Vinyltitanium Trichloride

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The preparation and properties of vinyltitanium trichloride and its adducts with tetrahydrofuran and 1,2-dimethoxyethane are described. The nature of the vinyl–titanium bond and the mechanism of decomposition of vinyltitanium trichloride are discussed.

THERE has been considerable interest in organotitanium chemistry since it has been shown that stable compounds of the type R_nTiCl_{4-n} may be isolated if other stabilising ligands, especially bidentate ligands such as 1,2-dimethoxyethane or *NNN'N'*-tetramethylethylenediamine, are present [1-5] or if the groups R contain no β-hydrogen atoms.[6-10] Thus complexes such as $MeTiCl_3$–dimethoxyethane [4,5] and $(Me_3C{\cdot}CH_2)_4Ti$ [9] may be stored for short periods at room temperature. It has been suggested that in both cases stabilisation can be attributed to the removal of the low energy β-elimination path for decomposition, either by blocking, with additional ligands, the co-ordination sites necessary for the reaction to proceed, or by choosing alkyl groups which have no β-hydrogen atoms.[8-11] The vinyl group partially meets the latter criterion (since β-hydrogen elimination is expected to be considerably more difficult than from simple alkyl groups). However, only one fully-characterised vinyltitanium compound has been reported, *viz.* chlorovinylbis(π-cyclopentadienyl)titanium(IV),[12] although vinyltitanium compounds have often been proposed as reaction intermediates [13-15] and some alkenyltris(diethylamido)titanium(IV) derivatives (but not the parent complex) have been isolated recently.[16] We now report the preparation and properties of vinyltitanium trichloride.

Tetravinyl-lead reacts with titanium(IV) chloride at −78 °C in a 1 : 1 mole ratio to give trivinyl-lead chloride and a purple compound, vinyltitanium trichloride:

$$(CH_2{=}CH)_4Pb + TiCl_4 \longrightarrow (CH_2{=}CH)_3PbCl + CH_2{=}CHTiCl_3$$

However, the two products cannot readily be separated since they have similar solubilities in organic solvents. Fortunately we found that hydrogen chloride reacts only with the trivinyl-lead chloride at −78 °C to give ethylene and the highly insoluble divinyl-lead dichloride, which can be filtered off, and pure vinyltitanium trichloride can then be isolated on evaporation of the solvents from the filtrate. In the preparation of vinyltitanium trichloride a small excess of tetravinyl-lead was usually used; this excess was then removed in the subsequent reaction with hydrogen chloride. Vinyltitanium trichloride is a purple solid which is stable at −78 °C but which decomposes rapidly above −30 °C. It is therefore less stable than methyltitanium trichloride.[1] This low thermal stability made conventional analysis of the product very difficult but its constitution as vinyltitanium trichloride was established by the following reactions:

(1) On allowing to warm to room temperature in dichloromethane the product decomposed quantitatively to titanium(III) chloride and a mixture of ethylene, butadiene, and some acetylene. The total amount of

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organic products corresponded exactly to that expected from one vinyl group per titanium atom.

(2) It reacted quantitatively with chlorine at −78 °C to give titanium(IV) chloride and polyvinyl chloride in the mole ratio required by the equation:

$$CH_2{=}CHTiCl_3 + Cl_2 \longrightarrow TiCl_4 + \frac{1}{n}(CH_2{=}CHCl)_n$$

(3) It reacted with bromine to give a 1 : 1 mixture of 1,1,2-tribromoethane and 'bromotrichlorotitanium(IV),' which was analysed as its adduct with tetrahydrofuran, bromotrichlorobis(tetrahydrofuran)titanium(IV).

'Bromotrichlorotitanium(IV)' may be expected to exist as a mixture of $TiCl_nBr_{4-n}$ species where $n = 0$—4, and it is possible that the tetrahydrofuran adduct is also a mixture. However the fact that the correct analysis for bromotrichlorobis(tetrahydrofuran)titanium(IV) was obtained is proof that the initial product contained one vinyl group per titanium atom.

