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CATALYTIC PROPERTIES OF E^{IVB}-SUBSTITUTED TUNGSTEN CARBONYL COMPLEXES (E^{IVB} = Ge, Sn) IMMOBILIZED ON A SILICA SUPPORT

J.P. VAN LINTHOUDT, L. DELMULLE and G.P. VAN DER KELEN
Laboratory for General and Inorganic Chemistry-B, University of Gent, Krijgslaan 271, B-9000 Gent (Belgium)

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Summary

The catalytic activity in olefin disproportionation of a 3,3-dimethyl-1-butene substrate has been investigated for a series of E^{IVB}—$W(CO)_3C_5H_5$ species (E^{IVB} = Ge, Sn) chemically bonded to a high surface silica carrier. Different product distributions and conversion factors were obtained by thermal and UV activation of the catalysts, whereas variation of the E^{IVB} element had little effect. In all cases, isomerization was observed rather than disproportionation, probably because of steric interaction between the rather bulky t-Bu groups at the active W sites.

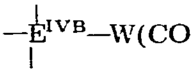
I. Introduction

It is well known that many transition metal complexes and ions exhibit catalytic activities primarily due to the availability of empty *d*-orbitals which permit several oxidation states and coordination numbers and allow coordination of neutral molecules. Furthermore, certain relationships have been established between the nature of the metal and the type of reaction for which it is most effective. Tungsten and molybdenum derivatives seem to be particularly active catalysts for the disproportionation of olefins (metathesis) [1]. The initial catalysts disclosed by Banks and Bailey [2] were all of the heterogeneous type, and consisted of W or Mo oxides and hexacarbonyls physically fixed on alumina supports. Later, several soluble disporportionation catalysts of the Ziegler-type were developed in which a transition metal halide (mostly WCl_6) interacts with an alkylaluminium halide in the presence of oxygen-containing compounds such as phenols or alcohols [3]. However, compounds based on W or Mo are not the only active catalysts in the disporportionation of alkenes. Thus it was recently shown that Re_2O_7 promoted by a small amount of $SnMe_4$ is a very active and selective catalyst for the disporportionation of olefins carrying functional heteroatom groups [4].

One of the problems encountered in olefin metathesis is the interference from side reactions of the polymerization, isomerization, or even Friedel-Crafts alkylation type, the last only occurring when soluble multi-component W/Al catalyst systems are used.

It was found that some catalyst modifications, e.g. incorporating minor amounts of alkali or alkaline earth metal ions [5,6] led to a suppression of double bond isomerization while others, such as MgO added to a $WO_3.SiO_2$ catalyst, resulted in an increased double bond isomerization [7]. However, it must be emphasized that double bond migration does not always have a negative influence on the disproportionation yield during a metathetical process. Indeed, in the case of symmetrical olefins double bond migration has to occur prior to disproportionation because symmetrical alkenes cannot yield new olefins by metathesis.

It was in the light of these facts and problems that we investigated the catalytic activity of a series of bifunctional catalyst systems based upon W, Ge and Sn directly bonded to each other by σ-bonds:



$—E^{IVB}—W(CO)_3Cp$, E^{IVB} = Ge, Sn; Cp = η^5-C_5H_5

Instead of anchoring the catalysts on a solid support by physical adsorption like Banks [1], we rather preferred to fix them by a chemical reaction in order to obtain a better resistance to elution.

II. Experimental

1. Support

A high surface area (200 ± 25 m^2 g^{-1} BETT) silica carrier of the Aerosiltype, supplied by Degussa, was used. This support had to be preheated at 110°C and 1 atmosphere during 12 hours before use in order to remove physically adsorbed water. After this, the concentration of active silanol groups amounts to about 2.6 $\not\equiv Si-OH$ units/100 $Å^2$ [8].

