

Journal of Organometallic Chemistry, 150 (1978) 321-344
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Interaction of VCl_4 with α -olefins.
 π -complex formation, with concomitant oligomerisation,
isomerisation and methathesis reactions

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(Received October 6th, 1977)

Summary

Stable π -complexes of olefins with tervalent vanadium have been isolated from the reaction of olefins with vanadium tetrachloride at $-78^\circ C$. The isolation of such complexes is of considerable significance in relation to the frequently proposed formation of intermediate π -complexes in catalytic systems. At higher temperatures concomitant oligomerisation, isomerisation and methathesis reactions were observed, giving rise to a complex array of products whose analysis indicates that insertion into a labile V-Cl bond is a key step in the above catalytic activity.

Transition metal olefin complexes have been frequently cited as intermediates in catalytic systems, notably in Ziegler-Natta polymerisation¹ and metathesis reactions². However in the absence of isolable olefin complexes of catalytically active transition metals there would appear to be little direct evidence for these proposals³. This is not necessarily surprising since it has been suggested⁴ that the instability of these complexes is a

Table 1 - Interaction of VCl_4 with olefins

RUN	Olefin Ligand Structure	mol	Ti or V	MCl_4 mol	Solvent	Temperature °C	Complex Isolated	Observations/Remarks
1.	4-MP-1	0.08	V	0.02	hexane	-78°C	$VCl_3 \cdot 2L \cdot 0.6$	Volatiles distilled off, at low temperature, at -78°C. VCl_4 in distillate-reduction incomplete.
2.	4-MP-1	0.10	V	0.01	hexane	-78°C	$VCl_3 \cdot 1.8$	Volatiles pumped off at low temperature, after 24 hours at -78°C.
3.	4-MP-1	0.15	V	0.005	-	-78°C	-	Allowed to warm up after 24 hrs at -78°C. At about -100°C reaction mixture becomes viscous-indicative of oligomerisation.
4.	4-MP-1	0.15	V	0.01	-	-78°C	-	Oligomerisation occurs after standing at -50°C for 5 hours.
5.	cis-4-MP-2	0.10	V	0.01	hexane	-78°C	$VCl_3 \cdot 1.0$	Allowed to warm to +30°C after 24 hrs at -78°C - no oligomerisation.
6.	3,3-DMP-1	0.08	V	0.01	hexane	-78°C	-	Allowed to warm to +30°C after 1 hour at -78°C - no oligomerisation
7.	2-MP-2	0.08	V	0.01	hexane	-78°C	$VCl_3 \cdot 2L \cdot 0.6$	As for run 6
8.	4-MP-1	0.20	V	0.01	-	30°C	-	On initial mixing brown solution exothermic oligomerisation reaction ensues after 10 minutes. Reaction quenched with MeOT.
9.	4-MP-1	0.20	Ti	0.01	-	30°C	-	Olefin distills into $TiCl_4$ to give yellow solution. Slightly exothermic.
10.	4-MP-1	0.04	V	0.04	benzene	30°C	$VCl_2 \cdot 1L \cdot 0.2H \cdot 1$	Exothermic oligomerisation occurred on mixing. Complex separated from oligomer.

prerequisite of catalytic activity. Consequently, a hitherto unsubstantiated claim in the patent literature⁵ that stable olefin complexes of vanadium are isolable, is of considerable interest—especially since vanadium compounds are active catalysts in co-ordinate anionic polymerisation.

This paper describes an investigation of the interaction of vanadium tetrachloride with olefins, resulting in the synthesis of olefin-complexes and the discovery of oligomerisation, isomerisation and metathesis side reactions. Analysis of reaction products indicates that olefin insertion into a vanadium chlorine bond is a key step in the catalytic activity. Similar insertion reactions could explain the catalytic activity of other transition metal halides in co-ordinate polymerisation, isomerisation and metathesis reactions, in the absence of co-catalysts.

RESULTS and DISCUSSION

Synthesis of vanadium olefin complexes

In contrast to earlier claims⁵, complexes of unhindered terminal olefins could only be prepared under carefully defined conditions (See Table 1). In every attempt to prepare complexes of 4-methylpentene-1 (4-MP-1) at room

Table 1(a) - Interaction of complexes with solvents

Solvent	Observation
Benzene, hexane	Insoluble
Acetonitrile	Dissolves immediately at room temperature with formation of light green crystals of $VCl_3 \cdot 3CH_3CN$
Ethanol	Dissolves immediately with formation of oily oligomer, and coloured solution.

temperature, a vigorous exothermic oligomerisation ensued, and the vanadium compound was converted to either uncomplexed VCl_3 (run 8) or, had very low hydrocarbon content (run 10).

Isolable vanadium complexes of 4-MP-1 not contaminated with oligomers, and with stoichiometries approaching $VCl_3 \cdot 2L$ were only obtained when the two components were reacted at $-78^\circ C$ for 24 hr and all volatiles pumped off at low temperatures (Run 2).

The description of the preparation and method of isolation of VCl_3 complexes in the patent literature⁵ suggests that complex formation was accompanied by oligomerisation⁶.

On the other hand, complexes of internal olefins (Run 5) and sterically hindered α -olefins (Run 6) could be prepared readily without side reactions although again stoichiometries were variable and in every case less than 2:1.

