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Cluster Catalysis of Olefin Hydrosilylation and Isomerization Thermal Reaction Using $Co_4 (CO)_{10}(PPh)_2$

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الحفز الحراري لاضافة السايلان وتفاعلات
التشكل للألكينات باستخدام الكوبالت العنقودي

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ABSTRACT

The cobalt cluster $[Co_4(CO)_{10}(PPh)_2]$, $\underset{\sim}{1}$, has been evaluated as a catalyst for 1-octene thermal hydrosilylation and isomerization reactions. The kinetics indicate that the hydrosilylation reaction occurs via cluster catalysis at temperatures ranging from 50-70°c. The 1-octene isomerization was selective to trans-2-octene only. The kinetics indicate that at 50°c or lower isomerization reaction occurs via cluster

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catalysis. whereas at 70°c or higher. catalysis by lower nuclearity species is involved. The effects of solvent, silane, temperature, and catalyst and reactant concentrations, on the rates of hydrosilylation and isomerization reactions, have been investigated. Plausible mechanisms, based on experimental data, have been proposed .

ملخــص

تم تقييم الكوبالت العنقودي ١ كحفـاز حـراري فـي تفـاعلات اضـافـة السـايلان، وكذلك تفاعلات التشكل لـ -١- اوكتين. وقد بينـت الدراسـة الحركيـة ان اضـافـة السـايلان تحدث عن طريق الحفز العنقودي بين درجات الحرارة ٥٠ – ٧٠ °م. وان تفـاعل التشكل كان انتقائيا واعطى -٢- اوكلتين فقط . وكذلك بينت الدراسـة الحركيـة ان تفـاعل التشكـل على درجة حرارة ٥٠ °م أو أقل يحدث بواسطة الحفز العنقودي في حين انه علـى درجة حرارة ٧٠ °م او اكثر يحدث بواسطة تكسير الحفاز العنقودي الى اجـزاء اصـغر. وكذلك تمت دراسة تأثير المذيب والسايلان ودرجة الحرارة والحفاز وتركيز المواد المتفاعلة علـى معدل سرعة هذه التفاعلات. وأخيرا تم اقتراح ميكانيكية للتفاعلات معتمدة على الظروف والنتائج العملية .

Introduction

Metal- and mixed-metal-atom clusters have been employed as catalysts and/or catalyst precursors in some chemical reactions, such as hydroformylation [1-4], hydrogenation [5-6], carbonylation [7-9] and water gas shift [7] reactions .

Hydrosilylation and isomerization reactions of terminal olefins have been conducted using several metal-and mixed-metal-atom clusters as catalyst precursors . Examples of such species are $[HRu_3(CO)_{11}]^-$, [8], $Ru_3(CO)_{12}$, [10], $Os_3(CO)_{12}$, [10] and other species. Cluster 1 , shown below, has been also used as a catalyst for photochemical, but not thermal, hydrosilylation and isomerization reaction of olefins [11], and hydroformylation and acetylation of carbon monoxide [12a] .

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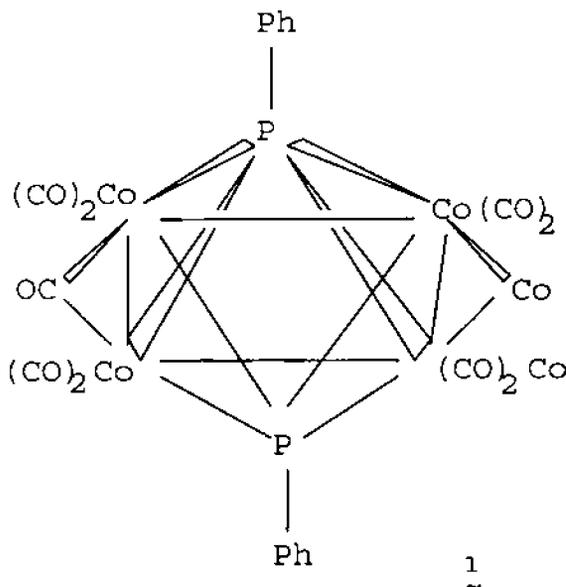
In this work, cluster $\underline{1}$ has been employed as a catalyst for thermal hydrosilylation and isomerization reactions of 1-octene. It is assumed that this cluster is stable to fragmentation, due to the presence of capping ligands. Emphasis has been devoted to see if cluster catalysis occurs. One simple technique to do this is the Laine's kinetic criterion [12b]. In this technique, it is argued that plots of turnover frequency, the change of moles of a product or a reactant per unit of time per mole of cluster, versus cluster concentration can be used to see if catalysis occurs while the cluster concentration is an indication of catalysis by lower nuclearity fragment species. On the other hand, an increase in turnover frequency with increasing cluster concentration is an indication of cluster catalysis. In this report I have used the Laine's kinetic criterion to study the catalytic behaviour of $\underline{1}$ in thermal hydrosilylation and isomerization reactions of 1-octene. The effects of other parameters on the rate of the reaction have also been studied. The stability of the original cluster to fragmentation under the reaction conditions will therefore be tested experimentally in this report .

Experimental

All Chemicals and solvents were purchased from Aldrich Chemical Company Ltd. in a pure form. Cluster $\underline{1}$ was prepared as described elsewhere [13].

A Pye Unicam SP 200 infrared spectrophotometer was used to record the IR spectra. For U.V./visible spectra, a Pye Unicam SP8-100 spectrophotometer was used .

All catalytic reactions were conducted in a 100 ml three - necked round -bottomed flask equipped with subaseal stoppers, a refluxing column, a thermostated bath, and a magnetic stirrer.

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In a typical catalytic experiment, the stirred thermostated reactor was charged with the catalyst, the solvent (enough to make total volume of reaction mixture 10 ml), the silane, the internal standard reference benzene (5 ml) and the olefin.