2. Catalyst preparation and anchoring

Two different reaction pathways have been followed:

A. Reaction between Aerosil and $ClE^{IVB}[W(CO)_3Cp]_3$

Reactions: $2\ C_5H_6 + 2\ Na \rightarrow 2\ NaC_5H_5 + H_2\uparrow$

$$NaC_5H_5 + W(CO)_6 \rightarrow NaW(CO)_3C_5H_5 + 3\ CO\uparrow$$

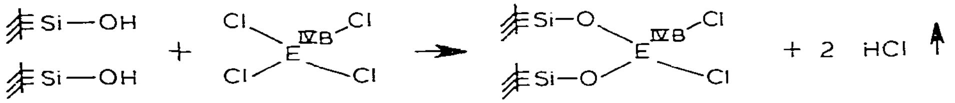
$$SnCl_4 + 3\ NaW(CO)_3C_5H_5 \rightarrow ClSn[W(CO)_3C_5H_5]_3 + 3\ NaCl\downarrow$$

$$\not\equiv Si-OH + ClSn\left[W(CO)_3C_5H_5\right]_3 \longrightarrow \not\equiv Si-O-Sn\left[W(CO)_3C_5H_5\right]_3 + HCl\uparrow$$

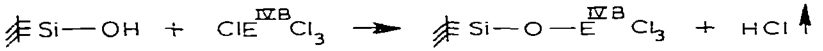
Procedure: To a solution of 8.63 mmol $SnCl_4$ or 8.63 mmol $GeCl_4$ in n-Bu_2O is added a suspension of $NaW(CO)_3Cp$ in THF prepared by the reaction of NaC_5H_5 with 25.89 mmol $W(CO)_6$. After refluxing this mixture during 60 hours, 10 g of predried Aerosil (±8.63 mmol $\not\equiv Si-OH$) is added and the pulpy mixture is kept for one week with gentle heating under a N_2 atmosphere. The supernatant liquid layer is separated by centrifugation and decantation from the solid phase, and the latter is washed several times with an acetone water mixture and finally with pure acetone. The catalyst is then dried under vacuo and the resulting lumps are pulverized in a mortar to yield a fine yellow powder.

B. Reaction between NaW(CO)₃Cp and Aerosil pretreated with $E^{IVB}Cl_4$ solutions

First, 10 g of predried Aerosil is allowed to react with 8.63 mmol of $SnCl_4$ or $GeCl_4$ in n-Bu_2O during 4 days at 60°C. This gives a light-grey coating of the silica surface. During this treatment two possible reactions can take place, depending upon the distance between neighbouring silanol groups at the silica surface:



or



Next, a suspension of freshly prepared $NaW(CO)_3Cp$ in THF is added and the suspension is well-stirred and heated at 60°C during 5 days. Finally, the catalyst is isolated and purified as described in section II.2.A.

3. Elemental, IR spectroscopic and thermogravimetric analysis of the catalysts before use

The W weight content was determined by the AAS technique and varied from 3.57% in the Ge compounds to 6.12% in the Sn derivatives. Corresponding to a weight content of 6.12% W, a C weight content of 3.73% was found by elemental analysis indicating a W to C atomic ratio of 1 : 9, which agrees quite well with the theoretical value of 1 : 8.

The thermogravimetric recordings of the $\not\equiv Si-O-Sn[W(CO)_3Cp]_3$ type catalysts were characteristic of a two step decomposition as depicted in Fig. 1. A first step is observed between 200°C and 300°C, a second between 380°C and 570°C. Since the latter is about half as high as the former and taking into ac-

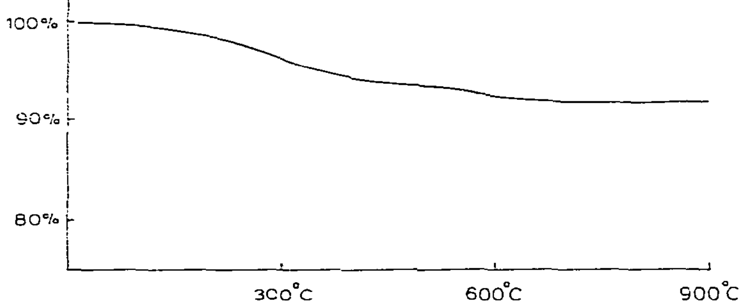


Fig. 1. TGA of a $\not\equiv Si-O-Sn[W(CO)_3Cp]_3$ type catalyst.

