which reacts with hexafluoro-2-butyne to give a high yield of *cis*-$(CH_3)_2AsC(CF_3)=C(CF_3)As(CH_3)_2$. A cyclic structure is suggested for the complex.

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Note added in proof. Since this article was written, a paper by Parshal[12] has appeared describing the reactions of hexafluorocyclobutanone with phosphine to give $(CF_3)_2C(OH)PH_2$ and $[(CF_3)_3P(OH)]_2PH$.

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SHORT COMMUNICATIONS

Zirconium and titanium derivatives of indene and fluorene

Among the π-complexes of the transition metals, the compounds of the type R_2MCl_2, where R = indenyl or fluorenyl and M = Ti or Zr, have to our knowledge, received only a brief mention in patents concerning their use as catalysts in olefine polymerisation[1]. The preparation, properties and IR spectra of these complexes are described in this paper.

Indenyl derivatives of titanium and zirconium

The first step in the preparation of these compounds is similar to that used for the preparation of the dicyclopentadienyl derivatives. Indenylsodium and the anhydrous metal tetrahalide in molecular proportions 2:1 are reacted together in THF. The main difference is the method for isolating the pure product from the reaction mixture; solvent extraction cannot be used in this case owing to the rapidity with which the product decomposes in solution, at least under normal conditions. This separation can readily be effected with good yields by rapid washing of the solid reaction products with water, thus dissolving all mineral compounds present and leaving a pure insoluble residue. Sublimation can also be used, but this gives lower yields owing to partial decomposition.

Fluorenyl derivatives of titanium and zirconium

Metalation of fluorene with sodium in THF leads to very poor yields of the metal derivative. Although lithium[2] and potassium[3] are reported to give 9-fluorenyl metal derivatives in this solvent, their use in the present preparation did not seem to lead to successful results. Metalation via ethyllithium or phenyllithium was also unsuccessful. It was found, however, that the reaction products of potassium with fluorene in diethyl ether, and sodium or potassium in dimethoxyethane[5] can quite satisfactorily be used as intermediates, at least in preparing the zirconium derivative.

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Experimental

(*1*) *Diindenylzirconium dichloride*. Sodium (4 g) was reacted with indene (20 ml) in dry THF (50 ml) under reflux (nitrogen) for 8 h. The residual sodium was removed, and after the contents of the vessel had been allowed to cool, they were poured gradually over a suspension of 10 g of anhydrous $ZrCl_4$ in THF, with stirring for 2 h. Dry HCl gas was then bubbled through the reaction mixture, and most of the solvent distilled off under vacuum. Diethyl ether was added until there was no further precipitate. The precipitate was filtered on a Büchner funnel, washed rapidly with water containing 10% conc. HCl, water and finally ethyl alcohol, and then dried with diethyl

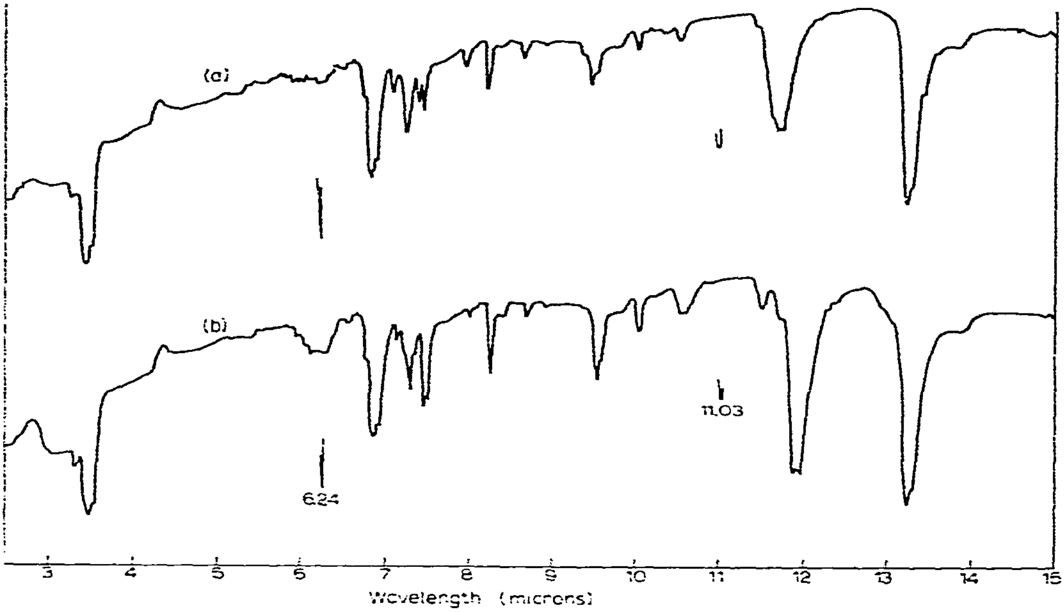

Fig. 1. Infrared spectra in nujol of: (a), $(C_9H_7)_2TiCl_2$; (b), $(C_9H_7)_2ZrCl_2$.