(4) It formed adducts with tetrahydrofuran and 1,2-dimethoxyethane which, as expected,[4,5] were considerably more stable than the parent compound and could be fully analysed. These adducts, both of which were air-sensitive green solids which decomposed slowly at room temperature, were shown to be trichlorovinylbis(tetrahydrofuran)titanium(IV) and trichlorovinyl(dimethoxyethane)titanium(IV) respectively. They presumably have the same structures as the corresponding adducts of methyltitanium trichloride.[4]

The i.r. spectra of both adducts contain peaks at 1590 cm^{-1} which can be assigned to the C=C stretching vibration of the vinyl group. This frequency is considerably lower than that of the parent olefin and is similar to the values found in the vinyl derivatives of the Group IVB elements, where the reduction has been attributed, at least in part, to the effect of p_π–d_π bonding from filled π-orbitals of the vinyl group to empty d-orbitals on the metal.[17,18] The same effect could well contribute to the lowering of the frequency in the present case. It is particularly interesting that in chlorovinylbis(π-cyclopentadienyl)titanium(IV), in which the d-orbitals on titanium are already engaged in bonding to the strong π-donor cyclopentadienyl groups, the C=C stretching frequency[12] has the normal value of 1635 cm^{-1}. There is presumably hardly any p_π–d_π bonding, of the type discussed above, in the titanium–vinyl bond of this compound.

The u.v.–visible spectra of the adducts of vinyltitanium trichloride (see the Table) each contained two peaks in the region 10 000—25 000 cm^{-1} whereas the similar derivatives of methyltitanium trichloride give only one such peak. For methyltitanium trichloride the band in this region, which causes the intense colouration, has been assigned to the excitation of a non-bonding electron on chlorine into the titanium–methyl σ^* orbital.[19] In this excited state the titanium–carbon bond would be considerably weakened and the stability of the organotitanium compound may be critically dependent on the energy of this transition. Factors which influence the stability of transition-metal alkyls have been discussed in detail by several authors.[11,20-23] However the fact that the transition moves to lower energy in the adducts with Lewis bases (with increased stability) suggests that electronic excitation followed by homolysis of the titanium–alkyl bond is not the major decomposition path.

U.v.–visible spectra (10 000—26 000 cm^{-1}) of some organotitanium compounds

	Absorption maximum (cm^{-1})	ε	
CH_3TiCl_3	25 000[a]	75	Ref. 19
CH_3TiCl_3,2thf[b]	20 800[c]	150	Ref. 2*d*
CH_3TiCl_3,dme[d]	20 300[e]		Ref. 5
$CH_2{=}CHTiCl_3$,2thf	21 500[f]	45	This work
	15 200[f]	20	
$CH_2{=}CHTiCl_3$,dme	21 300[f]	41	This work
	15 800[f]	23	

[a] *n*-Hexane solvent. [b] thf = Tetrahydrofuran. [c] Tetrahydrofuran solvent. [d] dme = 1,2-Dimethoxyethane. [e] Diffuse reflectance. [f] Dichloromethane solvent.

Other proposed decomposition mechanisms for organotitanium compounds include the β-elimination mechanism,[11] non-promotional homolysis,[22] and intermolecular coupling of alkyl groups.[22] The observed decomposition products of vinyltitanium trichloride (ethylene, butadiene, and a little acetylene) are not consistent with the β-elimination mechanism which should give mostly acetylene and hydrogen, but are most readily explained by homolysis of the titanium–vinyl bond followed by further reactions of the vinyl radicals produced. It is also possible that at least some of the butadiene could be formed by intermolecular coupling of vinyl groups probably through a bimolecular intermediate containing bridging chloride or vinyl groups. The adducts would then be more stable since the necessary co-ordination sites for such bridging to occur would be blocked.

In an attempt to prepare vinylvanadium trichloride from tetravinyl-lead and vanadium(IV) chloride, we obtained trivinyl-lead chloride and vanadium(III) chloride, with butadiene or its polymer as the only organic product. Intermolecular coupling of vinyl groups from an intermediate, but very unstable, vinylvanadium trichloride is the most likely reaction mechanism in this case.

