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Cluster *versus* non-cluster catalysis in olefin thermal isomerization and hydrosilylation in the presence of $Ru_3(CO)_{12}$

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Abstract

The ruthenium cluster $Ru_3(CO)_{12}$ (**1**) has been evaluated as a catalyst precursor for the thermal reactions of 1-octene with $(EtO)_3SiH$ in a mixture of dioxane and benzene at temperatures of 50–75°C. At 70°C or higher, olefin isomerization and hydrosilylation reactions were observed; the products, *trans*-2-octene and $C_5H_{11}CH_2CH_2CH_2Si(OEt)_3$ (**2**) were identified. The reactions were accompanied by a side reaction that involved generation of hydrogen gas. The sum of the rates of appearance of **2** and H_2 equalled the rate of disappearance of $(EtO)_3SiH$. No significant isomerization was observed in the absence of $(EtO)_3SiH$. Maximum turnover number values of 750, 70, and 70 were obtained for isomerization, hydrosilylation, and H_2 production reactions, respectively. At 60°C or lower, no hydrosilylation or hydrogen production was observed, and the only product was *trans*-2-octene. No detectable disappearance of $(EtO)_3SiH$ was observed. Acetophenone was also hydrosilated by use of cluster **1**, as catalyst; the only product obtained was $(EtO)_3SiOC(Ph)(H)(CH_3)$. Kinetic studies indicated that the reactions of 1-octene and the reaction of acetophenone involved a catalytically active species of lower nuclearity. There was evidence of concurrent cluster catalysis, especially during the first few minutes of the reaction.

1. Introduction

Catalysis by metal- and mixed-metal-atom carbonyl clusters in various thermal and photochemical reactions has received increasing attention in the past decade [1–6].

Studies have been carried out on catalysis by ruthenium carbonyl and carbonylate clusters of the types $[Ru_3(CO)_{12}]$ and $[HRu_3(CO)_{11}]^-$ in thermal and photochemical isomerization reactions of terminal olefins [7–11]. In some reports, it was suggested that the $[Ru_3(CO)_{12}]$ cluster remained intact while catalyzing the olefin isomerization [10,11]. On the other hand, the clusters $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_{11}]^-$ have been reported to undergo fragmentation into lower nuclearity catalytically active species in hydroformylation reactions [12–14]; this seemed reasonable since the hydroformylations required more vigorous conditions. In hydroformylation conducted under mild conditions, the cluster $[HRu_3(CO)_{11}]^-$ was judged to remain intact [15–17].

Studies have also been made of olefin hydrosilylations with other metal carbonyl clusters as catalyst precursors. Examples of such clusters are: $Co_4(CO)_{10}$-$(PPh)_2$ [3,4], $[HOs_3(CO)_{11}]^-$ [6], $[HFe_3(CO)_{11}]^-$ [6], and $[HRu_3(CO)_{11}]^-$ [2].

Here, we report the results of our studies in which the cluster $[Ru_3(CO)_{12}]$, **1**, was used as a catalyst precursor for 1-octene isomerization and hydrosilylations. Since cluster **1** is known to be unreactive towards substrates such as olefins [18], it was expected that the presence of the triethoxy silane would enhance the activation of the olefin on the cluster. The main part of the study involved use of Laine's kinetic criterion [19] to find out whether **1** remains intact while catalyzing the reactions. This criterion states that if the reaction kinetics reveal an increase in turnover frequency with increasing cluster concentration, then cluster catalysis is involved. On the other hand, a decrease in turnover frequency with increasing cluster concentration indicates that catalysis involves lower nuclearity fragments.

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2. Experimental details

The cluster **1**, the reactants and the solvents were purchased from Aldrich Chemical Co.

The infrared spectra were recorded on a Pye Unicam SP200 infrared spectrophotometer.

Catalytic reactions were conducted in a 100 ml three-necked round-bottomed flask equipped with suba-seal stoppers, a cooled condenser column, a thermostated bath and a magnetic stirrer. When needed, the reaction was equipped with a constant-pressure gas burette connected to the upper end of the condenser column.