The reaction was monitored by taking small aliquots after specified time periods. Each aliquot was immediately chilled in a stoppered capillary tube, and analysed by IR spectrophotometry. Specially made calibration curves were used .

Special procedures were adopted to characterize the reaction products. In these, the reaction was allowed to reach completion (complete consumption of 1-octene). The reaction mixture was then fractionally distilled. The fractions were then characterized by their boiling point ranges and by their IR spectral fingerprint comparison with authentic samples and with literature IR spectra [14].

Results

Addition of 1-octene to a thermostated stirred catalytic mixture of cluster $\underline{1}$ and the silane $(EtO)_3SiH$ in different solvents, (with benzene as an internal reference standard), resulted in two concurrent reactions. As shown in eqn. (1), olefin hydrosilylation and olefin isomerization reactions were observed, with a reasonable activity, viz turnover number values up to 1800 were obtained within 20 min .

$$(EtO)_3 \ SiH + \bigwedge\bigvee\bigvee / \xrightarrow{\underset{\sim}{1}} \bigwedge\bigwedge\bigvee + \bigwedge\bigwedge\bigwedge \ \underset{H}{Si(OEt)_3} \tag{1}$$
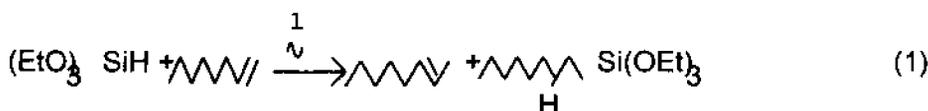
Under our working conditions, the isomerization reaction was the dominant one. Product ratios of (isomerization product) : (hydrosilylation product) up to 10 : 1, respectively, were observed. Reaction products were separated from the reaction mixture by

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fractional distillation. IR spectral analysis confirmed the appearance of trans-2-octene as a sole isomerization product. No other isomers were observed. No unsaturated silylated species, of the type $-C=CSiR3$ or $-C\equiv C-SiR_3$, were observed.

The hydrosilylation reaction progress was monitored by following the decay of the $\{A_{SiH}/ A_{benzene}\}^*$ with time. The consumption of $(EtO)_3SiH$ with time was then calculated based on calibration curves of $\{A_{SiH}/ A_{benzene}\}$ vs. [Silane concentration]. Similarly, the consumption of 1-octene was calculated using $\{A_{1-octene}/ A_{benzene}\}^{**}$ and correlating them with calibration curves of $\{A_{1-octene}/ A_{benzene}\}$ vs. [1-octene concentration].

In addition to the reference standrad benzene solvent, other several solvents were tried. The rate of consumption of 1-octene was in the order rate: CCL_4 < heptane < dioxane <1-octene only.

Therefore, unless otherwise stated, dioxane, was used throughout all reaction.

In the 50-70°c range, the olefin was consumed in less than 25 min. This was evidenced by complete disappearance of the olefin. Before the complete consumption of 1-octene, no matter what its initial concentration was, the reaction continued with no stopping and with no change in the reddish-brown colour. After reaction completion,

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* A_{SiH} = absorbance of Si-H bond at 2210 cm^{-1} characteristic for (EtO)3 SiH;

** $A_{benzene}$ absorbance of benzene at 1950 cm^{-1}.

     $A_{1-octene}$ = absorbance of 1-octene at 1650 cm^{-1}.

a green colour developed, turning into blue, dark blue and then into black residue. The original reddish-brown solution was the only catalytically active solution among the series. It was active on reuse, as shown in Table (1).

Table (1) :   Comparison of turnover number values of fresh and used catalytic mixtures

	Hydrosilylation	Isomerization
fresh catalyst turnover number (20 min.)	100	760
used catalyst turnover number (20 min.)	24	760

Reaction conditions : Cluster $\underset{\sim}{1}$ (0.021 g, 2.87 x 10 mol) ;

triethoxysilane (1.85 ml, 0.01 mol), 1-octene (2.35 ml, 0.015 mol), dioxane (0.8 ml), benzene (5 ml) at 76°c.

The Hydrosilylation Reaction :

The rate of the 1-octene hydrosilylation reaction was affected by many reaction parameters, such as the silane, the solvent and the concentrations of the cluster and the reactants.

Blank experiments, conducted with no cluster. showed no hydro-silylation reaction. Cluster $\underset{\sim}{1}$ catalysed the reaction between $(EtO)_3SiH$ and 1-octene but not that between Et_3SiH & 1-octene. Therefore, unless otherwise stated, all reactions were conducted using $(EtO)_3SiH$.

The rate of the hydrosilylation reaction was affected by the type of the added solvent. This is evident from values of turnover numbers shown in Table (2).

Table (2) :   Values of turnover numbers calculated for the hydrosilylation reaction in different solvents .

Solvents	THF	Dioxane	Heptane	CCl_4
turnover number after 10 min.	12	42	49	v. small
after 20 min.	35	101	66	42
after 40 min.	49	216	77	-
after 60 min.	-	-	101	-
after 90 min.	66	-	153	-

Reaction conditions : Cluster $\underline{1}$ (0.201g, 2.87 x 10 $^{-5}$ mol),

triethoxysilane (1.85 ml,, 0.01 mol); 1-octene (2.35 ml, 0.015 mol), benzene reference (5 ml); solvent (0.8 ml), temperature 76° c.