In company with other tervalent vanadium compounds, the olefin complexes are sensitive to both oxygen and moisture, but samples sealed under vacuum show no visual decomposition after several months. In addition, the complexes show unexpected thermal stability in the light of their predicted formation as transients. Thus the 4-MP-1 complex decomposes only slowly to yield a volatile colourless oil, and a solid brown residue after heating for several hours at $150^\circ C$ under vacuum.

Characterisation

Attempts to unambiguously characterise the reaction products have been hindered because of difficulties encountered with purification and in obtaining suitable solvent systems, *vide infra*. Nevertheless the evidence presented below strongly points towards the formation of stable vanadium-olefin complexes, *viz*:-

a) Colour

The light brown colour of the complexes is in complete contrast to the violet colouration of VCl_3 . Nevertheless, the valence state of the products has been shown to be exclusively V^{III} , and furthermore the Cl/V

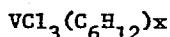
ratios are in all cases close to 3. These observations clearly support the formation of a VCl_3 complex.

b) i.r. analysis

A distinct double bond absorption is observable at 1595 cm^{-1} , indicative of the presence of a complexed olefin molecule - the C=C stretch is lowered by about 50 cm^{-1} compared with the free olefin.

c) Elemental analysis

The analyses of the complexes correspond to an empirical formula:



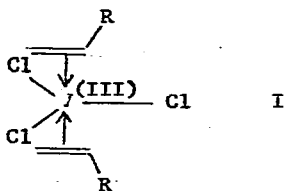
where, in certain cases x approaches 2. The variability of x on preparative conditions and the lack of an exact stoichiometric ratio may well reflect the presence of impurities such as uncomplexed VCl_3 , which it has not proved possible to remove by standard purification techniques, or, alternatively it may represent incomplete co-ordination by rather bulky olefin ligands. Notwithstanding the above, the observed empirical formulas are suggestive of the formation of an olefin complex.

d) Interaction with solvents

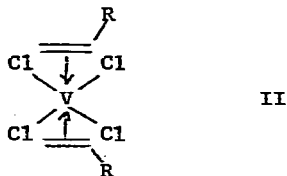
Attempts to discover a suitable solvent system for the above complexes were unsuccessful since the solvents examined proved to be either inert or to solubilise the complex with concomitant displacement of the olefin ligand (Table 1(a)). The observed resistance of the complexes to dissolution in hydrocarbon solvents clearly indicates that the olefin ligand is chemically bound in the complex. On the other hand the action of acetonitrile (Table 1(a)) demonstrates that the compound is unusually reactive since the normal preparation of $VCl_3 \cdot 3CH_3CN$ involves refluxing VCl_3 in acetonitrile for several hours⁷, whereas, the olefin ligand is almost immediately displaced from the complex at room temperature.

Structure

Since the only known⁷ neutral complexes of vanadium trichloride with unidentate ligands are of the type VCl_3L_2 and VCl_3L_3 it seems likely that stoichiometries of less than 2 represent incomplete formation of the olefin complex rather than a unique species of the type $VCl_3.L$ as suggested earlier⁵. By analogy with vanadium compounds of similar stoichiometry the olefin complexes would be expected to exhibit a trigonal bipyramidal structure (I)

*Reaction pathway*

It seems likely that the reaction of VCl_4 with an olefin leads initially to the rapid formation of tetravalent complexes such as II. This is evidenced by the immediate colour change on mixing the two components.



The trivalent compound is then formed by slow reduction of complex II with simultaneous loss of chlorine. Reduction of tetravalent vanadium has previously been observed on reaction of VCl_4 with excess dialkyl sulphides⁸, alkyl cyanides⁹ and tertiary amines¹⁰.

Synthesis of Titanium olefin complexes

A preliminary experiment was carried out with titanium tetrachloride to establish whether its reactivity was similar to the vanadium analogue. In contrast to the vanadium system no facile reduction of the tetravalent olefin complex of titanium occurs. Thus on exposing titanium tetrachloride

to 4-MP-1 vapour under vacuum, the olefin rapidly distills⁵² into the titanium tetrachloride; complex formation being evidenced by the resultant yellow colouration. However, on standing at room temperature for several days no further reaction or reduction was apparent. Similar observations have been made by previous workers, who have reported complex formation between $TiCl_4$ and; cis and trans stilbene¹², isobutene¹³, 1,1-diphenylethylene¹⁴, 1-hexene and cyclohexene¹⁵, and other substituted olefins¹⁶.

Oligomerisation

Since 4-MP-1 is susceptible to cationic polymerisation and since the activity of VCl_4 should be typical of *classical* cationic initiators such as $TiCl_4$ and $AlCl_3$ it would seem reasonable to assume that the observed oligomerisation reactions occur via cationic intermediates. However, there are certain features which are indicative of an alternative mechanism, *viz.*;

1. Cationic initiation by metal halides is generally¹⁷ thought to require co-catalysis by proton donors such as water. In these experiments the olefin and solvent water contents were below 0.1 ppm¹⁸.
2. Oligomerisation was not initiated at $-78^\circ C$, whereas, rapid polymerisation at low temperature is a characteristic feature of many cationic systems¹⁹.
3. Oligomerisation of internal and hindered olefins does not occur, whereas, such reactions have been reported for cationic systems¹⁹.
4. The concomitant isomerisation reactions, *vide infra*, show a strong resemblance to previously reported oligomerisation reactions with a titanium based catalyst system, which were shown to follow an anionic mechanism^{20a}.
5. The presence of alkanes in the reaction mixture, *vide infra*, is indicative of the formation of organo-metallic intermediates.