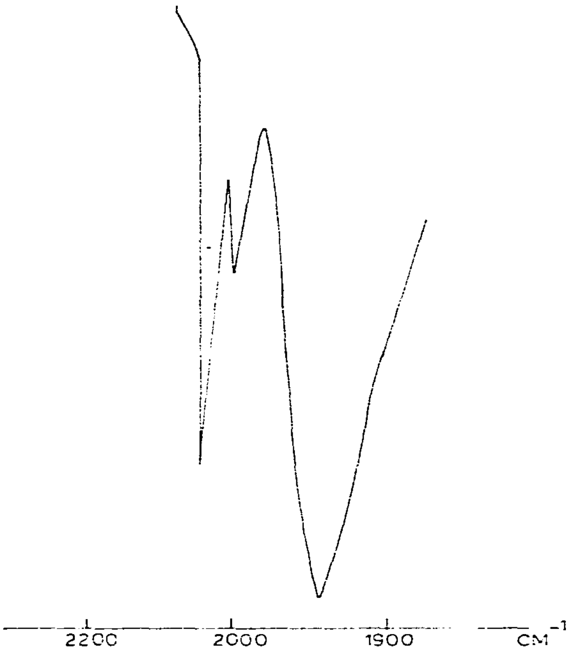


Fig. 2. IR spectrum (CO region) of a ≡Si—O—Ge[W(CO)$_3$Cp]$_3$ type catalyst.

count their magnitudes of 3 and 1.5%, they must obviously be assigned to the loss of 2 and 1 CO units, respectively. In other words, TGA suggests a chemical non-equivalency between the 3 CO ligands, one being more strongly bonded to W than the others. Since some regions (1300—950 cm^{-1}, 850—750 cm^{-1} and 550—350 cm^{-1}) of the IR spectra of the heterogenized catalysts are obscured by strong and broadened bands from the silica matrix, attention was paid only to the CO vibrations between 1800—2000 cm^{-1} as well as to the olefinic $>C=C<$ region near 1600 cm^{-1}. As shown in Fig. 2 for the case of a ≡Si—O—Ge[W(CO)$_3$Cp]$_3$ catalyst, there are 3 absorption bands ν_i in the CO region, suggesting a C_s symmetrical environment of the W center [9]. This confirms the conclusion reached by TGA on the non-equivalency of the 3 CO ligands. The CO vibrations depend on the nature of the E^{IVB} element as is shown in Table 1. The cyclopentadienide ring yields two characteristic absorptions of medium intensity near 1630 and 1700 cm^{-1}.

TABLE 1

IR ABSORPTION BANDS IN THE CO REGION (cm^{-1})

ν (cm^{-1})	—Ge[W(CO)$_3$Cp]$_3$	—Sn[W(CO)$_3$Cp]$_3$
ν_1	2036	2020
ν_2	2001	2000
ν_3	1944	1925

4. *Investigation of the catalytic activity towards olefinic disproportionation of 3,3-dimethyl-1-butene*