Plots of catalyst turnover number values (taken at different reaction times) against cluster concentrations have been made using different reaction temperatures as shown in Figure (1). The fact that the turnover number increased with higher cluster concentration indicates that the hydrosilylation

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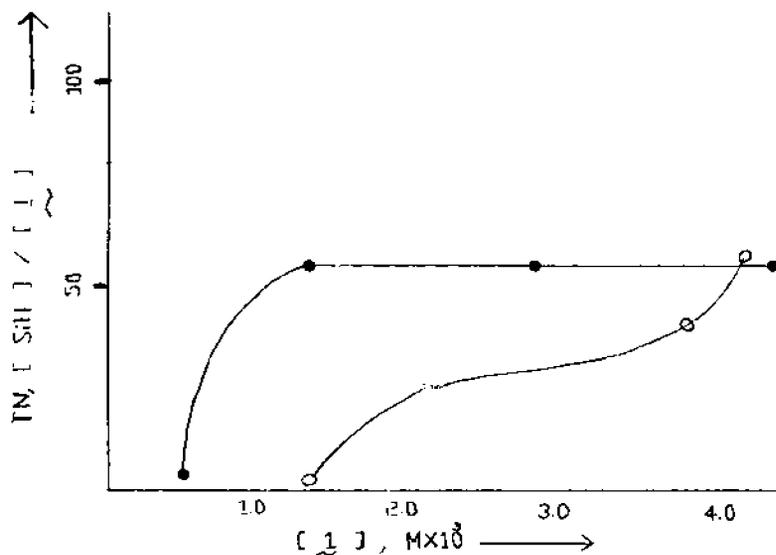
Figure (1):   Plots of turnover number values (T.N.) vs. cluster
coacentration for 1-octéne hydrosilylation reactions,
after 15 min. reaction times
Reaction conditions : Triethoxy (1.85 ml, 0.015 mol);
benzene reference (5 ml); dioxane (0.8 ml).
Reaction temperatures : ● at 50°c; O at 70°c.

reaction occured by cluster catalysis throughout our working
conditions. This conclusion is based on the discussion presented by
Laine [12]. It should be noted here, that although the hydrosilylation
reaction occurs via cluster catalysis, partial fragmentation of some
mother cluster molecules may occur. In addition to turnover studies,
tentative kinetic studies have been made. Based on plots of ln[initial
rate]vs. ln[cluster concentration], the relatively slow hydrosilylation
reaction, made it difficult to find the order of the reaction with respect
to the reactants .

With silane concentrations higher than 0.5M, the reaction was approximately 1st order with respect to the silane .

The Isomerization Reaction :

The isomerization reaction of 1-octene, to yield trans-2-octene in the absence of any silane, was conducted at 76°c . The reaction progressed slowly, with maximum turnover numbers of 450 (within 30 min.) were observed. When Et_3SiH was used the isomerization reaction was immeasurably slow.

The reaction was much faster when $(EtO)_3SiH$ was used, and turnover numbers up to 1700 (within less than 20 min.) were observed. Figure (2) summarizes these results .
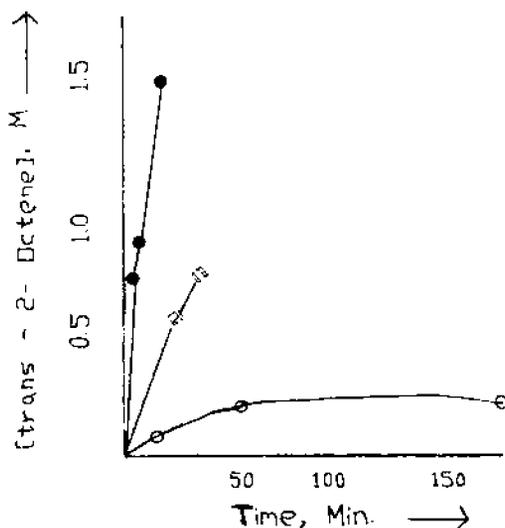
Figure (2):   Reaction profiles showing the effect of type of tertiary silane on rate of 1-octene isomerization reaction.
Reaction conditions : Cluster 1 (0.0105g, 1.434 x 10 -5 mol) 1-octene (2.35 ml, 0.015 mol); benzene reference (5 ml); dioxane (enough to make total solution 10 ml); silane (0.01) mol).
Silanes : triethoxysilane ●; no silane ◇ ; triethylsilane O.

The effect of the type of the solvent on the rate of 1-octene isomerization was investigated. Table (3) shows that the rate of the reaction in different solvents varies in the order :

rate : CCl_4 < THF < heptane < dioxane

Table (3) : Values of turnover numbers for 1-octene isomerization in different solvents .

Solvents	THF	Dioxane	Heptane	CCl_4
turnover number after 10 min.	45	481	139	-
after 15 min.	-	-	-	139
after 20 min.	63	760	491	-
after 40 min.	98	-	630	153
after 60 min.	-	-	-	153
after 90 min.	136	-	-	-

Reaction conditions :   Cluster $\underset{\sim}{1}$ (0.021 g, 2.87 x 10^{-5} mol); triethoxysilane (1.85 ml, 0.01 mol); 1-octene (2.35 ml, 0.015 mol); benzene reference (5 ml) and solvent (0.8 ml). Temperature 76°c.

The effect of the $(EtO)_3SiH$ concentration on the rate of the isomerization has been studied. As stated earlier, the reaction proceeded in the absence of the silane, with turnover numbers up to 410 within 20 min. A much faster reaction was observed when $(EtO)_3SiH$ was added, and turnover number values of 1700 were obtained under otherwise identical conditions, Table (4). These observations indicate that the isomerization reaction occurs via two concurrent reaction pathways, as will be discussed later .

Table (4) : **Effect of (EtO)$_3$SiH concentration on rate of 1-octene isomerization .**

initial molar concentration of (EtO)$_3$SiH	0.0000	0.00725	0.08610	1.00000
turnover number after 10 min.	260	488	700	1260

Reaction conditions :　　Cluster 1 (0.0105 g, 1.434 x 10^{-5} mol);
1-octene (2.35 ml, 0.015 mol); dioxane solvent
(enough to make total volume 10 ml); benzene
reference (5 ml). Temperature 70°c.

