

## Reactions of Various Organotitanium Compounds with Potentially Bidentate Alkenyloxo- and Related Ligands<sup>1</sup>

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Monoalkoxo-derivatives of titanium(IV) have been synthesised from the potentially bidentate ligand but-3-en-1-ol as four-co-ordinate monomers:  $[\text{TiCl}_3(\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ , (I);  $[(\text{cp})_2\text{TiCl}(\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ , (II); and  $[(\text{cp})_2\text{TiMe}(\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$ , (III) (cp =  $\eta$ -cyclopentadienyl). The 1:1 complex of titanium tetrachloride and 4-methoxybut-1-ene is a chloro-bridged dimer containing six-co-ordinate titanium,  $\{\text{TiCl}_4(\text{MeOCH}_2\text{CH}_2\text{CH}=\text{CH}_2)\}_2$  (IV). A variation in the chemical shifts of the olefinic protons in complex (IV), and in (I) and its six-co-ordinate derivatives, has been observed in n.m.r. spectra but it is not considered to be sufficient to imply titanium-olefin bonding. Attempts to prepare models of Ziegler-Natta catalysts by methylation of these compounds have not been successful. Brief reports of reactions of dimethyltitanium dichloride with some uni- and bi-dentate ligands are also given.

CONSIDERABLE interest is attached to low-temperature and -pressure polymerisation of  $\alpha$ -olefins by catalysts incorporating titanium and other early transition metals. The titanium catalysts vary considerably with respect to the oxidation state of the metal atom, the nature of the attached ligands, and the presence or absence of various alkylating agents (usually alkylaluminium compounds). It is generally accepted that the active site in the catalyst is an alkylated titanium atom and that the reaction path is similar to that envisaged in the Cossee mechanism.<sup>2</sup> The growth step according to this mechanism involves occupation of a vacant co-ordination site at the six-co-ordinate titanium centre by a monomeric olefin unit prior to migration of an alkyl group, initially  $\sigma$ -bonded to the titanium atom. A new vacant co-ordination site and a different alkyl group  $\sigma$ -bonded to the titanium atom are thus produced. A recent theoretical investigation has quantified a number of the postulates of the Cossee mechanism.<sup>3</sup>

The primary role of the alkylaluminium compound in the catalyst mixture is considered to be alkylation of the titanium atom. A secondary function is suggested in homogeneous catalysis based on dichlorobis( $\eta$ -cyclopentadienyl)titanium(IV).<sup>2</sup> Henrici-Olivé and Olivé<sup>4</sup> have shown that the nature of the complexed organo-

aluminium compound has a marked influence on the lability of the titanium-carbon  $\sigma$ -bond.

Although an extensive literature exists concerning these catalysts there is little direct chemical evidence for the essential steps, which are titanium-olefin and titanium-alkyl-olefin interactions. The formation of coloured solutions on addition of a variety of substituted olefins to titanium tetrachloride has been attributed to formation of 1:1 charge-transfer complexes,<sup>5</sup> although thermochemical studies have shown that the heats of formation in these reactions are extremely small,<sup>6</sup> in accord with the transitory nature of this interaction. Strong olefin complexes have only been reported with titanium(III), *viz.* the series of allylbis( $\eta$ -cyclopentadienyl)titanium(III) compounds.<sup>7,8</sup> In similar allyl and vinyl compounds of titanium(IV), however, the alkenyl groups appear to be  $\sigma$ -bonded to the metal atom.<sup>9-12</sup>

In the present work a number of compounds of titanium(IV) have been synthesised by use of the potentially bidentate ligand but-3-en-1-ol, which co-ordinates to the titanium atom by an alkoxo-(-OCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>) or ether (MeOCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>) linkage. The terminal olefin group is available to occupy a second co-ordination site at the titanium centre such that possible titanium-olefin interaction may be investigated. In some cases a  $\sigma$ -bonded methyl group was introduced at the titanium

<sup>1</sup> Presented in part at the 14th Internat. Conf. Co-ordination Chem., Toronto, 1972.

<sup>2</sup> J. Boor, *Ind. and Eng. Chem. (Product Res. and Development)*, 1970, **9**, 437.

<sup>3</sup> D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1972, 1972.

<sup>4</sup> G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn.*, 1968, **7**, 821; *Adv. Polymer Sci.*, 1969, **6**, 421.

<sup>5</sup> H. L. Krauss and J. Nickl, *Z. Naturforsch.*, 1965, **B20**, 630.

<sup>6</sup> B. Hessett and P. G. Perkins, *Chem. and Ind.*, 1970, 747.