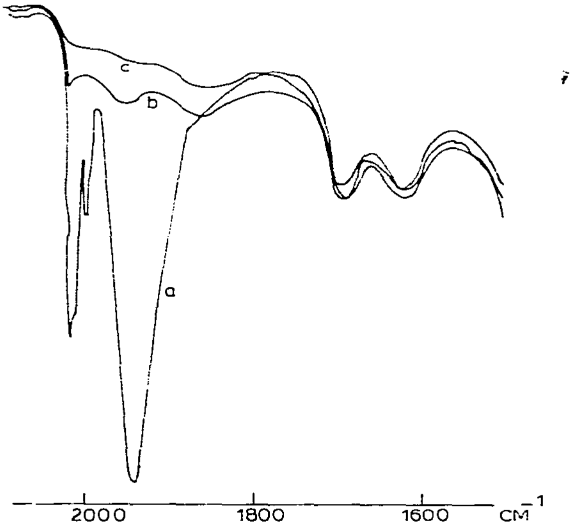
4.1. Catalyst activation

It is well known [10] that most transition metal carbonyl complexes exhibit only minor catalytic activity before activation. During the activation stage one or more CO entities are expelled from the central coordination sphere of the metal yielding vacant sites at the carrier surface which subsequently account for catalytic activity.

Catalyst activation was performed by thermal treatment as well as UV irradiation.

4.1.1. UV activation

UV activation was carried out under a N_2 atmosphere be means of a mercury lamp. In order to obtain homogeneous illumination the solid sample was rotated. During irradiation the original yellow colour disappeared and the sample became colorless. After activation, all contact with air or moisture was strictly avoided. (Studies on $Mo(CO)_6.Al_2O_3$ catalysts [11] have shown that exposing to the air after activation leads to deactivation.) Comparison of the



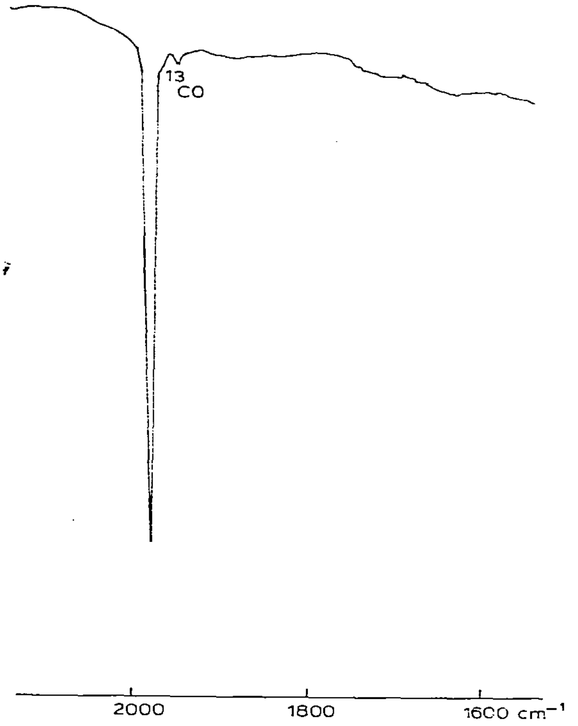


Fig. 3. IR spectrum (olefinic and CO region) of a $\equiv$Si—O—Sn$[W(CO)_3 Cp]_3$ type catalyst before (a), after 1 h (b) and after 3 h (c) of UV activation.

Fig. 4. IR spectrum (olefinic and CO region) of a $\equiv$Si—O—Sn$[W(CO)_3 Cp]_3$ type catalyst after thermal activation.

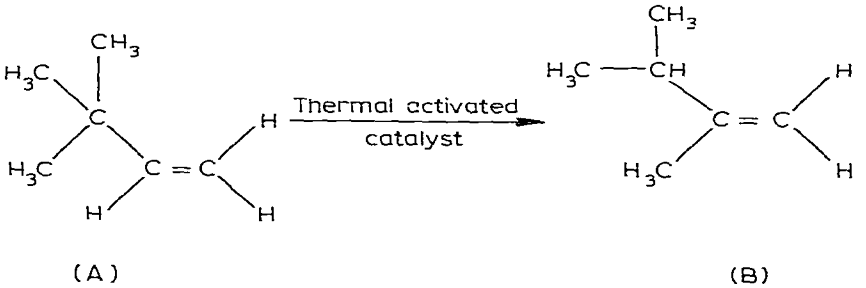
IR recordings before (a), after 1 h (b) and after 3 h (c) of UV activation showed that nearly all the CO ligands had been expelled after 3 hours of irradiation (Fig. 3). Furthermore, as can be seen from the 1600—1700 cm^{-1} region, the cyclopentadienide ligands are unaffected by UV treatment.