Finally we note that vinyltrichlorobis(tetrahydrofuran)titanium(IV) in dichloromethane is a catalyst, though not a very efficient one, for the polymerisation of ethylene.

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EXPERIMENTAL

All preparations and reactions were carried out *in vacuo*; solid products were handled in an atmosphere of dry nitrogen, and starting materials were prepared and purified by standard methods. Volatile products were identified by their saturated vapour pressures at various temperatures,[24-27] vapour densities, and i.r. spectra, after separation by fractionation *in vacuo*. Non-condensable products were identified and estimated by combustion analysis. Lead and halide estimations were by standard methods; titanium(IV) was determined gravimetrically as TiO_2 and Ti^{III} by titration with iron(III) ammonium sulphate under nitrogen. I.r. spectra were recorded using a Perkin-Elmer 257 spectrophotometer and u.v. spectra using a Unicam SP 700C spectrophotometer.

Preparation of Vinyltitanium Trichloride.—Tetravinyl-lead (3·49 mmol),[28,29] titanium tetrachloride (2·89 mmol), and dichloromethane (10 ml) were condensed into a reaction vessel provided with a sinter and break seals at −196 °C and the vessel sealed and allowed to warm to −78 °C when a purple colour developed. The vessel was opened at a break seal, hydrogen chloride (5·04 mmol) was condensed in, and the vessel was resealed and allowed to warm to −78 °C. The vessel was then opened and the divinyl-lead dichloride (3·48 mmol) was filtered off at the sinter. The volatile material was pumped off at −78 °C and shown to be CH_2Cl_2, C_2H_4 (3·86 mmol), and HCl (1·15 mmol) leaving vinyltitanium trichloride in quantitative yield as a purple solid, decomp. −30 °C.

Decomposition of Vinyltitanium Trichloride.—In a similar experiment the vinyltitanium trichloride from tetravinyl-lead (3·38 mmol) and titanium tetrachloride (4·37 mmol) was allowed to warm to 20 °C in dichloromethane solution. The decomposition products were shown to be trivinyl-lead chloride (3·12 mmol), titanium(III) chloride (3·02 mmol), acetylene (0·29 mmol), ethylene (1·33 mmol), and butadiene (0·80 mmol). If excess tetravinyl-lead was used considerably higher quantities of butadiene and some polybutadiene were formed together with metallic lead.

Reaction with Chlorine.—Chlorine (7·42 mmol) was condensed onto vinyltitanium trichloride [from tetravinyl-lead (3·32 mmol) and titanium tetrachloride (4·55 mmol)] and dichloromethane (10 ml). The purple colour disappeared very rapidly on warming to −78 °C. The volatile products were dichloromethane, chlorine (4·30 mmol), and titanium tetrachloride (4·29 mmol). The white residue was shown by its i.r. spectrum to be polyvinyl chloride (0·194 g).

Reaction with Bromine.—Bromine (12·34 mmol) was condensed onto a solution of vinyltitanium trichloride [from tetravinyl-lead (5·13 mmol) and titanium tetrachloride (5·00 mmol)] in dichloromethane (10 ml). After warming to room temperature the volatile products were removed and shown to be dichloromethane, bromine (2·49 mmol), and 1,1,2-tribromoethane (4·50 mmol). Tetrahydrofuran was condensed onto the involatile material to give 'trichlorobromobis(tetrahydrofuran)titanium(IV)' as a yellow solid (4·85 mmol). $C_8H_{16}BrCl_3O_2Ti$ requires Cl, 28·15; Br, 21·1; Ti, 12·65. Found: Cl, 27·8; Br, 21·8; Ti, 12·35%.