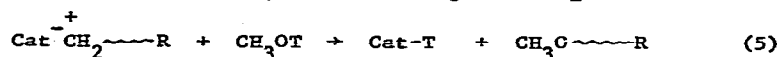
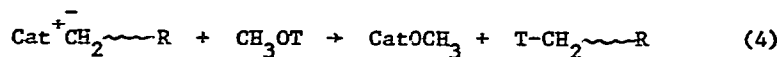
In order to probe the nature of the oligomerisation mechanism, recourse was made to the *classical* diagnostic test of quenching with tritium labelled alcohols²¹. Labelling of the oligomer should be indicative of an anionic

Table 2 - Analysis of Oligomer

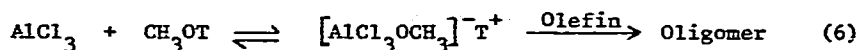
Oligomer Source	% Cl	$\bar{M}_n(\text{Cl})^a$	\bar{M}_n^b	Activity (dpm/g)	$\bar{M}_n(\text{T})^c$
Run 3	1.4	2,500	1,270	8.4×10^6	42,000
Run 8	0.3	11,600	n.d.	-	-
AlCl_3	n.d.	-	n.d.	3.7×10^7	9,500

- a - Number average molecular weight calculated assuming one Cl atom per chain.
- b - Determined by vapour pressure osmometry.
- c - Number average molecular weight calculated assuming one label per chain. Details of calculation given in reference 21.

mechanism (eq. 4), whereas, the absence of label should result from a cationic mechanism (eqn. 5).



Quenching of the vanadium catalysed oligomerisation system resulted in highly active oligomers (Table 2). However, a control experiment employing AlCl_3 as initiator, where the monomer was not rigorously dried²², showed similar incorporation. It must be concluded that the alcohol quench method is ambiguous under these circumstances, where the monomer is susceptible to cationic polymerisation. Probably active oligomers may be formed during the quench reaction, involving the labelled alcohol as co-initiator, e.g.;

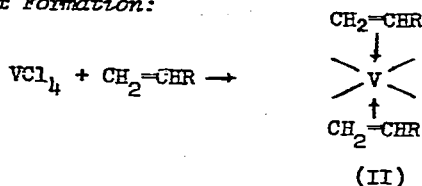


Although the possibility of a cationic mechanism cannot be excluded, the features of the oligomerisation and in particular the nature of the volatile

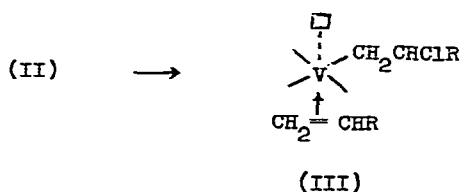
reaction products formed concomitantly (Table 3) are more readily accountable by scheme 1.