<sup>7</sup> H. A. Martin and F. Jellinek, *J. Organometallic Chem.*, 1967, **8**, 115.

<sup>8</sup> H. A. Martin and F. Jellinek, *Rec. Trav. chim.*, 1967, **86**, 1263.

<sup>9</sup> J. A. Waters and G. A. Mortimer, *J. Organometallic Chem.*, 1970, **22**, 417.

<sup>10</sup> B. J. Hewitt, A. K. Holliday, and R. J. Puddephatt, *J.C.S. Dalton*, 1973, 801.

<sup>11</sup> H.-J. Neese and H. Bürger, *J. Organometallic Chem.*, 1971, **32**, 213.

<sup>12</sup> H. Bürger and H.-J. Neese, *J. Organometallic Chem.*, 1972, **36**, 101.

centre in an attempt to reproduce a model for the polymerisation process.

#### EXPERIMENTAL

n-Pentane, benzene, toluene, and chloroform solvents were dried as described previously for n-hexane and dichloromethane.<sup>13</sup> n-Butyl- and methyl-lithium (Fluka) and dichlorobis( $\eta$ -cyclopentadienyl)titanium(IV) (Ralph Emmanuel) were used as obtained. But-3-en-1-ol (Fluka), NNN'N'-tetramethyldiaminoethane (tmde), and triethylamine were briefly stirred with powdered calcium dihydride and vacuum distilled prior to use. Diethyl ether and tetrahydrofuran (thf) were initially dried over lithium tetrahydridoaluminate and then distilled from sodium diphenylketyl immediately prior to use. Titanium tetrachloride was purified, and trichloro(methyl)titanium(IV) prepared as described previously.<sup>13</sup>

*Preparations.*—All preparations involving potentially atmosphere-sensitive materials were carried out using the apparatus and techniques described previously.<sup>13</sup>

*4-Methoxybut-1-ene.* This was prepared in moderate yield by addition of but-3-en-1-ol (14.5 g, 0.2M) to sodium (4.0 g, 0.17 g-atom) in diethyl ether (20 cm<sup>3</sup>) followed by reaction with iodomethane (25 g, 0.17M) in diethyl ether (40 cm<sup>3</sup>). The pure compound (b.p. 68.5 °C) was obtained on careful fractional distillation. The n.m.r. spectrum exhibited the correct signal integration and showed absence of diethyl ether and starting materials.

*(But-3-enyloxo)trichlorotitanium(IV), (I).* n-Butyl-lithium (15 cm<sup>3</sup> of a 2.1M-solution, 0.032M) was added to a stirred solution of but-3-en-1-ol (2.3 g, 0.032M) in hexane (20 cm<sup>3</sup>) at -78 °C, and the stirred solution allowed to warm to room temperature. The resulting solution was then added dropwise to a cold (-78 °C) stirred solution of titanium tetrachloride (8.1 g, ca. 0.04M) in hexane (75 cm<sup>3</sup>). The resultant cream-coloured slurry was warmed to room temperature and allowed to settle overnight before filtering off finely divided lithium chloride. On cooling to -78 °C the filtrate deposited a white *product* which was filtered off and recrystallised from fresh hexane (20 cm<sup>3</sup>) at -78 °C. The *product* was dried *in vacuo* and sealed in a vacuum manifold (yield 2.5 g, 35%). The low yield is largely attributed to mechanical difficulties of separating the *product* from lithium chloride.

*(But-3-enyloxo)chlorobis( $\eta$ -cyclopentadienyl)titanium(IV), (II).* But-3-en-1-ol (5.7 g, 0.078M) in benzene (30 cm<sup>3</sup>) was added dropwise over 2 h to a stirred suspension of dichlorobis( $\eta$ -cyclopentadienyl)titanium(IV) (19.6 g, 0.078M) in triethylamine (9.1 g, 0.09M) and benzene (600 cm<sup>3</sup>). After stirring for a further 5 h at room temperature the solvent was removed and the resultant orange solid repeatedly extracted with diethyl ether (60 cm<sup>3</sup>). Careful addition of hexane (ca. 20 cm<sup>3</sup>) and cooling produced the *compound* as a low melting (m.p. ca. 40 °C) orange solid which was filtered off, washed with hexane (20 cm<sup>3</sup>), and dried *in vacuo* before being sealed in a vacuum manifold and stored at -20 °C.