In a typical catalytic experiment, the stirred thermostated reactor was charged with the cluster, the solvent (enough to make total volume 10.0 ml), the silane and the internal standard reference (benzene, 5.0 ml). The olefin was then syringed in through the suba-seal stopper. In experiments involving gas volume measurements, pressure leakage tests were performed at the time of burette zero setting prior to reaction.

The progress of the hydrosilylation reaction was monitored by observing the disappearance of the organosilane. Allowance was made for the volume of hydrogen evolved. The extent of hydrosilylation was therefore evaluated by subtracting the amount of evolved hydrogen from the amount of consumed $(EtO)_3SiH$. The extent of isomerization was given by the amount of reacted 1-octene less the amount of reacted $(EtO)_3SiH$. The amount of *trans*-2-octene produced was also measured spectrophotometrically.

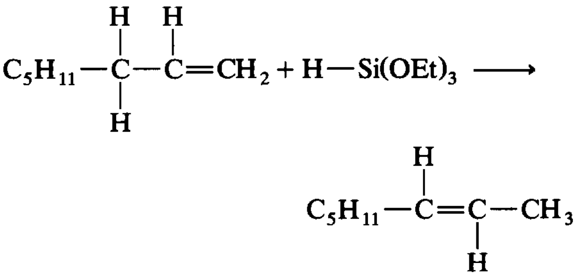
Measurements of the amounts of reaction products and unreacted starting materials were made throughout the reaction; for this, small aliquots were withdrawn after specified times, immediately chilled in stoppered capillary tubes, and analysed by IR spectrophotometry.

The hydrosilylations of acetophenone and 1-octyne were conducted similarly. The rates of disappearance of $(EtO)_3SiH$ and the substrate were used to assess the extents of reaction. No gas evolution was observed in either case.

3. Results

3.1. The isomerization reaction

When 1-octene was added to a mixture of cluster **1** and $(EtO)_3SiH$ in dioxane containing benzene as internal standard at 60°C or lower, isomerization occurred (eqn. (1)). The product was exclusively *trans*-2-octene. Turnover number (TN) values up to 700 were obtained within 11 min. Comparison of fingerprint IR spectral data for the reaction product with literature [20] values and with those of authentic samples were conclusive. No products other than *trans*-2-octene were present. No detectable disappearance of $(EtO)_3SiH$ was observed. However, in the absence of $(EtO)_3SiH$, no detectable isomerization reaction was observed even for prolonged reaction times.



$$C_5H_{11}-\underset{H}{\overset{H}{C}}-\overset{H}{C}=CH_2+H-Si(OEt)_3 \longrightarrow C_5H_{11}-\overset{H}{C}=\underset{H}{C}-CH_3 \qquad (1)$$

The progress of the reaction was monitored by determining the rate of disappearance of the IR absorption band characteristic for 1-octene at 1645 cm^{-1}. The rate of appearance of *trans*-2-octene was monitored by use of its characteristic IR band at 960 cm^{-1}. In each case, the absorbance was measured relative to that of the benzene internal standard at 1960 cm^{-1}, and related to specially prepared calibration curves.

The rate of 1-octene isomerization was affected by change in temperature. The activation energy for the reaction was calculated from plots of ln(initial rate) *versus* $1/T$ (K), and found to be 25.0 kcal mol^{-1}.

The dependence of the rate of the reaction on the reactant concentrations was also studied, and the results are shown in Figs. 1–4. Plots of ln(initial rate)