Scheme 1 - Oligomerisation

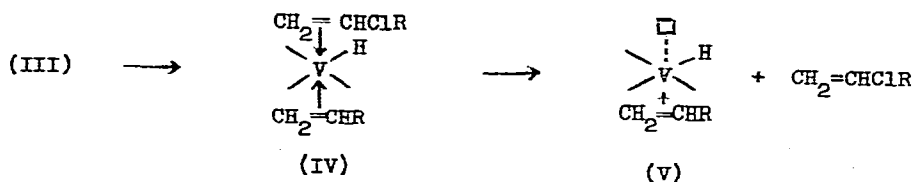
1. *Complex Formation:*



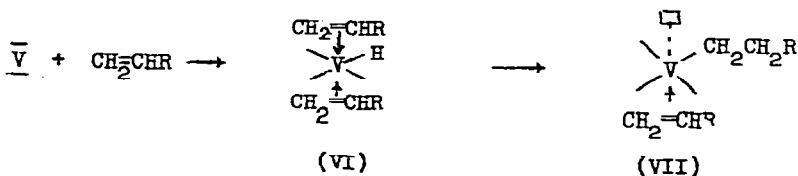
2. *Insertion into V-Cl bond:*



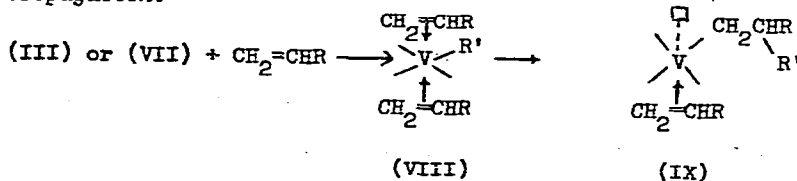
3. *Displacement:*



4. *Insertion into V-H bond:*



5. *Propagation:*



6. *Reduction:*

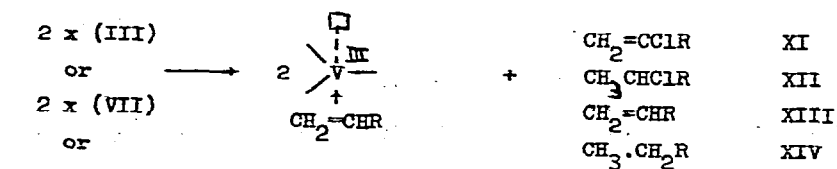


Table 3 - Analysis of volatiles from run 3

Compound	% ^a	Compound
1. Isobutene	trace	8. 2-methylpentene-2 (2-MP-2)
2. 2-methyl butane	1	9. cis or trans-hexene-3
3. 2-methylbutene-1 ^b or trans-pentene-2	trace	10. 2,3-dimethylbutene-2 (2,3-DMB-2)
4. 2-methylbutene-2 (2-MB-2)	1	11. Unidentified heptene isomer ^d
5. 2-methylpentene	11	12. 2-chloro-4-methylpentane
6. 4-methylpentene-1 ^c (4-MP-1)	40	13. 2-chloro-4-methylpentene-1
7. 2-methylpentene-1 (2-MP-1)	2	14. 1,2-dichloro-4-methylpentane

a - This does not include isomers less volatile than 1,2-dichloro-4-methylpentane which were present but not identified.

b - It was not possible to distinguish these isomers.

c - Cis-4-methylpentene-2, may be present in small amounts under this p

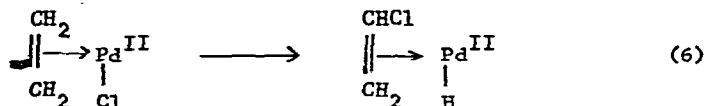
d - C₇ confirmed by ms analysis.

Insertion

The key step in the scheme is the proposed insertion into a V-Cl bond which appears to be without precedent for Gp. IV and V transition metals. This reaction is analogous to the well documented²⁴ insertion of olefins into M-C bonds. Supporting evidence is to be found in the chlorine content of the oligomers (Table 2) and the formation of chloro¹¹olefin (XI) and alkyl chloride (XII)²³. Furthermore, the formation of some such organometallic intermediate is clearly indicated by the presence of alkane.

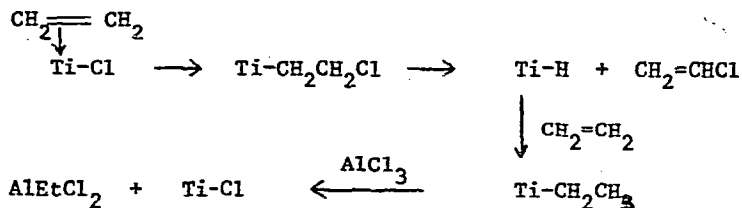
The literature does contain some evidence for similar reactions with

hydride formation in a palladium catalyst system by nucleophilic attack of Cl^- ion on the coordinated olefin. This idea was later endorsed by Cramer and Lindsey²⁶ who formulated it schematically as shown in 6.



The net effect of this is clearly indistinguishable from an olefin insertion into a Pd-Cl bond followed by a displacement step. Support for this mechanism was deduced from the presence of chloroolefin in the product mixture. Similar experimental evidence was provided by Tayim²⁷ who showed that vinyl chloride could be produced by the interaction of ethylene with a PdCl_2 catalyst. Tayim postulated a mechanism including insertion and displacement steps similar to the present proposals.

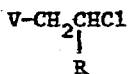
All these examples are with palladium, and it would be dangerous to infer too much about insertion into V-Cl bonds from this evidence. However, there is a certain amount of circumstantial evidence that insertion can occur into Ti-Cl bonds. Thus recently the polymerisation of ethylene by the catalyst system $\text{TiCl}_4/\text{AlCl}_3/\text{Al}$ has been reported²⁸. Analysis of volatiles showed the presence of AlEtCl_2 , AlEt_2Cl , and AlEt_3 , which could have been formed by steps such as:



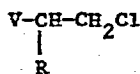
An alternative route could involve insertion into an Al-Cl bond²⁹.

Direct of insertion

The formation of exclusively³⁰ 2-chloro-4-methylpentene-1 and 2-chloro-4-methylpentane indicates that reaction occurs by primary (P) rather than secondary (S) insertion.



(P)



(S)

This is in contrast to the findings of Takegami et al^{31a-c} who observed that olefin insertion into V-Et bonds at -78°C occurred predominantly by secondary insertion.

Displacement step The displacement of the alkyl ligand as olefin is considered to occur by β -hydrogen abstraction - an essential feature of isomerisation and oligomerisation mechanisms^{24,32}.

Insertion into V-H bond Transition metal hydrides form active homogeneous catalysts for hydrogenation, isomerisation, and dimerisation reactions³³. The common feature of these reactions is olefin insertion into a M-H bond.

Indirect evidence for the formation of vanadium hydrides is provided by the analysis of the vanadium complex isolated from run 10, which shows that the H content is considerably higher than that required for the ratio C_6H_{12} . Furthermore, the formation of alkanes (Table 3) is most reasonably explained by the intermediacy of such hydride species.

Propagation

The growth step in the oligomerisation reaction can be considered to occur by insertion into a V-C bond. Analogous propagation steps have been proposed for the oligomerisation of ethylene by $\text{CH}_3\text{Ti}^{\text{IV}}\text{Cl}_3$ ^{20b} and $\text{CH}_3\text{Ti}^{\text{III}}\text{Cl}_2$ ^{20c}, where insertions was considered to occur into Ti-C bonds.