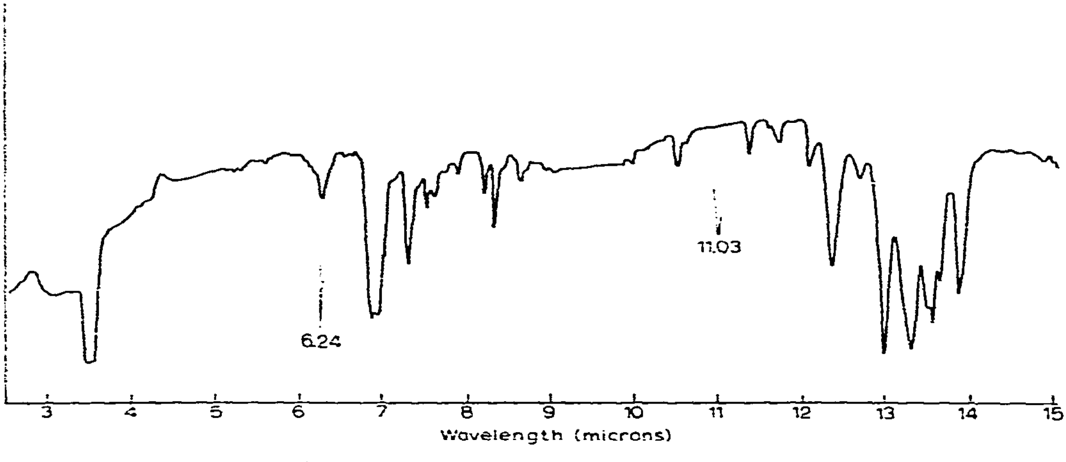

Fig. 2. Infrared spectrum of $(C_{13}H_9)_2ZrCl_2$ in nujol.

ether to give 8 g of a yellow crystalline product (m.p. 264°). This compound can be further purified by vacuum sublimation. Any attempt to recrystallise it in an organic solvent leads to its immediate decomposition. (Found: C, 54.92; H, 3.37; Cl, 17.53; Zr, 23.08. $C_{18}H_{14}Cl_2Zr$ calcd.: C, 55.09; H, 3.57; Cl, 18.08; Zr, 23.25%.)

(2) *Diindenyltitanium dichloride.* This can be prepared by the same method using anhydrous $TiCl_4$; a dark brown crystalline product is isolated (m.p. 210°), which also decomposes in organic solvents (it is possibly slightly more stable than the zirconium analogue). (Found: C, 59.26; H, 4.35; Cl, 20.27. $C_{18}H_{14}Cl_2Ti$ calcd.: C, 61.92; H, 4.01; Cl, 20.33%.)

Infrared spectra were taken as Nujol mulls with a Perkin-Elmer Infracord. The spectra of both compounds are remarkably similar (Fig. 1).

(3) *Difluorenylzirconium dichloride.* Small pieces of sodium (2 g) were added to fluorene (10 g) in pure dry dimethoxyethane (30 ml) and allowed to react overnight with stirring under nitrogen. Excess sodium was removed, and the solution gradually introduced into a suspension of $ZrCl_4$ (10 g, an excess over the theoretical requirement) in 20 ml dimethoxyethane. The colour of the suspension rapidly turned dark orange, with the formation of a crystalline product. After one hour stirring, a large excess of diethyl ether was added to precipitate the solid products which were filtered off, rapidly washed with 10% HCl, water and finally ethyl alcohol and dried with ether to give 3 g of an orange crystalline powder which decomposed without melting. The insolubility of the product in ether permits an easy separation from excess fluorene. Since the complex decomposes easily in organic solution the reaction must be carried out using the minimum quantity of solvent. (Found: Cl, 14.1; Zr, 19.1. $C_{26}H_{18}Cl_2Zr$ calcd.: Cl, 14.3; Zr, 18.5%.) Infrared spectrum: Fig. 2.

(4) *Difluorenyltitanium dichloride.* Attempts to prepare this compound in the same manner as the zirconium derivative did not lead to the expected result. Although a very stable crystalline product could be isolated in acceptable yields, its identity could not be checked as its metal content could not be ascertained. This matter is being further investigated.

The ease with which the complexes described above decompose in organic solvents has interfered with the preparation of the homologues of dicyclopentadienylzirconium oxide chloride[4,5] and dicyclopentadienyltitanium oxide chloride[6,7], both of which show an intense and characteristic absorption band between 13 and 14 microns.

Laboratoire de Photosynthèse,
Centre National de la Recherche Scientifique
Gif-sur-Yvette, S. et O. (France)

EDMOND SAMUEL
RALPH SETTON

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