4.1.2. Thermal activation

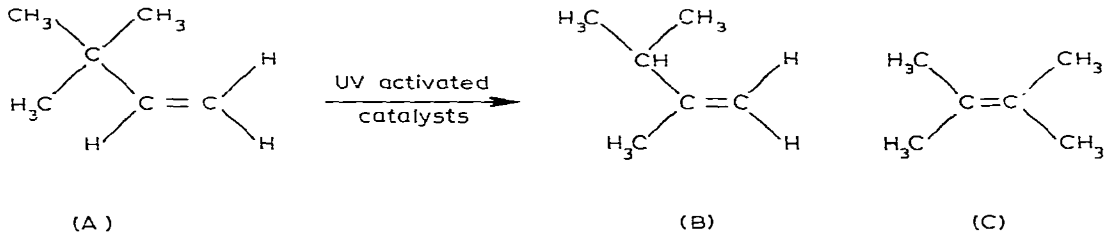
Thermal activation of the sample was performed by heating for 12 hours at 300°C in an electric furnace under a constant N_2 or H_2 flow. In agreement with results of the TGA, the IR spectra showed that under these conditions only 2 of the 3 CO ligands were expelled from the W coordination sphere (Fig. 4). The nature of the protecting gas also proved to be of some importance since the absorptions in the 1600—1700 cm^{-1} region disappeared after thermal treatment under H_2, probably due to hydrogenation of the Cp rings.

4.2. Catalytic experiments and results

All the catalytic experiments were performed by heating a mixture of 1.4 g (1.7×10^{-2} mol) substrate with 0.3 g catalyst during one week at 150°C in a 25 ml sealed ampoule. After cooling and opening the ampoule and separation of the solid particles, the liquid layer was analyzed by GCMS and ^{1}H NMR. Comparison of these results with those of blank tests, confirmed the catalytic activity of the heterogenized W catalysts. Furthermore, it was found that efficiency and product distribution both depended upon the way the catalysts had been activated, whereas the nature of the E^{IVB} element had no influence on these parameters. In the case of thermally activated catalysts the following reaction took place:



Component B was identified by a M^+ peak at $m/e = 84$ and by its ^{1}H NMR spectrum, as shown in Fig. 5. The reaction mixture contained about 7% of compound B and 93% of unreacted 3,3-dimethyl-1-butene (compound A). With UV activated catalysts, the reaction mixture consisted of three components:



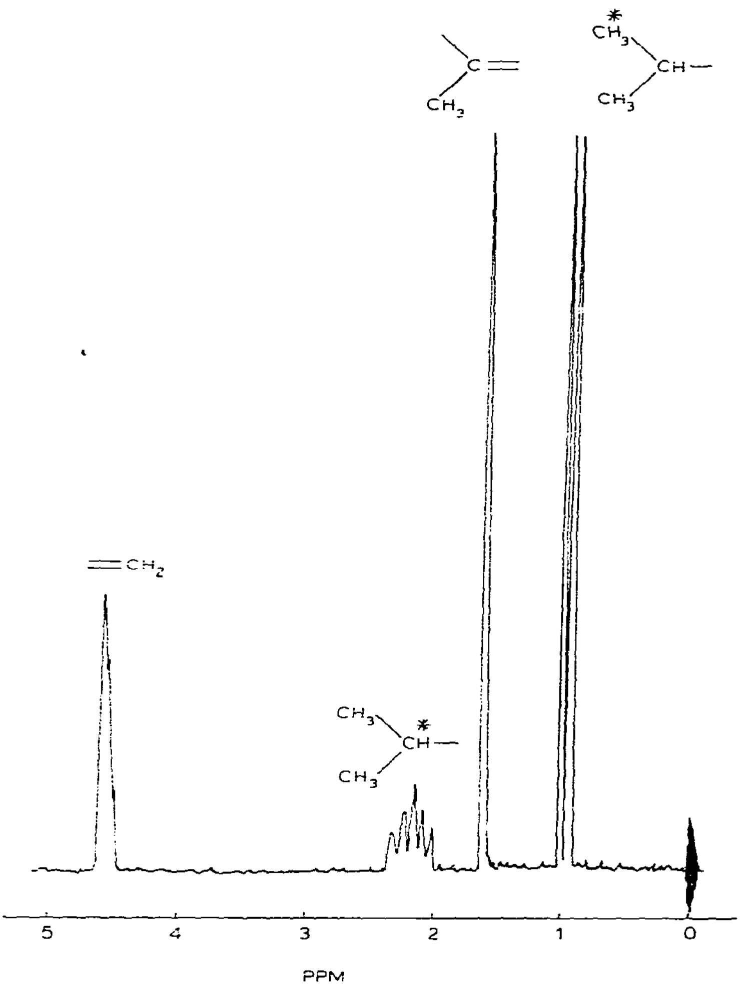


Fig. 5. 90 Mc ^{1}H spectrum of $(CH_3)_2CH\underset{\underset{CH_3}{|}}{C}=CH_2$.

Compound C was characterized by a M^+ peak at $m/e = 84$ and a ^{1}H singlet at 1.56 ppm. Higher conversions were obtained and the relative amount of A, B and C were 42%, 16% and 42% respectively.

4.3. Discussion of results

Instead of disproportionation, which would have yielded 2,2,5,5-tetramethyl-3-hexene and ethylene, only isomerization processes were observed in all experiments. An explanation of this unexpected result was found in a kinetic and mechanistic study of olefin metathesis by Banks [12]. From this work it appeared that when an olefinic substrate is contacted with an $E^{IVB}(CO)_6$ catalyst (E^{IVB} = W, Mo), three types of reaction are possible: 1) disproportionation (metathesis) by scission of the carbon double bond; 2) polymerization; and 3) isomerization. Furthermore, ^{14}C investigations [13] showed that reactions of olefinic

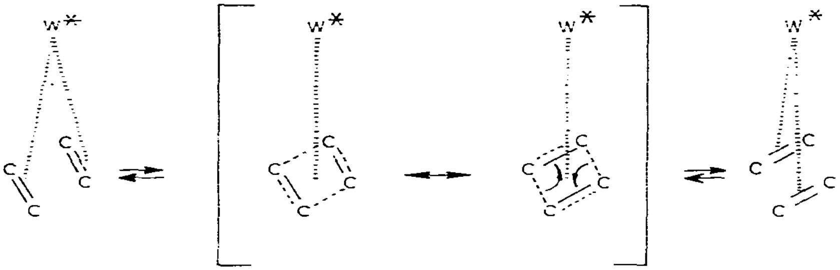


Fig. 6. 4-centre disproportionation mechanism.

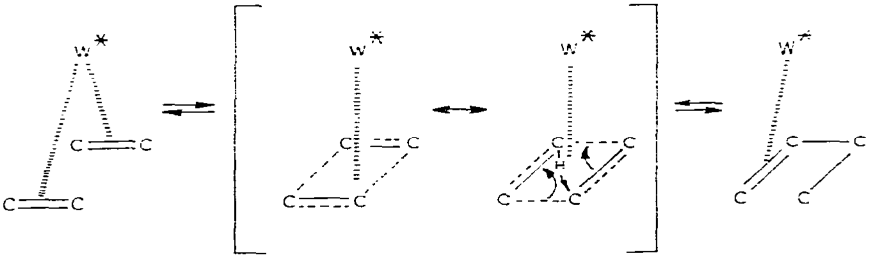


Fig. 7. 4-centre polymerization mechanism.