The molecular weight of the oligomer should be controlled by the displacement and reduction steps. Molecular weight determination (Table 2) shows that an average of 15 growth steps occur before propagation is interrupted by either reduction or displacement. Furthermore, comparison of the molecular weight determined by vapour pressure osmometry with that calculated from the chlorine content (Table 2) shows that there is on average one combined chlorine atom for every two oligomers. This must mean that

insertion into V-H bonds is important for oligomerisation initiation, in addition to the V-Cl insertion.

The absence of oligomerisation reactions with the internal olefins *cis*-4-methylpentene-2 (*cis*-4-MP-2) and 2-methylbutene-2 (2-MB2) and with the olefin 3,3-dimethylbutene-1 (3,3-DMB-1) can be ascribed to the very slow insertion of these sterically hindered olefins, into either the initial V-Cl bond, or, the V-C bond, compared to the rate of reduction of the V^{IV} olefin complex to the apparently inactive V^{III} complex. Evidence that the initial insertion does occur in the case of *cis*-4-MP-2 is provided by the detection of alkyl chlorides in the volatiles from the reaction product.

Although polymerisation of internal olefins has been achieved with conventional Ziegler-Natta systems it is generally believed³⁴ that a prior isomerisation step to the α -olefin is necessary. This supports the contention that insertion of the hindered olefin into the V-C bond is either very slow or completely inhibited.

Reduction The formation of significant proportions of alkanes and alkyl chlorides (Table 3) is indicative of reduction reactions. It is important to note that these components were present in the colourless volatiles distilled from the oligomerisation mixture under vacuum *before* quenching with alcohol, and consequently are formed³⁵ during the course of reaction and not by reaction of the vanadium alkyl with quench agent.

Alkane formation, before quenching, has recently been reported in the isomerisation polymerisation³⁶ of 4-methylpentene-2 with a $\text{TiCl}_3/\text{AlR}_3$ catalyst and in the polymerisation³⁷ of vinylcyclohexane with $\text{TiCl}_4/\text{AlR}_3$ catalyst. It was speculated³⁷ that alkane formation occurred through disproportionation of an alkylated titanium intermediate.

Olivé and Olivé¹¹ have suggested that alkane formation accompanying reduction of the transition metal occurs via a bimolecular mechanism and this model forms the basis of the proposed reduction step in this system.

The presence of alkanes provides strong support for the contention that oligomerisation proceeds via an anionic rather than a cationic mechanism.

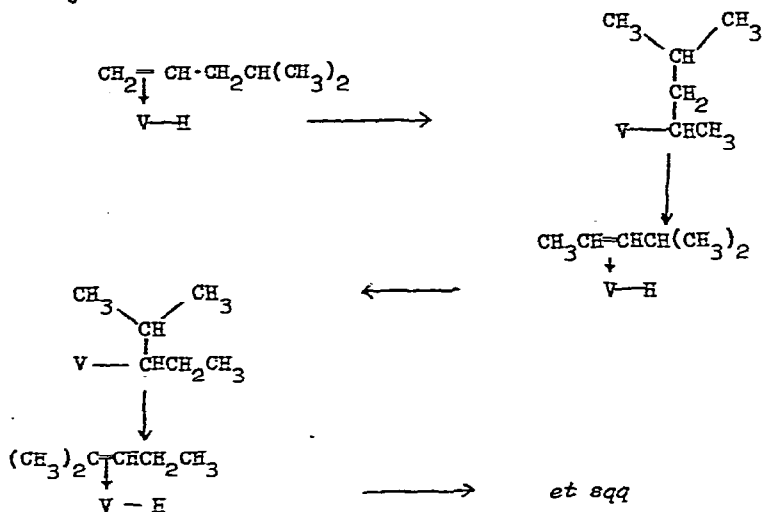
Isomerisation

The positive identification of appreciable quantities of 2-methylpentene-2 (2-MP-2) and 2-methylpentene-1 (2-MP-1) in the reaction mixture clearly demonstrates the presence of isomerisation reactions catalysed by VCl_4 .

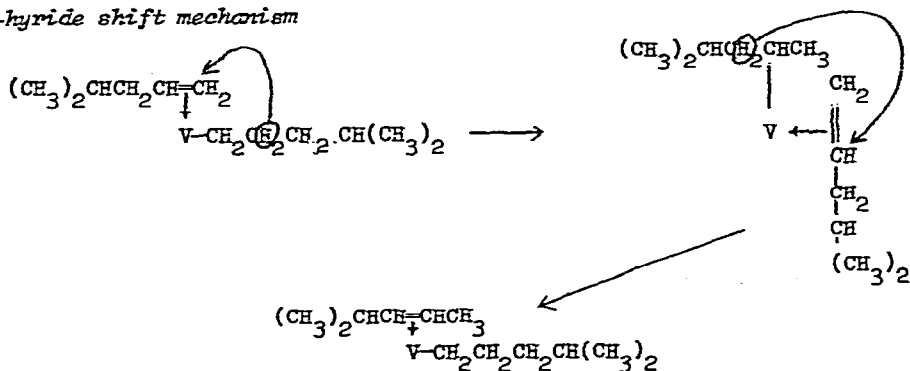
Isomerisation could proceed via a metal hydride addition and elimination mechanism²⁵ since the generation of vanadium hydride species is consistent with the scheme for oligomerisation (*vide supra*). For isomerisation to

Scheme 2 - Isomerisation

(a) Metal hydride addition and elimination:



(b) β -hydride shift mechanism



Note: For clarity non-reacting ligands are omitted from the above structures.

occur insertion would be necessary to give a secondary vanadium alkyl. Initial isomerisation leads to the formation of cis and trans 4-MP-2, but subsequent isomerisation of these isomers will result in the formation of 2-MP-2 and 2-MP-1 (Scheme 2(a)).