The effect of 1-octene concentration on the rate of the isomerization reaction has also been studied in dioxane benzene at 70° c. Plots of ln (initial rate) against ln[1-octene] showed a first order reaction with respect to the olefin .

No conclusive plots of ln(initial rate) against ln[$\underset{\sim}{1}$] were obtained. However plots of catalyst turnover numbers against cluster concentrations were conclusive. At 70°c or higher, the turnover number value decreased with increasing cluster concentration. This was observed for different reaction times. Figure (3) shows examples of such relation after 10 min. reaction time.
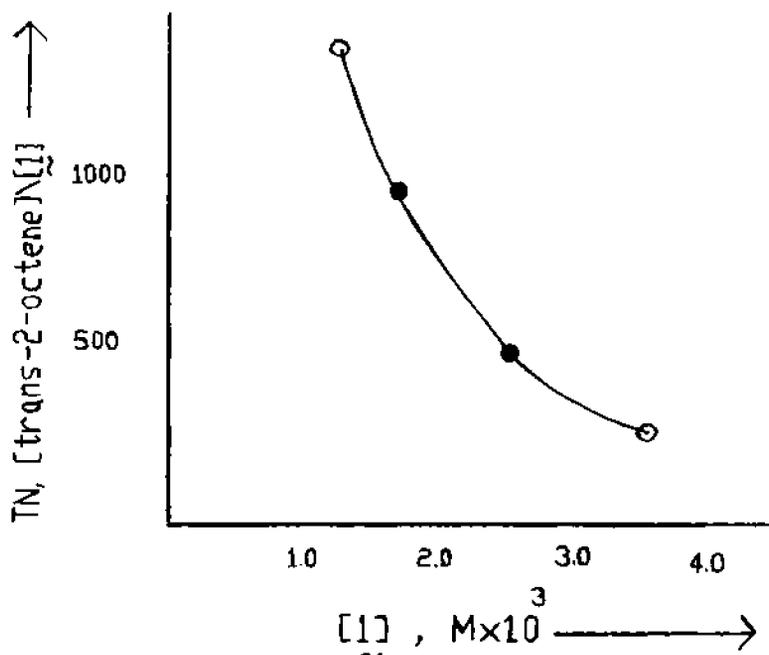
Figure (3) :   Plot of turnover number values (T.N.) vs. cluster
concentration for 1-octene isomerization reaction,
after 10 min. reaction times . reaction conditions :
triethoxysilane (1.85 ml. 0.01 mol); 1-octene (2.35
ml, 0.051 mol); benzene reference (5 ml); dioxane
(0.8 ml); at 72 °C.

At lower temperatures, 50°c or lower, a different behaviour was observed. Figure (4) shows that at 50°c the turnover number values, measured after 10 min., increased with increasing cluster concentrations. Measurements taken after different reaction times showed similar behaviour.
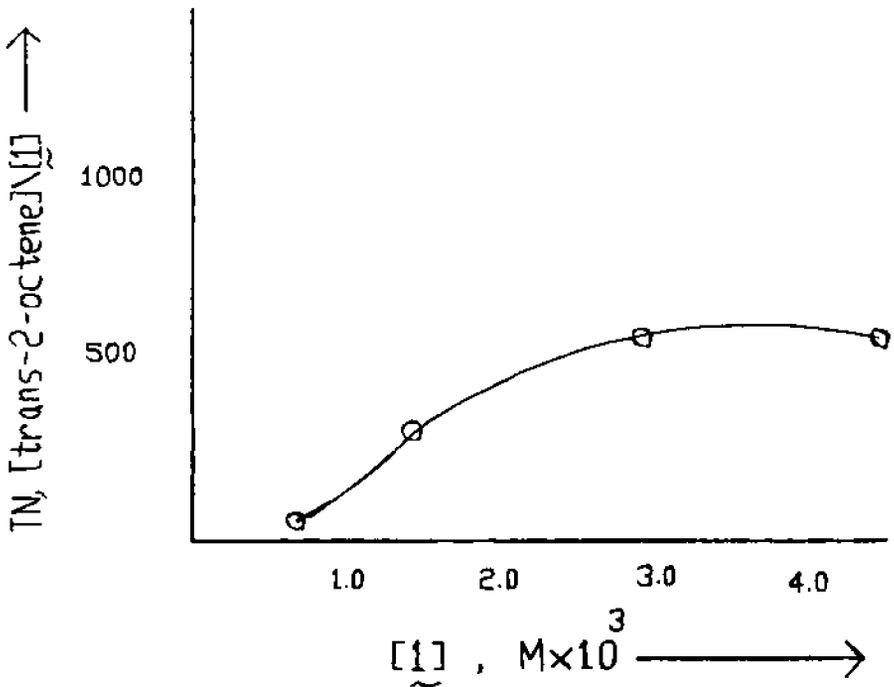
Figure (4) : Plot of turnover number values (T.R.) vs. cluster concentration for 1-octene isomerization reaction after 10 min . reaction times.

Reaction conditions : (2.35 ml, 0.015 mol); benzene references (5 ml) ; dioxane (0.8 ml); at 50°c.

Discussion

The Hydrosilylation Reaction :

Plots of turnover number values vs. cluster concentration, (Fig. 1), indicate that the hydrosilylation reaction occured via cluster catalysis, at temperature range 50-70°c. This means that cluster species are responsible for the catalytic activity while remaining intact. This does not, however, disprove partial fragmentation of original cluster molecules. In fact, there is some evidence in favour of fragment formation as will be seen later.