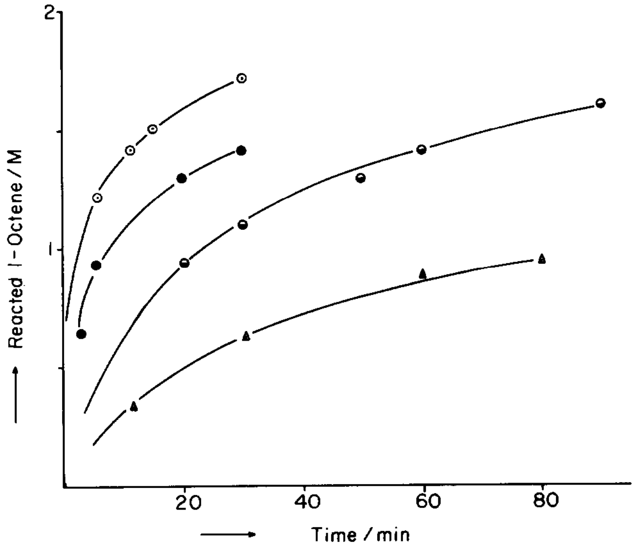


Fig. 1. Reaction profiles showing the effect of initial 1-octene concentration on rate of isomerization reaction. Conditions: in dioxane (variable to make total volume 10 ml)/benzene (5 ml) using **1** (0.0160 g, 2.50×10^{-5} mol) and $(EtO)_3SiH$ (1.85 ml, 1.00 M) at 60°C. 1-Octene concentrations: △, 0.74 M; ⊖; 1.12 M; •; 1.50 M; ⊙, 1.75 M.

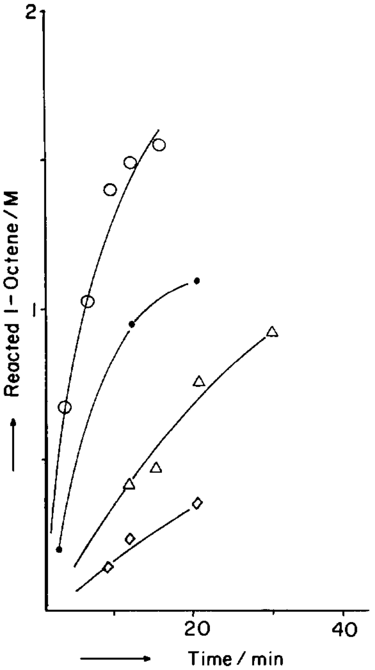


Fig. 2. Reaction profiles showing the effect of initial 1-octene concentration on rate of isomerization reaction. Conditions: in dioxane (variable to make total volume 10 ml)/benzene (5 ml) using **1** (0.0630 g, 9.85×10^{-5} mol) and $(EtO)_3SiH$ (1.85 ml, 1.00 M), at 70°C. 1-Octene initial concentration: ◇, 0.38 M; △, 0.70 M; ●, 1.10 M; ○, 1.50 M.

versus ln[initial 1-octene] and versus ln[initial $(EtO)_3SiH$] showed that the reaction orders were 1.2 and 1 with respect to 1-octene and $(EtO)_3SiH$, respectively. Similar values were observed at 70°C. These results were observed for respective olefin and silane concentrations of 2.0 and 1.0 M or below. At higher silane concentrations, a fall in the rate was observed.

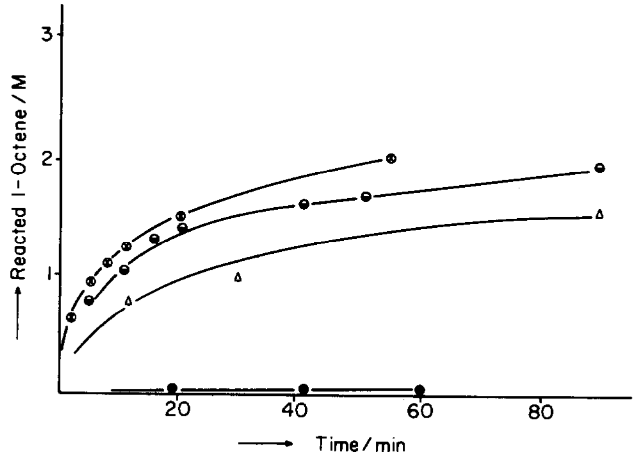


Fig. 3. Reaction profiles showing the effect of initial $(EtO)_3SiH$ concentration on the rate of 1-octene isomerization reaction. Conditions: in dioxane (variable to make total volume 10 ml)/benzene (5 ml) using **1** (0.0160 g, 2.50×10^{-5} mol) and 1-octene (2.35 ml, 1.50 M) at 60°C. $(EtO)_3SiH$ concentrations: ●, 0.00 M; △, 0.34 M; ⊖, 0.50 M; ⊗, 1.00 M.