An alternative mechanism, which was suggested by Bestian and Claus^{20a} to explain isomerisation during the course of oligomerisation reactions could also be applicable and is shown schematically (2(b)). This scheme involves a β -hydride shift from the alkyl group to the α -carbon of the complexed olefin and avoids the necessity of a secondary insertion reaction.

The proportions of olefin isomers determined in this study differ markedly from those reported in earlier studies of 4-MP-1^{32,38-41} isomerisations. In particular the absence of trans 4-MP-2 and possibly⁴² cis 4-MP-2 seems conspicuous. This is probably attributable to the non-equilibrium nature of the isomerisation due to rapid deactivation of the catalyst and preferential removal of certain olefin isomers in oligomerisation, reduction and metathesis reactions.

It appears significant that olefin isomerisation has been reported^{37,43} with TiCl_3 , and that the rate of isomerisation is accelerated by the addition of AlEt_3 ⁴³. This may suggest the involvement of a titanium alkyl as in the β -hydride shift mechanism, or, alternatively the titanium alkyl may be a precursor of a titanium hydride species. The former is probably the more likely since chain transfer with monomer (analogous to the β -hydride shift) is a more important molecular weight regulating step than spontaneous termination (hydride formation) in Ziegler-Natta polymerisation at moderate temperatures⁴⁴.

Isomerisation does not appear to occur with $\text{VCl}_3/\text{AlR}_3$ based catalyst systems, or, with $\text{TiCl}_4/\text{AlR}_3$ systems under conditions where reduction to Ti^{III} is remote³⁷. Thus it would appear that only Ti^{III} and V^{IV} systems are catalytically active in isomerisation and this in turn points to the importance of a d' configuration in these reactions.

Methathesis

The presence of isobutene, C₅ olefins and alkanes, C₆ olefins with skeletal rearrangements and C₇ olefins provide ample proof of a VCl₄ catalysed methathesis reaction⁴⁵. Although methathesis reactions have been intensively investigated over the past decade^{2,46-48}, the vanadium system presents several novel features. The vanadium methathesis catalyst appears to be the first reported system involving Gp. V elements, and is one of the few catalysts which do not require activation by an organometallic promoter⁴⁹. Furthermore, the vanadium system has significant activity at relatively low temperatures (c.a. -20°C) compared to those necessary for many methathesis reactions. The methathesis reaction is of course not selective in that concomitant oligomerisation and isomerisation occur.

The activity of the VCl₄ system may be due to the ready formation of vanadium alkyl species, *vide supra*, since it has been suggested that σ -bonded alkyl species can undergo transformation into carbene metal intermediates which many authors believe are key intermediates in methathesis reactions.

The formation of the observed methathesis products may be rationalised by Scheme 3.

Since the rate of olefin methathesis is sterically controlled, reactions such as 5 should be relatively important, assuming that *cis* and *trans* 4-MP-2 are formed in significant proportions during the isomerisation reactions. The failure to detect 3-methylbutene-1 in the product mixture may result from the facile isomerisation of this olefin to 2-methylbutene-2 and this in fact may be the source of that olefin rather than the methathesis step outlined in reaction 2.

The absence of significant quantities of α -olefins formed by methathesis, may also in part be explained by the preferential oligomerisation of these olefins.

Experimental Section

Materials

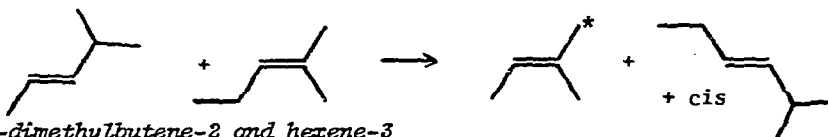
Olefins, hexane and benzene were all high purity grades which were

Scheme 3 - Methathesis

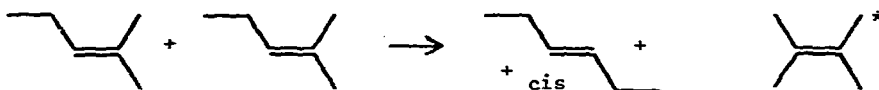
1. Isobutene



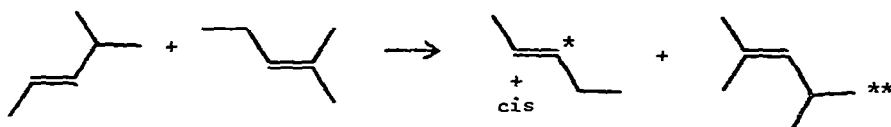
2. 2-methylbutene-2



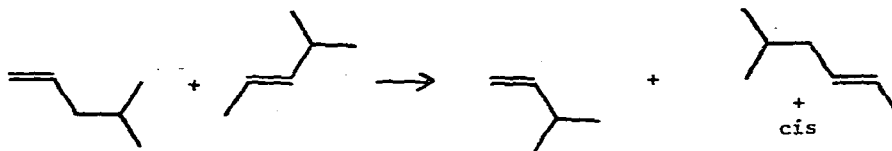
3. 2,3-dimethylbutene-2 and hexene-3



4. pentene-2



5. Probable reaction



*Note: These olefins were positively identified. ** C₇ olefins were detected in the reaction mixture but not unambiguously identified.