*(But-3-enyloxo)bis( $\eta$ -cyclopentadienyl)methyltitanium(IV), (III).* Methyl-lithium (2.7 cm<sup>3</sup> of a 1.93M-solution, 0.0052M) was added dropwise to a stirred solution of compound (II) (1.47 g, 0.0052M) in diethyl ether (50 cm<sup>3</sup>) at -78 °C. The stirred solution was warmed to room temperature over 1 h and the solvent removed *in vacuo*. The resultant red gum was extracted with n-hexane (30 cm<sup>3</sup>) and the red solution

filtered free of lithium chloride. The n-hexane solvent was removed *in vacuo* to produce a red *oil* which was purified by short-path distillation at 70 °C under high vacuum on to a liquid-nitrogen-cooled probe.

*Bis[tetrachloro(4-methoxy-but-1-ene)titanium(IV)], (IV).* 4-Methoxybut-1-ene (0.6 g, 0.007M) was added under vacuum to a stirred solution of titanium tetrachloride (18.4 g, 0.096M) in n-pentane (30 cm<sup>3</sup>) at -40 °C. The resulting yellow mass was warmed to room temperature and held there briefly before being cooled to -20 °C. The yellow *product* was removed by filtration, washed with cold (-20 °C) pentane (2 × 10 cm<sup>3</sup>) before being dried *in vacuo* at 0 °C, and stored in a vacuum manifold at -20 °C.

*(But-3-enyloxo)trichlorotitanium(IV)-NNN'N'-Tetramethyldiaminoethane (1/1), (V).* To compound (I) (0.78 g, 0.003M) in n-hexane (20 cm<sup>3</sup>) was added NNN'N'-tetramethyldiaminoethane (tmde) (0.40 g, 0.003M) in hexane (10 cm<sup>3</sup>). Reaction was immediate and the white *product* was filtered off and washed with hexane (20 cm<sup>3</sup>) before evacuation and sealing in a vacuum manifold.

*Methylaluminium dichloride.* Trimethylaluminium (K and K; 1.01 g, 0.015M) and freshly sublimed aluminium trichloride (4.1 g, 0.03M) were stirred together *in vacuo* while being warmed to ca. 120 °C. The solid was extracted with pentane (40 cm<sup>3</sup>) and the solution filtered free of a slight residue. On being cooled to -78 °C the filtrate deposited crystals of methylaluminium dichloride which were filtered off, dried *in vacuo*, and transferred to a vacuum manifold, m.p. 74 °C (lit., 72.7 °C) (Found: C, 10.7; H, 2.6. MeAlCl<sub>2</sub> requires C, 10.6; H, 2.7%).

*Dichlorodimethyltitanium(IV).* This compound was prepared as described previously<sup>14</sup> using the starting materials, apparatus, and techniques described for trichloro(methyl)titanium(IV).<sup>13</sup> Dimethylzinc (3.46 g, 0.036M) was added under vacuum to a stirred solution of titanium tetrachloride (6.38 g, 0.036M) in n-pentane (130 cm<sup>3</sup>) at -78 °C over 1 h. The resultant dark brown slurry was stirred for a further 0.5 h at this temperature before being warmed to -20 °C during 1 h when the colour lightened. The mixture was filtered at -20 °C and the orange filtrate deposited black crystals on being cooled to -78 °C. Crystallisation was complete after 0.5 h at this temperature, and the black solid was filtered off and recrystallised from n-pentane (15 cm<sup>3</sup>) at -78 °C. The quantitative yield of dichloro(dimethyl)titanium(IV) was transferred to a vacuum manifold as a concentrated n-pentane solution and stored thus at -78 °C in the absence of light *in vacuo*.

*Reactions of Compounds (II) and (III).*—(II) and MeAlCl<sub>2</sub>. Methylaluminium dichloride (0.30 g, 0.0027M) in toluene (20 cm<sup>3</sup>) was added dropwise to compound (II) (0.77 g, 0.0027M) in toluene (26 cm<sup>3</sup>) at -78 °C. The stirred solution was warmed to room temperature and the solvent removed *in vacuo*. n-Hexane (20 cm<sup>3</sup>) was added and a red precipitate, which exhibited an i.r. spectrum identical to that of dichlorobis( $\eta$ -cyclopentadienyl)titanium(IV), was filtered off. The filtrate deposited a very air-sensitive yellow gum on evaporation of the solvent (Found: C, 47.7; H, 4.2; Cl, 30.3. [(cp)<sub>2</sub>TiCl<sub>2</sub>] requires C, 48.2; H, 4.0; Cl, 28.5%).

