Hydrides of Bis(cyclopentadienyl)zirconium

By B. KAUTZNER, P. C. WAILES,* and H. WEIGOLD
(*Division of Applied Chemistry, C.S.I.R.O., P.O. Box 4331, Melbourne*)

Summary Several new hydrides of zirconium have been prepared by the action of lithium aluminium hydride on various bis(cyclopentadienyl)zirconium chlorides.

AMONG the Group IVA elements the only hydrides which have been isolated are two of zirconium, *viz.* $(\pi\text{-}C_5H_5)_2ZrH_2$ and $(\pi\text{-}C_5C_5)_2Zr(H)BH_4$, both of which were prepared by the action of trialkylamines on the bis(tetrahydroborate), $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$.[1] We report a convenient new synthesis of $(\pi\text{-}C_5H_5)_2ZrH_2$, (I) and of three new zirconium hydrides.

On addition of $LiAlH_4$ (1 mol.) in tetrahydrofuran to $(\pi\text{-}C_5H_5)_2Zr(Cl)OZr(Cl)(\pi\text{-}C_5H_5)_2$ [2] in the same solvent, abstraction of both chlorine and oxygen occurs and pure (I) is slowly precipitated. From $LiAlH_4$ (0·25 mol.) and $(C_5H_5)_2ZrCl_2$, $(\pi\text{-}C_5H_5)_2Zr(H)Cl$, (II) is formed and precipitates immediately from tetrahydrofuran. The same product is obtained in a purer state when $LiAl(OBu^t)_3H$ (1 mol.) is used instead of $LiAlH_4$. Like the dihydride (I), (II) is remarkably insoluble and involatile and is undoubtedly polymeric.

When a further quantity of $LiAlH_4$ (1 mol.) in solution is added to a suspension of (II) in tetrahydrofuran, a clear solution is obtained. After removal of LiCl with benzene a new hydride, $(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$, (III) slowly deposits from solution in benzene–tetrahydrofuran.

From $(\pi\text{-}C_5H_5)_2Zr(Cl)Me$, the hydride $(\pi\text{-}C_5H_5)_2Zr(H)Me$, (IV) can be obtained using either $LiAlH_4$ or $LiAl(OBu^t)_3H$. All of these compounds have broad bands in the i.r. greatly displaced from the region normally associated with metal hydrides (*ca.* 2000 cm.$^{-1}$). The broadness of the bands together with their displacement seems to indicate bridging hydrogen.[1,3] That these bands are due to hydrides was shown by preparing the corresponding deuterides from $LiAlD_4$. The i.r. frequencies of both hydrides and deuterides are shown in the Table.

TABLE

I.r. frequencies of hydrides and deuterides

Compound	Frequency (cm.$^{-1}$, KBr disc) Zr–H	 Zr–D
$(\pi\text{-}C_5H_5)_2ZrH_2$, (I)	1520, 1300	1100, 960
$(\pi\text{-}C_5H_5)_2Zr(H)Cl$, (II)	1390	1020[a]
$(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$, (III)	1425	1055
	(1790, 1700 $[AlH_4]$)	(1310, 1260 $[AlD_4]$)
$(\pi\text{-}C_5H_5)_2Ar(H)Me$, (IV)	1500, 1310	1090, 965

[a] Overlapping with C–H deform. of $(\pi\text{-}C_5H_5)$.

All of the hydrides were characterized by analysis, i.r. and by quantitative hydrolysis with 50% aqueous H_2SO_4. Hydrogen evolved was pumped into a calibrated volume by means of a Töpler pump and accurately measured. Attempts to detect the resonance of the hydridic proton of (II), the most soluble hydride, in the ^1H n.m.r. spectrum in tetrahydrofuran have not yet been successful. Other authors have found the same difficulty with bridging hydrides.[1,3]

(*Received, July 25th*, 1969; *Com.* 1140.)

---

[1] B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Inorg. Chem.*, 1967, **6**, 1979.

[2] A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailes, *Austral. J. Chem.*, 1965, **18**, 173.

[3] G. E. Coates and P. D. Roberts, *J. Chem. Soc.* (*A*), 1969, 1008.