A plausible mechanism   for the hydrosilylation reaction is shown in Figure (5).
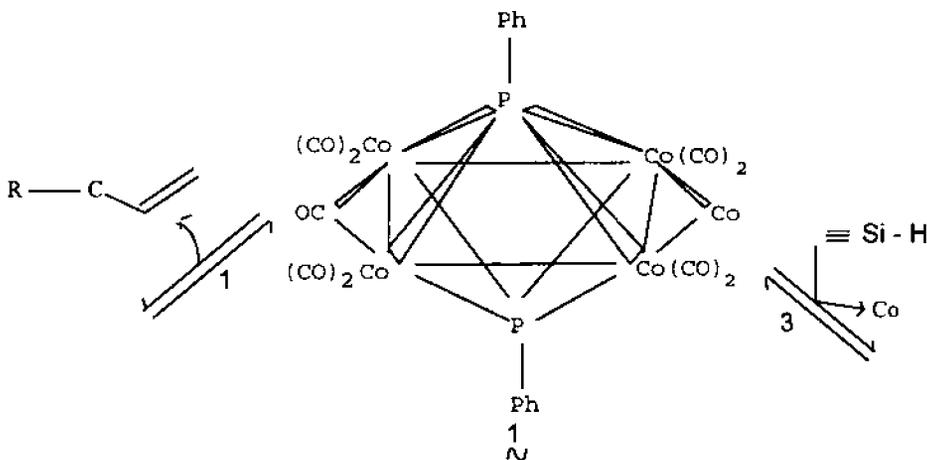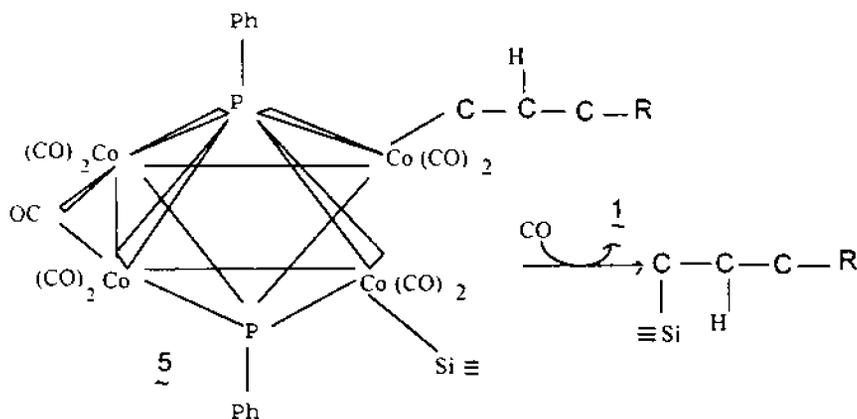
Figure (5):   A plausible mechanism for 1-octene hydrosilylation reaction catalysed by cluster $\underset{\sim}{1}$.

Cluster $\underset{\sim}{1}$ has been reported as catalyst (or catalyst precursor) for several reactions such as photochemical olefin hydrogenation [11] and hydroformylation [15] reactions. Based on preliminary investigations, the olefin activation, at one Co atom, has been proposed [15-16]. This process is accompanied by one Co-Co bond cleavage, as shown in step (1), (Fig 5).

Step (2) involves activation of the silane. This is consistent with other reports in which hydrogen activation is expected in reactions such as hydrogenation and hydroformylation [11, 15-16]. It is believed that tertiary silanes undergo reactions similar in nature to molecular hydrogen [17-18]. In fact, it is assumed that tertiary silanes are easier to activate than the H-H molecule [19]. The activation of the Si-H bond may occur via a unimolecular oxidative addition at one Co atom only. Alternatively, a binuclear oxidative addition may occur. Similar reactions are well known [20-23].

Another possible route involves steps (3-4), where the silane activation precedes the olefin activation.

Step (5) is an insertion reaction, and step (6) is a binuclear reductive elimination.

The mechanism presented in figure (5) explains several facts. Assuming steps (1 and 2) or (3 and 4) are quickly established equilibria, and step (6) is the slow step, and assuming steady states for intermediates $\underset{\sim}{2}$ and $\underset{\sim}{3}$, the dependance cluster, the silane and the olefin may be explained. Furthermore, the mechanism explains why $(EtO)_3SiH$ reacts faster than Et_3SiH, with the assumption that step(6) is the slow step. The Co and Si atoms have comparable electronegativities. In the case of R=EtO, the intermediate $\underset{\sim}{5}$ involves a Co-Si bond with both atoms having electron withdrawing groups, (viz the carbonyls are π-acidic ligands). On the other hand, with R=Et (electron - donating group), the coordinated Si becomes richer with electron charge and forms a more stable Co-Si bond. This is partly responsible for the slower reactivity of $\underset{\sim}{5}$ when Et_3SiH was used. Furthermore, with R=EtO, the coordinated Si atom, in $\underset{\sim}{5}$, would have a higher partial positive charge. This makes it more susceptible to the close proximity attack assumed to occur during the migration of the coordinated alkyl group. Such interaction is expected to be much slower in case of R=Et, where the coordinated Si will be richer with negative charge and less susceptible to nucleophiles.

The assumption, that step (6) is the slow step, also explains the high tendency of the olefin to isomerize, as will be discussed later.

The Isomerization Reaction :

The isomerization of 1-pentene into cis- and trans - 2 - pentence by cluster $\underset{\sim}{1}$ has been reported as a side reaction in hydroformylation processes [15].