further purified by fractionation from CaH₂ and storage over 4A molecular sieves⁵¹. Anhydrous TiCl₄ (ROC/RIC) of 99.95% purity was used as received. Anhydrous VCl₄ (ROC/RIC) was purified by vacuum distillation.

Reaction of olefins with metal halides

a) *At low temperatures* Experiments were carried out in the all glass apparatus shown schematically in Figure 1. The reaction vessel was evacuated overnight at 10⁻⁴ mmHg, and flamed out before transferring to a drybox. Appropriate amounts of metal halide were syringed into sidearm A, the reaction

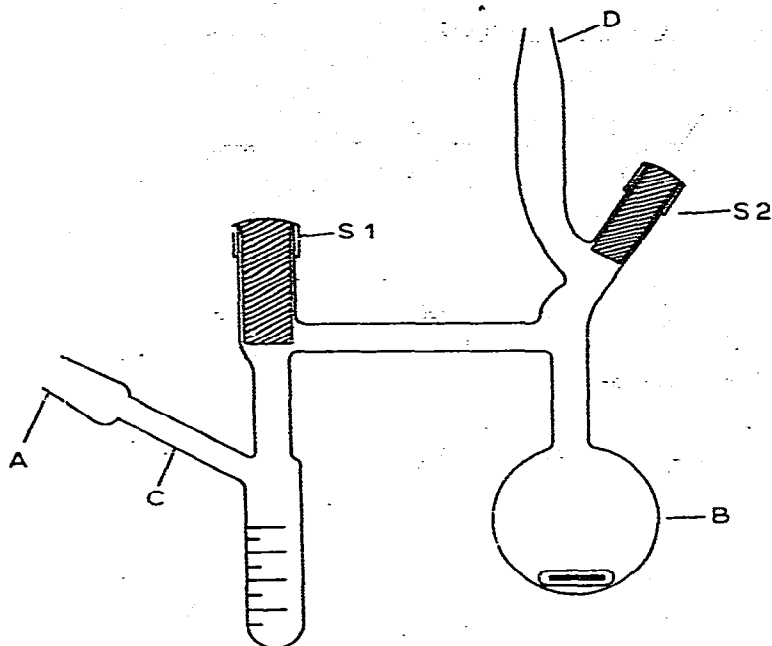


Figure: 1 Reaction vessel

vessel returned to the vacuum line and sealed at C. A measured quantity of halide was distilled into B, and then pumped at -78°C to remove dissolved chlorine. Olefin or olefin/hexane mixtures (which had been further dried by stirring over CaH_2 on the vacuum line) were then distilled into B, via D, at -78°C .

After reaction for the periods and temperatures indicated (*vide supra*), volatiles were distilled into a liquid nitrogen trap, through D, and products pumped dry. Solid products, where isolated, were washed with dry hexane and pumped under vacuum overnight.

RUN 1:- 0.08 mol of 4-MP-1 and 0.02 mol VCl_4 in hexane, were reacted at -78°C for 1 hour. Volatiles were pumped off whilst maintaining the reaction mixture at about -40°C . A light-brown amorphous solid was obtained. Analysis: V^{III} , 25.6; C, 20.65; H, 3.60; Cl, 50.1.

On standing (several days) a light brown solid separated from the coloured distillate, which had been stored under vacuum. Analysis: V^{III} , 18.2; Cl, 37.1; C, 32.77; H, 6.10;

RUN 2:- 0.1 mol of 4-MP-1 and 0.01 mol VCl_4 were reacted at $-78^\circ C$, for 24 hours, in hexane. Volatiles pumped off below $-40^\circ C$. Light brown amorphous solid obtained. Analysis: V^{III} , 16.3; Cl, 34.2; C, 40.2; H, 7.1. i.r. (C=C) nujol 1595 cm^{-1} . Attempted purification of product by vacuum sublimation was unsuccessful. Heating for several hours at $150^\circ C$, at 5×10^{-3} mmHg gave no sublimate product. Complex slowly decomposes with release of colourless oil. Residue analysis; C, 24.02; H, 3.76; shows loss of ligand after prolonged heating. M.Pt. $> 350^\circ C$. Complex begins to decompose at $250^\circ C$ with loss of oil.

RUN 3:- 0.15 mol of 4-MP-1 and 0.005 mol VCl_4 were reacted at $-78^\circ C$, for 24 hours with no added solvent. The red-brown reaction mixture was allowed to warm up slowly to room temperature. At $-50^\circ C$, a sample of volatiles was coloured showing the presence of unreduced V^{IV} . At about $-10^\circ C$ the reaction mixture suddenly *bumped* and became viscous. At room temperature the mixture was a dark brown viscous mass showing the presence of V^{III} complex and oligomer. Volatiles (3 ml) distilled from the mixture were colourless, showing the absence of V^{IV} , and were subjected to g.l.c. analysis.