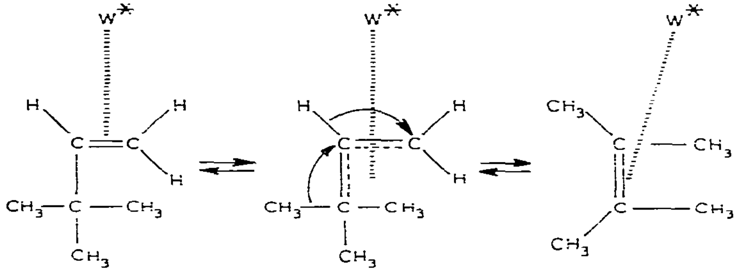


Fig. 8. Possible mechanism for the isomerization of 3,3-dimethyl-1-butene to 2,3-dimethyl-2-butene.

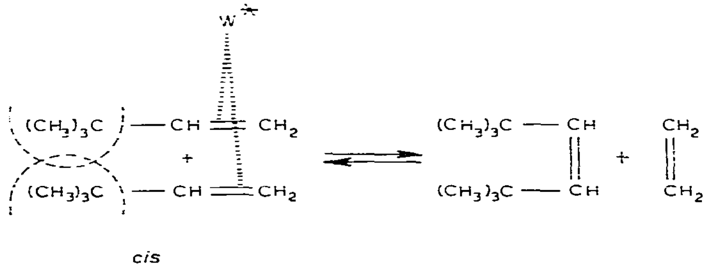


Fig. 9. 4-centre disproportionation of 3,3-dimethyl-1-butene in *cis*-position.

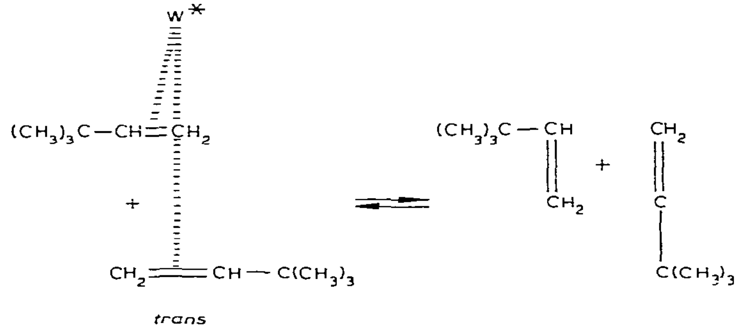


Fig. 10. 4-centre disproportionation of 3,3-dimethyl-1-butene in *trans*-position.

systems catalyzed by activated W centre (W*) proceed by a four-center mechanism. From these features Banks suggested that disproportionation must involve simultaneous bonding of two olefins by the W* center, followed by scission of carbon bonds without a H shift (Fig. 6).

Polymerization too should proceed by simultaneous bonding of two substrate molecules, but instead of two carbon bonds only one is ruptured, and this is accompanied by a H^- shift (Fig. 7). In contrast, isomerization processes require the attachment of only one olefin entity to the W* site, followed by a carbon bond cleavage, and in the case of 3,3-dimethyl-1-butene a H^- as well as a CH_3^- migration. As depicted in Fig. 8, this mechanism accounts for the formation of the highly symmetrical 2,3-dimethyl-2-butene (compound C) from 3,3-dimethyl-1-butene (compound A).

That disproportionation is not observed with a 3,3-dimethyl-1-butene substrate is probably the result of steric crowding between the bulky t-Bu substituents of adjacent molecules when simultaneously bonded to the same W* site (Fig. 9). Moreover, in spite of reduced steric compressions associated with a *trans* orientation of the adjacent molecules, no new olefins can be formed by way of this intermediate complex (Fig. 10).

Finally, it should be mentioned that the formation of 2,3-dimethyl-1-butene (compound B) from 3,3-dimethyl-1-butene (A) requires only a H^- and CH_3^- shift, without any double bond migration.

Acknowledgement

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