In the present work, plots of turnover number values vs. cluster concentration are shown in Figures (3 & 4). Figure (3) indicates that, at 70°c or higher, the 1-octene isomerization catalysis occurs via lower nuclearity fragment species. The cluster is, therefore, believed to fragment into lower nuclearity species which are responsible for the catalytic action. It should be noted, however, that only a fraction of the cluster molecules fragment during the reaction, since at 70°c the hydrosilylation reaction occured via cluster catalysis, as was discussed earlier. Furthermore, cluster $\underset{\sim}{1}$ was tested as catalyst for the reaction of tertiary silanes with alcohols. If appreciable amounts of $HCo(CO)_n$ or $R_3SiCo(CO)_n$ fragments were present, the reaction mixture should catalyse the O-silylation reaction effectively. This is because such species are known to catalyse O-silylation reactions [20]. In the present work, cluster $\underset{\sim}{1}$ failed to catalyse the O-silylation reaction . This indicates that fragmentation to $HCo(CO)_n$ or $R_3SiCo(CO)_n$ species is not significant.

Another evidence, in favour of cluster abundance, came from colour remaining unchanged throughout the course of the reaction. Electron absorption spectra recorded for the reaction mixture, during the reaction, showed no significant change in maximum absorption frequency (573 nm).

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These observations demonstrate that at 70°c cluster ⅃ fragments into lower nuclearity species which are involved in catalysis of the isomerization reaction. This does not exclude catalysis by other remaining cluster molecules.

In fact, cluster catalysis at 70°c is evidenced from cluster catalysis concluced for isomerization at 50°c, (Fig. 4). No indication, of fragmentation, was observed at 50°c.

To account for these and other observations presented earlier, plausible mechanisms based on cluster catalysis have been proposed. It is assumed that the isomerization reaction occurs via two concurrent pathways.In one pathway, isomerization occurs with no tertiary silane, (Fig. 6). In this case isomerization via a π-allyl intermediate is expected. A similar mechanism has

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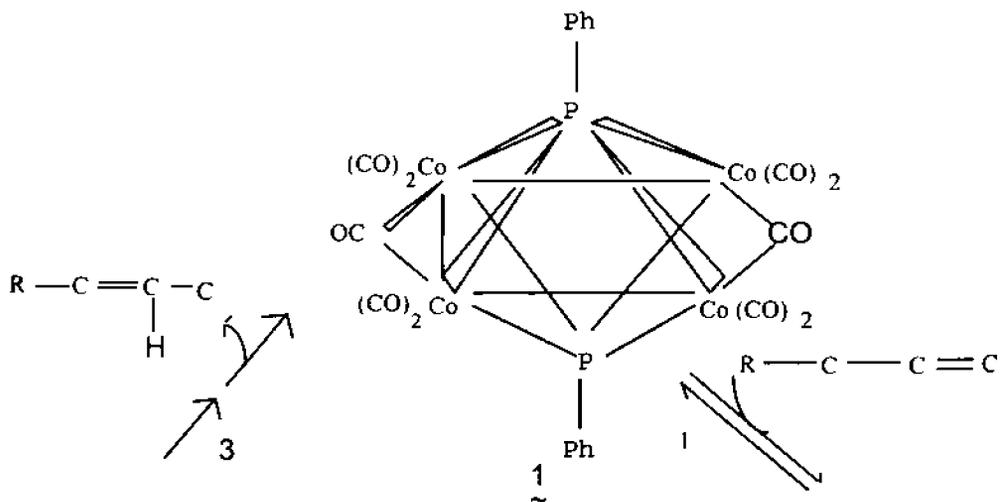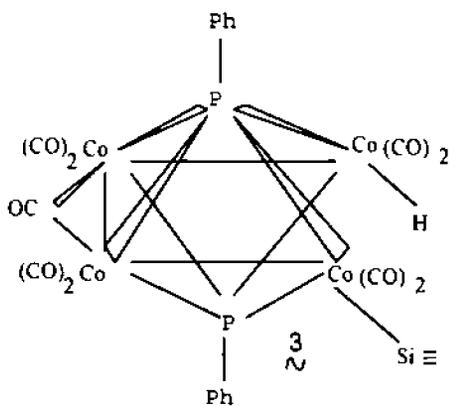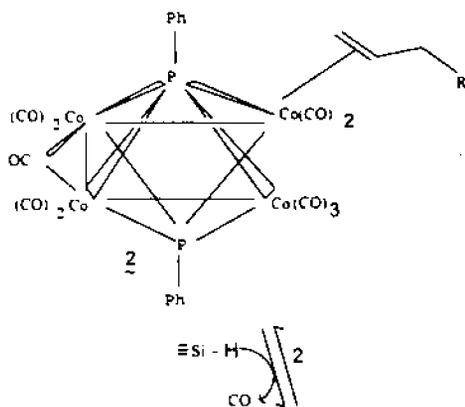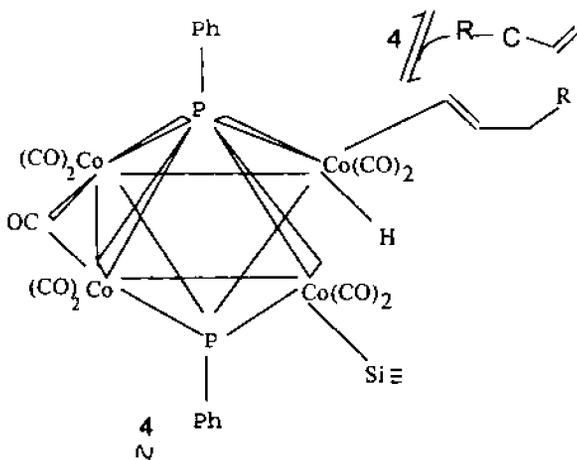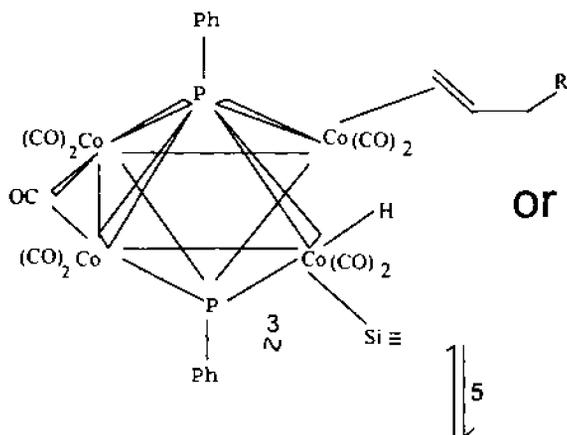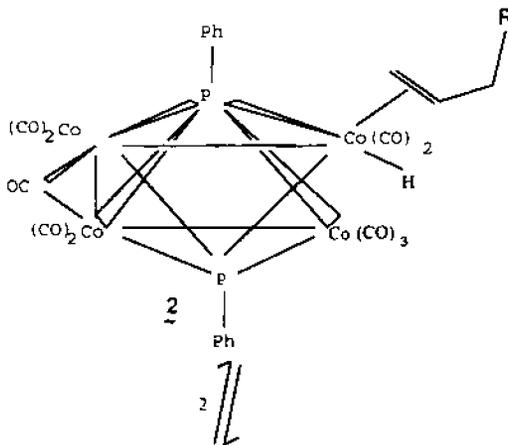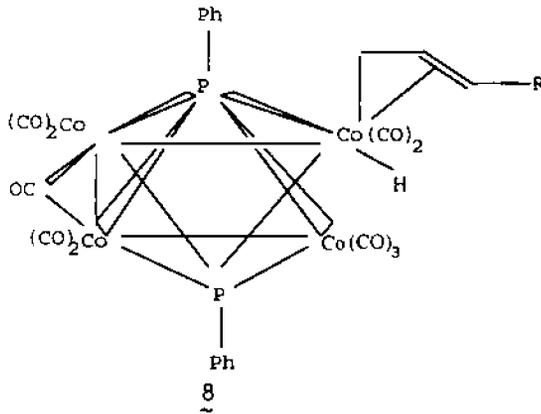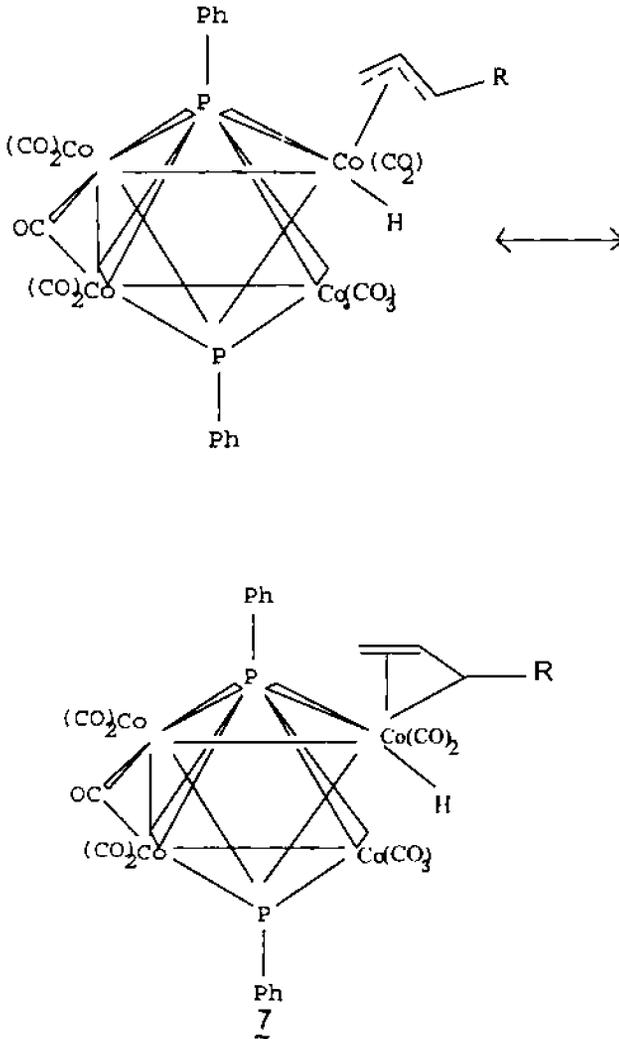
Figure (6): A plausible mechanism for 1-octene isomerization in the absence of silanes .