The viscous reaction mixture was diluted with 40/60 $^\circ C$ petroleum ether and poured into a large excess of methanol. The brown viscous oil which separated was purified by redissolving in pet. ether and subsequent chromatography on an alumina column to yield 8.7 g of colourless oligomer. M.W. = 1270 (Vapour pressure osmometry, $CHCl_3$). Analysis: Cl, 1.4

RUN 4:- 0.15 mol of 4-MP-1 and 0.01 mol VCl_4 , with no added solvent, were distilled together at $-78^\circ C$ and subsequently maintained at $-50^\circ C$ for 5 hours, and then for 20 hours at $-78^\circ C$. After 20 hours at $-78^\circ C$ the dark brown reaction mixture had become viscous. The products were not isolated.

RUN 5:- 0.1 mol of cis-4-MP-2 and 0.01 mol of VCl_4 , were reacted at $-78^\circ C$ for 24 hours, in the presence of hexane. The red-brown reaction mixture was warmed to room temperature, and was left for 2 days at room temperature during which time a light brown solid settled out. Analysis: V, 15.8; Cl, 36.2; C, 41.03; H, 6.88. i.r. (C=C) nujol 1600 cm^{-1} .

RUN 6:- 0.08 mol of 3,3-DMB-1 and 0.01 mol VCl_4 were reacted at $-78^\circ C$ for 1 hour in the presence of hexane. The reaction mixture was warmed to room temperature during which time a light brown solid settled out.

RUN 7:- As for run 6 except with 2-MB-2. Analysis: V (by diff.), 24.92; Cl, 55.0; C, 17.03; H, 3.05.

b) At ambient temperatures

Experiments were carried out in the apparatus already described. Metal halide was introduced into A and the vessel sealed at C. With stopcock S1 closed, olefin was distilled into B. Stopcock S2 was then closed and the apparatus removed from the vacuum line. The reagents were mixed by opening stopcock S1 and pouring the metal halide into the olefin.

RUN 8:- On slowly adding 0.01 mol of VCl_4 to a stirred 0.2 mol of 4-MP-1, a deep red-brown coloured solution was formed. There was no immediate precipitate and no heat liberated. After 10 min, with no visible change the reaction mixture was perceptibly warm. After 15 min a violent exothermic oligomerisation reaction ensued. The resultant product mixture was violet in colour indicating reduction of vanadium to uncomplexed V^{III} .

The reaction vessel was transferred to a dry box and the mixture quenched by addition of 3H labelled methanol. The oligomer was subsequently isolated and purified as described above, and then assayed by liquid scintillation counting as described elsewhere²¹.

RUN 9:- With 0.01 mol of $TiCl_4$ in A, and 0.2 mol of 4-MP-1 in B, stopcock S1 was opened. Immediately alkene distilled spontaneously⁵² into the $TiCl_4$ arm to yield a yellow coloured solution. The reaction was mildly exothermic (c.a., $+15^\circ C$). The increase in volume of the mixture was about 1 ml - equivalent to 0.008 mol of alkene, assuming additive volumes. On mixing the contents of A with the unreacted olefin a clear yellow solution resulted and a slight cooling of the mixture was observed. No precipitate occurred on

standing for 5 days and attempts to distil out the excess olefin under vacuum led to concomitant distillation of the coloured product.

RUN 10:-

This experiment was carried out in the dry box. 0.04 mol of 4-MP-1 was added to a solution of 0.04 mol of VCl_4 in benzene. After a few minutes an exothermic reaction occurred, leading to an increase in viscosity of the medium, and a brown precipitate. The precipitate was filtered off and freed from contamination with oligomer by repeated washing with dry benzene. Analysis: V (by diff.) 31.96; Cl, 53.90; C, 11.54; H, 2.60.

G.L.C. Analysis

Volatiles from run 3 and 5 were analysed by glc on the following columns; 10', 25%, dinonyl phthalate on chromosorb W at 100°C; 10', 20% $AgNO_3$ /glycol on chromosorb W at 35°C; 10', 5% SE30 on chromosorb W at 50°C and 100°C, using a Varian Aerograph Series 1800 Preparative Instrument.

Components were identified by comparison with the retention of standard compounds on all three columns. The identity of crucial components was further checked by gc-ms analyses which were run at 70 eV with an A.E.I. MS3074 Double Beam instrument fitted with a Pye Unicam Series 104 gas chromatograph unit.

Elemental analysis

Analysis of C, H and Cl were performed by a professional analyst. V^{III} content was determined by a potentiometric $KMnO_4$ titration as described in the literature⁵³.

Acknowledgements

The author wishes to thank the University of Malaya for funding this work under Vote F, and British Petroleum for supply of 4-methylpentene-1.

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$$\text{CH}_2=\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2 + \text{VCl}_4 \rightarrow \overset{+}{\text{CH}_2=\text{CH}-\text{CHCH}(\text{CH}_3)} + \text{VCl}_4\text{H}^-$$

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