(II) and Aluminium. Compound (II) (2.5 g, 0.008M) and pieces of aluminium foil (1.0 g, 0.037 g-atom) were stirred in tetrahydrofuran (thf) (40 cm<sup>3</sup>) overnight. The resultant green solution was filtered free of aluminium foil and the

<sup>13</sup> R. J. H. Clark and M. A. Coles, *J.C.S. Dalton*, 1972, 2454; *Inorg. Synth.*, in the press.

<sup>14</sup> L. A. M. Rodriguez and H. M. Van Looy, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1966, 4, 1951.

solvent removed *in vacuo*. Repeated extraction of the solid with diethyl ether (20 cm<sup>3</sup>) produced a residue of chlorobis( $\eta$ -cyclopentadienyl)titanium(III) {Found: C, 56.6; H, 4.8. [(cp)<sub>2</sub>TiCl] requires C, 56.2; H, 4.7%}.

(III) and MeAlCl<sub>2</sub>. Compound (III) (0.61 g, 0.0023M) in n-pentane (10 cm<sup>3</sup>) was added dropwise to a stirred solution of methylaluminium dichloride (0.77 g, 0.0023M) in n-pentane (40 cm<sup>3</sup>) at 0°C. A dark brown gum and a suspended brown material were produced immediately. The solid was decanted from the gum and filtered off. The brown filtrate deposited a red-brown solid on removal of the solvent. Spectroscopic analysis showed the solid materials to be free of the but-3-enyloxo-ligand. The dark gum represented the aluminium component of the reaction products and contained the but-3-enyloxo-ligand.

(III) and MeLi. Methyl-lithium (1.4 cm<sup>3</sup> of a 1.93M solution, 0.0027M) was added to a stirred solution of compound (III) (0.73 g, 0.0027M) in n-hexane (10 cm<sup>3</sup>) and diethyl ether (20 cm<sup>3</sup>) at -78°C. The solution turned yellow on warming to room temperature and a yellow-orange solid was produced on removal of the solvents. n-Hexane was added and partial solution occurred with a darkening of the mixture. The resulting brown solution was filtered free of a dark residue and deposited yellow needles on reducing the volume and cooling. The yellow

tion. The dark blue solid was filtered off and washed free of the brown oil with cold dichloromethane (2 × 10 cm<sup>3</sup>). The dried dark blue solid rapidly accumulated titanium(III) on storage *in vacuo* at -78°C, and thus conventional analyses were impossible. The product is probably<sup>13</sup> (Et<sub>4</sub>N)<sub>2</sub>[Me<sub>2</sub>TiCl<sub>4</sub>] but this could not be established for certain.

Analyses were carried out as reported previously.<sup>13</sup> Data for the titanium derivatives are listed in Table 1. Molecular weights were determined for benzene solutions of the compounds using a semi-micro ebulliometer (Gallenkamp MW-120). Naphthalene was the internal calibrant and the titanium derivatives were introduced to the apparatus as pellets, which had been previously prepared in a dry-box. I.r. spectra of the compounds were recorded on a Perkin-Elmer 225 spectrometer as Nujol mulls between caesium iodide plates, the mulls being prepared in a dry-box. N.m.r. spectra were recorded for degassed solutions of the compounds in sealed tubes using a Varian Associates HA100 instrument. The chemical shifts ( $\delta$ ) are given with reference to Me<sub>4</sub>Si or chloroform as solvent. Samples (ca. 20 g l<sup>-1</sup>) were made up in an apparatus, and by a procedure, described previously (figure 4, ref. 15). The dimethyl ether complex [TiCl<sub>3</sub>(OCH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)]<sub>2</sub>Me<sub>2</sub>O, (VI), was prepared in this apparatus by dissolving (I) in

TABLE I  
Analytical data for titanium compounds derived from but-3-en-1-ol

Compound	Colour	Found (%)						Calc. (%)					
		C	H	Ti	Cl	N	M	C	H	Ti	Cl	N	M
[TiCl <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )], (I)	White	20.6	3.0	21.1	46.0		239	21.3	3.1	21.3	47.2		225
[(cp) <sub>2</sub> TiCl(OCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )], (II)	Orange	58.5	5.9	18.0	12.4		287	59.1	6.0	16.8	12.5		284
[(cp) <sub>2</sub> TiMe(OCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> )], (III)	Red	67.4	7.5					68.2	7.6	18.1			
{TiCl <sub>3</sub> (MeOCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub> }, (IV)	Yellow	22.9	3.7	17.2	51.1		550	21.8	3.6	17.4	51.4		552
[TiCl <sub>3</sub> (OCH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub> ], tmdc, (V)	White	35.0	6.8		31.5	7.9		35.2	6.8	14.0	31.1	8.2	

cp =  $\eta$ -Cyclopentadienyl and tmdc = NNN'-tetramethyldiaminoethane.

needles were dried *in vacuo* and sealed in a vacuum manifold. The crystals darkened within 0.5 h at -20°C in the dark, deposited a metallic mirror, and evolved a considerable quantity of a gas in ca. 10 h under these conditions.