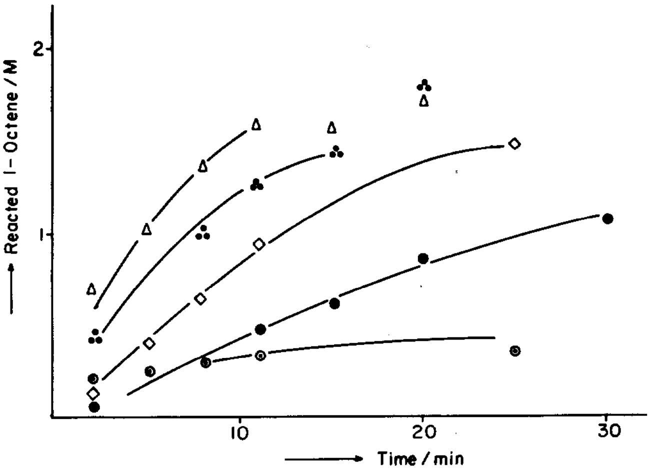


Fig. 4. Reaction profiles showing the effect of initial $(EtO)_3SiH$ concentration on rate of 1-octene isomerization reaction. Conditions: in dioxane (variable to make total volume 10 ml)/benzene (5 ml) using **1** (0.0630 g, 9.85×10^{-5} mol) and 1-octene (2.35 ml, 1.50 M) at 70°C. $(EtO)_3SiH$ concentrations: ⊙, 0.00 M; ●, 1.44 M; ◇, 0.33 M; ∴, 0.50 M; △, 1.00 M.

The effect of cluster concentration on the rate of isomerization was studied in the way described by Laine [19]. Plots of TN *versus* cluster concentration

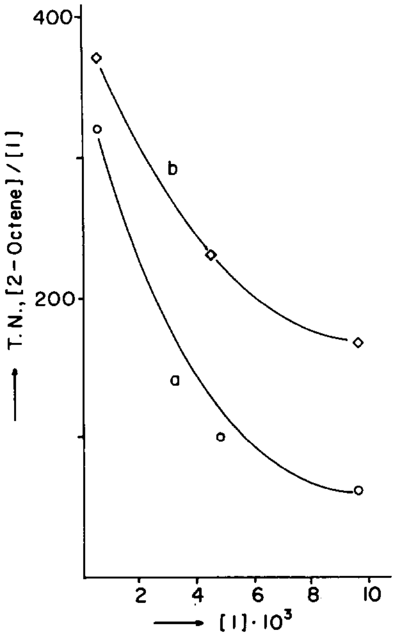


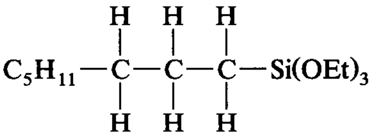
Fig. 5. Plots of TN values *versus* cluster **1** concentration for the 1-octene isomerization reaction at 60°C using dioxane (0.8 ml)/benzene (5 ml), 1-octene (2.35 ml, 1.50 M) and $(EtO)_3SiH$ (1.85 ml, 1.00 M). Measurements taken after 11 min (a), and 60 min (b).

(Figs. 5, 6) indicate that the isomerization reaction involves a lower nuclearity catalytic species resulting from fragmentation of the initial cluster.

3.2. *The olefin hydrosilylation reactions*

At 70°C or higher the olefin underwent the hydrosilylation described in eqn. (2). This was established by IR spectral analysis of

$$C_5H_{11}-CH_2-CH=CH_2 + H-Si(OEt)_3 \longrightarrow$$



$$C_5H_{11}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-Si(OEt)_3 \qquad (2)$$

the products using published IR data [20]. The IR band at 1250 cm^{-1}, arising from the Si–C bond in **2** grew progressively with time relative to the bond of the reference at 1960 cm^{-1}. At the same time the Si–H band at 2210 cm^{-1} disappeared. The concentration of **2** was calculated throughout the course of the reaction from the IR spectra. Maximum TN values of 70 were obtained within 30 min at 70°C. Plots of TN *versus* the cluster concentration were constructed after specified times. Figure 7 shows examples of such plots taken after 5 and 30 min. Figure 7a indicates that the hydrosilylation involves cluster catalysis, since the value of TN does not decrease with increasing cluster concentration. On the other hand, Fig. 7b indicates that catalysis involves a lower nuclearity species throughout the course of the reaction.