Trichlorovinylbis(tetrahydrofuran)titanium(IV).—Titanium tetrachloride (10·02 mmol) was treated with tetrahydrofuran (24·66 mmol) in dichloromethane (50 ml). The excess of tetrahydrofuran (4·62 mmol) and dichloromethane was removed and fresh dichloromethane (50 ml) and tetravinyl-lead (13·88 mmol) were condensed on. The mixture was warmed to room temperature and slowly became deep green in colour. After 18 h the vessel was opened and the solvent and the excess of tetravinyl-lead (3·81 mmol) removed. Fresh dichloromethane (50 ml) and hydrogen chloride (12·47 mmol) were added, the mixture warmed to room temperature and the precipitate of divinyl-lead dichloride (10·00 mmol) was filtered off. The volatile products were removed and shown to be dichloromethane, ethylene (10·01 mmol), and hydrogen chloride (2·44 mmol) leaving the *product* as a deep green solid in quantitative yield. The same compound could be prepared by treating vinyltitanium trichloride with tetrahydrofuran. U.v. spectrum in CH_2Cl_2; $\nu_{max.}$ 21 500, ε 45; 15 200 cm^{-1}, ε 20 l mol^{-1} cm^{-1}; i.r. ν(C=C) 1590 cm^{-1} (Found: Ti, 14·35; Cl, 30·2; tetrahydrofuran, 42·6. $C_{10}H_{19}Cl_3O_2Ti$ requires Ti, 14·7; Cl, 32·7; tetrahydrofuran, 44·4%). The compound was destroyed before analysis with aqueous KOH; polyethylene, identified by its i.r. spectrum, was formed as a by-product. Reaction with bromine gave, quantitatively, 1,1,2-tribromoethane and trichlorobromobis(tetrahydrofuran)titanium, identical with the compound prepared above.

Trichlorovinyl(dimethoxyethane)titanium(IV).—This was prepared as a green solid either by treating vinyltitanium trichloride with dimethoxyethane or by reacting tetrachloro-(dimethoxyethane)titanium with tetravinyl-lead as above. U.v. spectrum in CH_2Cl_2; $\nu_{max.}$ 21 300, ε 41; 15 800 cm^{-1}, ε 23 l mol^{-1} cm^{-1}; i.r. ν(C=C) 1590w cm^{-1} (Found: Ti, 17·35; Cl, 38·90; dimethoxyethane, 30·80. $C_6H_{13}Cl_3O_2Ti$ requires Ti, 17·65; Cl, 39·25; dimethoxyethane, 33·2%). The product reacted quantitatively with bromine in dichloromethane to give 1,1,2-tribromoethane and trichlorobromo-(dimethoxyethane)titanium(IV) as a yellow solid, which was recrystallised from dimethoxyethane (Found: Ti, 14·55; Cl, 33·1; Br, 24·15. $C_4H_{10}BrCl_3O_2Ti$ requires Ti, 14·8; Cl, 32·8; Br, 24·6%).

Attempted Preparation of Vinylvanadium Trichloride.—Vanadium tetrachloride (4·42 mmol), dichloromethane (50 ml), and tetravinyl-lead (9·47 mmol) were condensed into a reaction vessel provided with a sinter. On warming to room temperature a purple-brown solid precipitated. This was filtered off and found to be vanadium(III) chloride (4·36 mmol). The volatile products were removed from the filtrate and shown to contain dichloromethane, tetravinyl-lead (4·95 mmol), and butadiene (0·20 mmol). The white residue was extracted with dilute nitric acid. The insoluble fraction was identified as polybutadiene (0·11 g) by its i.r. spectrum, and the soluble fraction as trivinyl-lead chloride (4·44 mmol) by lead and chloride analyses.

A similar 1 : 1 reaction of tetravinyl-lead with tetrachlorobis(tetrahydrofuran)vanadium(IV) gave much butadiene, but the involatile products could not be separated.

Polymerisation of Ethylene by Trichlorovinylbis(tetrahydrofuran)titanium(IV).—Ethylene was bubbled through a solution of trichlorovinylbis(tetrahydrofuran)titanium(IV)

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(9·1 mmol) in dichloromethane (50 ml) at 25 °C for 5 h. The colour of the solution slowly changed from green to brown. The solvent was removed, the residue was extracted with boiling toluene, the insoluble portion was filtered off, and the toluene evaporated. Polyethylene (0·54 g), identified by its i.r. spectrum was left as a white solid. If all the vinyltitanium groups were converted to polyethylene, only 0·24 g of polymer would be formed.

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