Reactions of (Me)<sub>2</sub>TiCl<sub>2</sub>.—With tmdc. Tmdc (0.78 g, 0.005M) in n-hexane (15 cm<sup>3</sup>) was added to a stirred solution of dichloro(dimethyl)titanium(IV) (ca. 0.005M) in n-hexane (20 cm<sup>3</sup>) maintained at -10°C. On complete addition the suspension was cooled to -78°C and the resulting red-brown precipitate filtered off. After washing with cold (-40°C) n-hexane (15 cm<sup>3</sup>), the complex was dried *in vacuo* at 0°C and transferred to a vacuum manifold. A marked darkening in colour, accompanied by gas evolution, occurred within 0.5 h at room temperature. However a freshly prepared solution in dichloromethane exhibited an n.m.r. spectrum consistent with the formulation Me<sub>2</sub>TiCl<sub>2</sub>-tmdc [Me-Ti,  $\delta$  2.03 p.p.m. (rel. intensity 6); Me<sub>2</sub>N, 2.46 (11.7); and N-CH<sub>2</sub>, 2.66 (3.3)].

With Et<sub>4</sub>NCl. Tetraethylammonium chloride (1.04 g, 0.0062M) in chloroform (4 cm<sup>3</sup>) and dichloromethane (24 cm<sup>3</sup>) was added dropwise to dichloro(dimethyl)titanium(IV) (ca. 0.005M) in chloroform (10 cm<sup>3</sup>) at -78°C. A number of colour changes were apparent during the addition, ultimately resulting in formation of a dark blue precipitate and a brown oil. This mixture of products was unaffected by addition of further tetraethylammonium chloride solu-

tion. The dark blue solid was filtered off and washed free of the brown oil with cold dichloromethane (2 × 10 cm<sup>3</sup>). The dried dark blue solid rapidly accumulated titanium(III) on storage *in vacuo* at -78°C, and thus conventional analyses were impossible. The product is probably<sup>13</sup> (Et<sub>4</sub>N)<sub>2</sub>[Me<sub>2</sub>TiCl<sub>4</sub>] but this could not be established for certain.

## RESULTS AND DISCUSSION

Previous work<sup>15,16</sup> has indicated that octahedral compounds of trichloro(methyl)titanium(IV) with unsymmetrical bidentate ligands XCH<sub>2</sub>CH<sub>2</sub>Y (X and Y = OMe, SMe, and NMe<sub>2</sub>) adopt, at least at low temperature, the *mer*-configuration in which the harder ligand atom occupies the co-ordination site *trans* to that of the methyl group. An extension of this study to the preparation of analogous compounds of dichloro(dimethyl)titanium(IV) was largely frustrated by the extreme thermal instability of the products, which precluded execution of conventional chemical and i.r. analyses. The only such compound satisfactorily characterised was [Me<sub>2</sub>TiCl<sub>2</sub>]<sub>2</sub>tmdc, which is a red-brown solid and displays in dichloromethane the correct <sup>1</sup>H signal integration for the above formulation. By contrast to the variety and thermal

<sup>15</sup> R. J. H. Clark and A. J. McAlees, *J. Chem. Soc. (A)*, 1970, 2026.

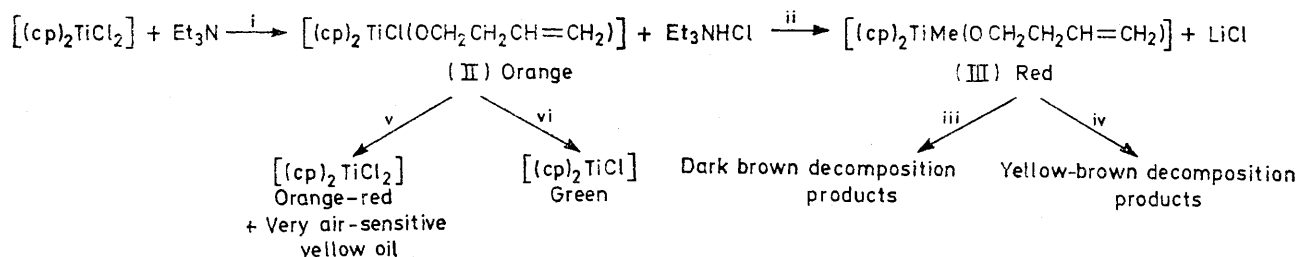
<sup>16</sup> R. J. H. Clark and A. J. McAlees, *Inorg. Chem.*, 1972, 11, 342.