been proposed for photocatalytic isomerization of 1-pentene to cis- and trans-2-pentenes [24]. In the present work the π-allyl mechanism justifies the selectivity of the isomerization to the trans-2-octene product. In the presence of $(EtO)_3SiH$, the rate of isomerization was appreciably enhanced. This is consistent with other reports in which fluorophosphine- bridged cobalt dimers were used as photocatalysts for isomerization reactions [25]. To account for the silane influence in this work, the mechanism shown in Figure (7) is proposed. Here, silane activation is involved as was proposed in figure (5) earlier, (steps 3-4). Once formed, complex 4 may undergo an insertion step in a **Markovnikov pattern, (Fig 7).**

The mechanism presented in Figure (7) explains also why the 1-octene isomerization is selective to rans-2-octene. The insertion (step 1) should yield the cobalt- alkyl species 9. The stereochemistry of complex 9 allows the -R and -CH$_3$ groups to be far a part when the complex comes to an eclipsed arrangement. The eclipsed arrangement is necessary for the deinsertion (step 3) to occur. Note that, for steric reasons, the deinsertion should invlove $H_{(a)}$ rather than $H_{(b)}$. Step (3) will immediately be followed by Lewis base dissociation (step 4) to yield the trans-2-octene. Comlex 4 that results from step (4) inters the catalytic cycle again, and so on.

Note that in the above catalytic cycle, (Fig 7), the role of the silane is restricted to create complex 4 only. The silane is not involved afterwards.