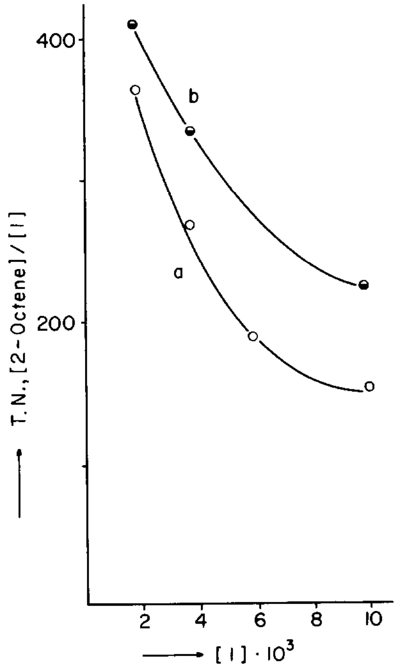


Fig. 6. Plots of TN *versus* cluster 1 concentration for the 1-octene isomerization reaction at 70°C using dioxane (0.8 ml)/benzene (5 ml), 1-octene (2.35 ml, 1.50 M) and $(EtO)_3SiH$ (1.85 ml, 1.00 M). Measurements taken after 11 min (a) and 90 min (b).

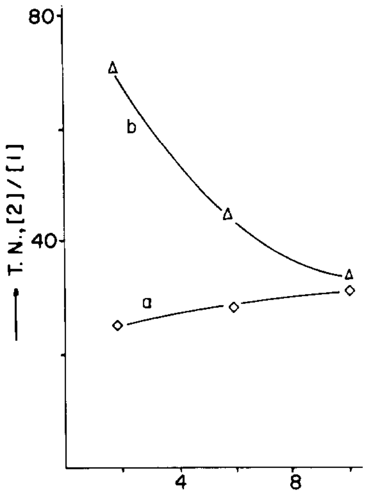


Fig. 7. Plots of TN *versus* cluster 1 concentration for the olefin hydrosilylation reaction at 70°C using dioxane (0.8 ml)/benzene (5 ml), 1-octene (2.35 ml, 1.50 M) and $(EtO)_3SiH$ (1.85 ml, 1.00 M). Measurements taken after 11 min (a) and 30 min (b).

The olefin hydrosilylation was accompanied by another side reaction that involved $H_{2(g)}$ evolution. On the basis of earlier reports [14,28,29], it can be assumed that this reaction is a dehydrogenative silylation yielding $C_5H_{11}CH_2CH{=}CHSi(OEt)_3$ (**3**) (eqn. (3)).

$$C_5H_{11}CH_2CH=CH_2 + HSi(OEt)_3 \longrightarrow$$
$$C_5H_{11}CH_2CH=CHSi(OEt)_3 + H_2 \qquad (3)$$

Two observations supported this assumption. First the number of moles of **3** (which was calculated by subtracting the amount of **2** from the amount of $(EtO)_3SiH$) consumed was equal to the number of moles $H_{2(g)}$ produced. Second, in a special experiment, 1-octyne was hydrosilylated, as shown in eqn. (4).

$$C_5H_{11}CH_2C\equiv CH + HSi(OEt)_3 \xrightarrow[\text{dioxane/toluene}\ 75°C]{Ru_3(CO)_{12}}$$
$$C_5H_{11}CH_2CH=CHSi(OEt)_3 \qquad (4)$$

No evolution of hydrogen gas was detected throughout the consumption of both the octyne and the silane. From previous reports [30], this reaction would be expected to yield **3**. The IR spectra of the product of hydrosilylation of 1-octyne closely resembled the IR spectra of the product of the side reaction of 1-octene. These results suggest that the product of the side reaction of 1-octene is **3**, but unfortunately the spectral analysis suggests that the product is not **3**, since no IR band near 1600 cm^{-1} appeared in any of the above