in the i.r. and the chemical shift of the olefinic protons in the n.m.r. spectrum showed only minor shifts relative to their values in the reference compound 4-methoxybut-1-ene, and these observations are indicative of negligible olefin-titanium interaction.

The methylated compound (III) was isolated from the reaction of (II) with methyl-lithium as a stable red oil which can be purified by short-path high-vacuum distillation at *ca.* 70 °C; prolonged heating under reflux in thf, toluene, or n-heptane resulted in the onset of deep-seated decomposition rather than methyl-olefin interaction at the titanium centre, as envisaged in the Cossee mechanism of the polymerisation process. I.r. and n.m.r. parameters of the olefin group of compound (III)

monomer<sup>3,4</sup> [structure (B)]. However attempts to increase the lability of the methyl group towards the available terminal olefin group in compound (III) by complex formation were unsuccessful. No reaction was apparent in the presence of chloride ion (as the tetraethylammonium salt), which might be expected to co-ordinate to the titanium atom of compound (III). The predominant reaction during attempted formation of a complex between (III) and methylaluminium dichloride [analogous to that in structure (B)] appeared to be transfer of the intact but-3-enyloxo-moiety to methylaluminium dichloride and production of bis( $\eta$ -cyclopentadienyl)-dimethyl and chlorobis( $\eta$ -cyclopentadienyl)methyltitanium(IV) (n.m.r. evidence). A complicated reaction was

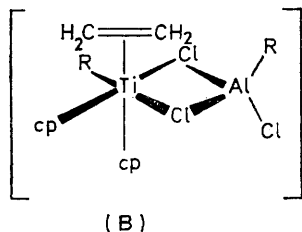


SCHEME 2

Reagents and conditions: i,  $CH_2=CHCH_2CH_2OH/C_6H_6$ ; ii, MeLi/Et<sub>2</sub>O, -20 °C; iii, MeAlCl<sub>2</sub>/n-C<sub>5</sub>H<sub>12</sub>, 0 °C; iv, n-C<sub>6</sub>H<sub>14</sub>-Et<sub>2</sub>O, -78 °C; v, MeAlCl<sub>2</sub>/toluene, -78 °C; vi, Al/thf.

suggest the absence of any significant olefin-titanium interaction. Attempted alkylation of compound (II) with methylaluminium dichloride in toluene produced dichlorobis( $\eta$ -cyclopentadienyl)titanium(IV) and an extremely air-sensitive yellow oil. This aluminium component was not fully characterised, but from i.r. evidence it appeared that the intact but-3-enyloxo-ligand was present. Similar behaviour was observed in reduction of compound (II) with aluminium foil using the method of Coutts *et al.*<sup>22</sup> Chlorobis( $\eta$ -cyclopentadienyl)titanium-(III) was produced as the major bis( $\eta$ -cyclopentadienyl)-titanium component instead of the desired (but-3-enyloxo)bis( $\eta$ -cyclopentadienyl)titanium(III).

It has been suggested that in homogeneous catalysis the alkylaluminium component forms compounds with



the alkylated dichlorobis( $\eta$ -cyclopentadienyl)titanium-(IV) entity and thus ensures the high co-ordination number at the titanium atom essential for facile interaction of the alkyl group  $\sigma$ -bonded to titanium with the olefin

<sup>22</sup> R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organometallic Chem.*, 1973, **47**, 375.

<sup>23</sup> J. P. Oliver, J. B. Smart, and M. T. Emerson, *J. Amer. Chem. Soc.*, 1966, **88**, 4101.

also apparent between compound (III) and methyl-lithium.

*N.m.r. Spectra.*—<sup>1</sup>H Chemical shifts ( $\delta$ ) of the compounds derived from but-3-en-1-ol are listed in Table 2.