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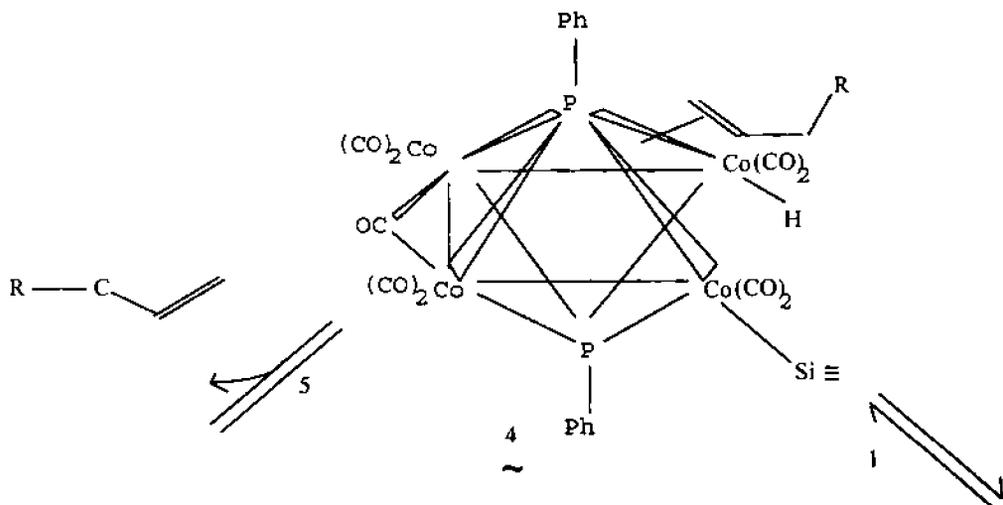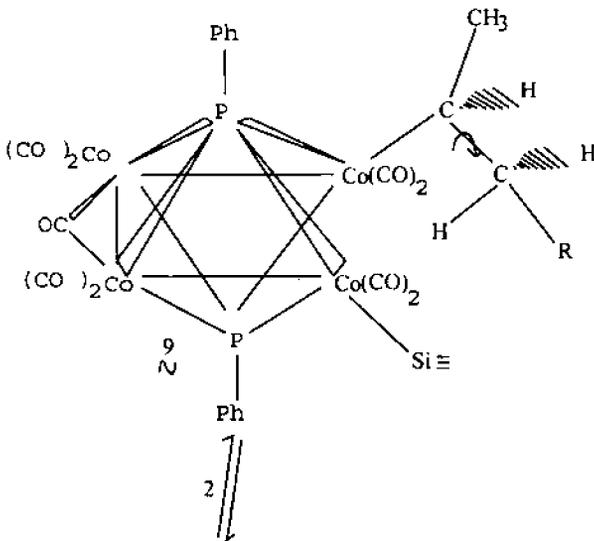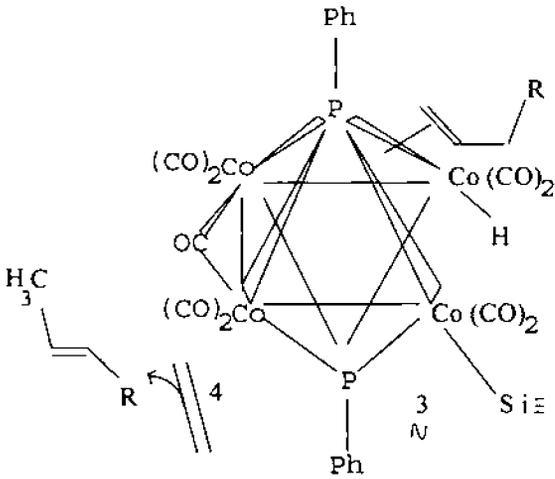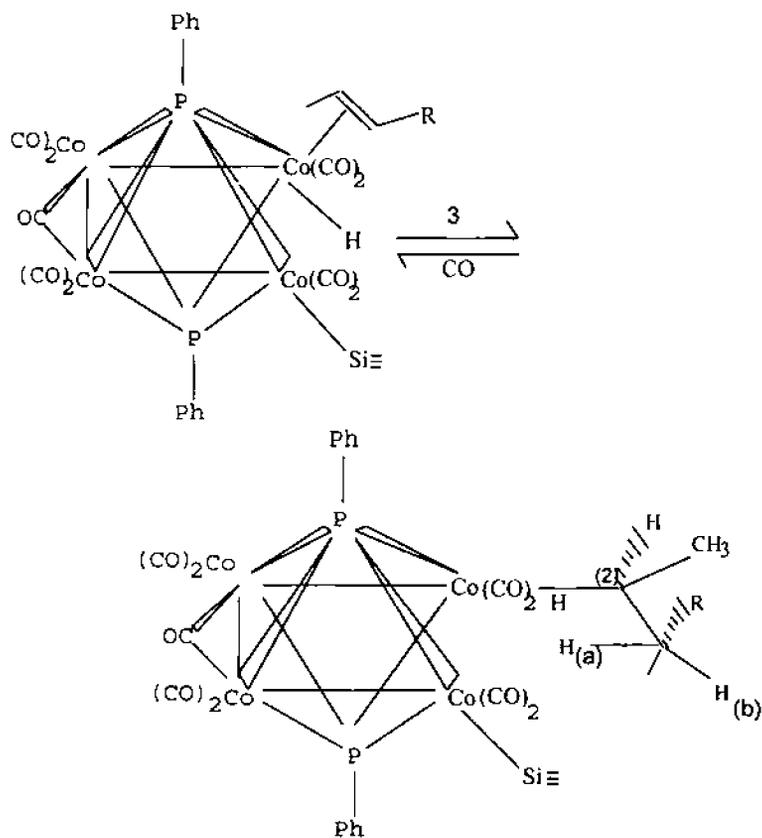
Figure (7):　A plauisible mechanism for 1-octene isomerization in the presence of silanes .

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