TABLE 2

<sup>1</sup>H N.m.r. chemical-shift values (p.p.m.)<sup>a</sup>

Compound	$H_2C=CH-CH_2-CH_2-O-$			
	(a)	(b)	(c)	(d)
$CH_2=CHCH_2CH_2OMe$ , Neat liquid	4.97	5.77	2.23	3.29
(IV), CCl <sub>4</sub> Solution	4.91	5.75	2.51	3.88
(I)	5.26	5.87	2.66	4.86
(VI)	5.21	5.90	2.68	5.08
(V)	5.04	5.83	<sup>c</sup>	4.97
(II), Relative to solvent CHCl <sub>3</sub>	5.05	5.74	2.17	4.43
(III), CHCl <sub>3</sub> Solution	5.12	<sup>b</sup>	2.04	4.06

<sup>a</sup> Downfield from internal Me<sub>4</sub>Si ( $\delta = 0$ ) in CDCl<sub>3</sub> except where indicated otherwise. <sup>b</sup> Obscured by cp signal at  $\delta$  5.86 p.p.m. <sup>c</sup> Obscured by tmde absorptions.

The olefinic protons, designated (a) and (b), produced identically shaped multiplets in the n.m.r. spectra and the values quoted correspond to the centred chemical shift of these multiplets. The chemical shift of olefinic protons has often been used as a probe to investigate metal-olefin interaction.<sup>23-26</sup> For complexes of silver(I) with a number of substituted olefins a general deshielding

<sup>24</sup> J. St. Denis, J. P. Oliver, and J. B. Smart, *J. Organometallic Chem.*, 1972, **44**, C32.

<sup>25</sup> H. C. Clark and R. C. Poller, *Canad. J. Chem.*, 1970, **48**, 2670.

<sup>26</sup> R. G. Jones, P. Partington, W. J. Rennie, and R. M. G. Roberts, *J. Organometallic Chem.*, 1972, **35**, 291.

of the olefinic protons by *ca.* 0.8 p.p.m. has been observed. This deshielding, together with changes in olefin coupling constants and a decrease in the olefin stretching frequency,  $\nu(\text{C}=\text{C})$ , in the i.r. spectrum, have been attributed to  $\sigma$ -donation of  $\pi$ -electron density to the metal atom. Weaker deshielding of olefinic protons has been correlated with perturbation by the metal atom in but-3-enyl-lithium<sup>23</sup> and bis(pent-4-enyl)zinc.<sup>24</sup> This technique has also been applied to a number of alkenyltin compounds.<sup>25,26</sup>

Chemical shifts of the olefinic protons ( $\delta_a$  and  $\delta_b$ ) in the titanium derivatives exhibited some variation as the co-ordination number and inductive effect (illustrated by  $\delta_a$ ) of the titanium atom changed. The variation of  $\delta_b$  in the series was small, although it has been noted previously that the chemical shift of this geminal proton shows the greatest sensitivity to a perturbation of the olefinic character.<sup>20</sup> Similarly the multiplet signal due to this proton was identically shaped and spaced in all the spectra, thus indicating little change in the coupling constants of the olefinic protons. However a larger variation in chemical shift of the terminal olefinic protons ( $\delta_a$ ) was apparent in compounds (I) and (IV)—(VI). The monomeric four-co-ordinate derivative (I) is an ideal candidate for titanium-olefin interaction and marked deshielding of  $\delta_a$  (and to a smaller extent of  $\delta_b$ ) occurred relative to the six-co-ordinate dimer (IV). If the deshielding of  $\delta_a$  in compound (I) were the result of titanium-olefin interaction, preferential occupation of vacant co-ordination sites by dimethyl ether and tmde in compounds (VI) and (V) should remove the perturbing influence on olefinic protons in these derivatives. In compound (V) shielding of  $\delta_a$  was indeed apparent, whereas in (VI)  $\delta_a$  was very similar to that in (I). The signal assigned to dimethyl ether in compound (VI) ( $\delta$  3.75 p.p.m.) was shifted considerably downfield relative to that of the free ligand ( $\delta$  3.24 p.p.m.), indicating that dissociation of (VI) is not responsible for this observation. We are unable to rationalise this apparent anomaly simply in terms of the presence or absence of titanium-olefin interaction, and it is considered that other factors, such as variation in the diamagnetic anisotropy<sup>26</sup> of the Ti-O bond and/or the conformation<sup>27</sup> of the but-3-enyloxo-chain in derivatives (I)—(VI) may be having an effect on the chemical shifts of the olefin protons.

*I.R. Spectra.*—The stretching frequency  $\nu(\text{C}=\text{C})$  and low-frequency bands exhibited by the titanium(IV) derivatives of but-3-en-1-ol are listed in Table 3. The small variation in  $\nu(\text{C}=\text{C})$  between 4-methoxybut-1-ene and compounds (I)—(VI) is consistent with negligible olefin-titanium interaction.

The dimeric compound (IV) is considered to contain six-co-ordinate titanium(IV) and two bridging chloride ligands by analogy with  $\{\text{TiCl}_4(\text{POCl}_3)_2\}_2$ .<sup>28</sup> I.r. spectra

<sup>27</sup> J. E. Anderson, personal communication.

<sup>28</sup> C. I. Brändén and I. Lindqvist, *Acta Chem. Scand.*, 1966, **14**, 726.

of these two compounds are very similar in the low-frequency region, with the exception of the presence of additional weak bands in  $\{\text{TiCl}_4(\text{POCl}_3)_2\}_2$  assignable, by comparison with that of the six-co-ordinate monomer  $[\text{TiCl}_4(\text{POCl}_3)_2]$ , to co-ordinated phosphoryl chloride.

TABLE 3  
I.r. data ( $\text{cm}^{-1}$ ) and assignments

Compound	$\nu(\text{C}=\text{C})$	Low-frequency bands [assignments]
$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OMe}$	1 641s 1 638m	
(I)		475vs [ $\nu(\text{TiCl})$ , $e$ ] 395vs, sh, 380vs [ $\nu(\text{TiCl})$ , $a_1$ ]
(II)	1 639s	395s, 370s, 350s, 264m, 234s [ $\nu(\text{TiCl})$ and $\nu(\text{Ti-cp})$ ]
(III)	1 636s	460s [ $\nu(\text{TiMe})$ ] 385vs [ $\nu(\text{Ti-cp})$ ]
(IV)	1 636m, sh, 1 638m	428s, br, 380s, br [ $\nu(\text{TiCl})_{\text{ter}}$ ] 273m [ $\nu(\text{TiCl})_{\text{br}}$ ] 415s, br, 390s, br [ $\nu(\text{TiCl})_{\text{ter}}$ ]
$\{\text{TiCl}_4(\text{POCl}_3)_2\}_2$		265m [ $\nu(\text{TiCl})_{\text{br}}$ ] 394m, 347vs, br, 325s, 300m [ $\nu(\text{TiCl})$ and $\nu(\text{Ti-ligand})$ ]
(V)	1 634m, sh, 1 637m	

The terminal (428 and 380  $\text{cm}^{-1}$ ) and bridging (273  $\text{cm}^{-1}$ ) titanium-chlorine stretching frequencies of compound (IV) are also similar to those of six-co-ordinate chloride-bridged  $\text{Et}_4\text{N}[\text{Ti}_2\text{Cl}_9]$  [ $\nu(\text{TiCl})_{\text{ter}}$  419 and 378  $\text{cm}^{-1}$ ,  $\nu(\text{TiCl})_{\text{br}}$  267 and 229  $\text{cm}^{-1}$ ].<sup>13</sup>

In accord with the low co-ordination number of the titanium atom in compound (I), the highest titanium-chlorine stretching frequency is similar to that observed in titanium tetrachloride and observed bands are assigned to  $e$  (475  $\text{cm}^{-1}$ ) and  $a_1$  (380  $\text{cm}^{-1}$ ) fundamentals.

The i.r. spectrum of compound (III) was simple, with the two most-prominent low-frequency bands being readily assignable to titanium-methyl stretching (460  $\text{cm}^{-1}$ ) and titanium- $\eta$ -cyclopentadienyl vibration (385  $\text{cm}^{-1}$ ).<sup>29</sup> Introduction of a chlorine atom into compound (II) complicates the i.r. spectrum considerably [*cf.*  $[(\text{cp})_2\text{TiCl}_2]$ ],<sup>29</sup> and it is clear that the many bands observed in the 200–400  $\text{cm}^{-1}$  region are admixtures of titanium-chlorine and titanium-ring vibrations.

*Conclusion.*—The results of these and earlier<sup>30</sup> investigations indicate the extreme reluctance of titanium(IV) to co-ordinate to an olefin grouping. Even in the extremely favourable case for olefin co-ordination [compound (I), four-co-ordinate metal atom in a high oxidation state], the olefin grouping remains free. The lack of lability of the methyl group towards the terminal olefin grouping in compound (III) indicates the complexity of the reaction mechanism in the homogeneous catalysis.

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<sup>29</sup> E. Samuel, R. Ferner, and M. Bigorgne, *Inorg. Chem.*, 1973, **12**, 881.

<sup>30</sup> D. A. Baldwin and R. J. H. Clark, *J. Chem. Soc. (A)*, 1971, 1725.