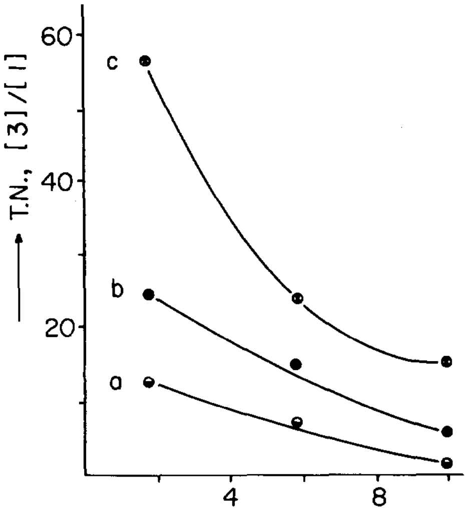


Fig. 8. Plots of TN *versus* cluster **1** concentration for the by-product **3** production at 70°C using dioxane (0.8 ml)/benzene (5 ml), 1-octene (2.35 ml, 1.50 M) and $(EtO)_3SiH$ (1.85 ml, 1.00 M). Measurements taken after 5 min (a), 11 min (b) and 60 min (c).

catalytic experiments. In each case, a band at ~ 2020 cm^{-1} was observed, and this cannot be assigned to product **3**. To allow better resolution, additional experiments were conducted without solvent, but again no band near 1600 cm^{-1} appeared; instead, the band at 2020 cm^{-1} appeared (in addition to the one at 960 cm^{-1} for *trans*-2-octene) at the expense of the 1-octene (1650 cm^{-1}) and $(EtO)_3SiH$ (2210 cm^{-1}).

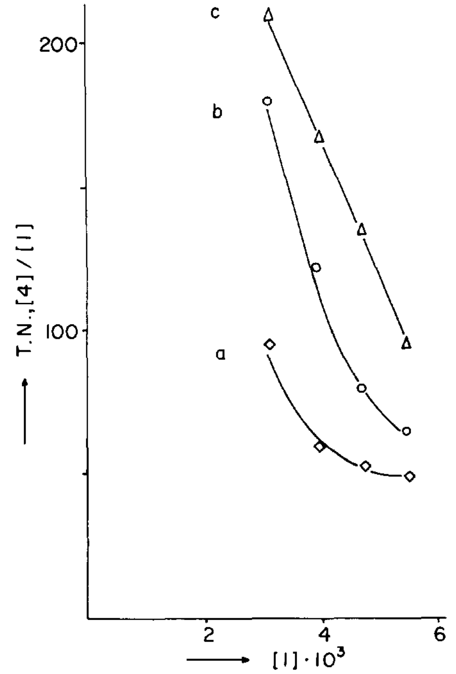
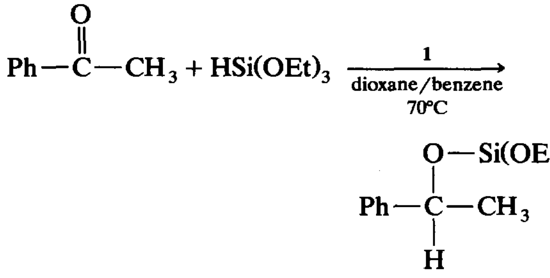


Fig. 9. Plots of TN *versus* cluster **1** concentration for the acetophenone hydrosilylation. Dioxane (0.8 ml)/benzene (5 ml), 1-octene (2.35 ml, 1.50 M) and $(EtO)_3SiH$ (1.85 ml, 1.00 M). Measurements taken after 30 min (a), 90 min (b) and 140 min (c). $T = 70°C$.

TN values up to 70 were obtained within 60 min. Plots of TN *versus* cluster concentration (based on $H_{2(g)}$ produced) (Fig. 8), indicated that catalysis was by lower nuclearity fragments. In Fig. 8, curves (a)–(c) seem to have different slopes. This implies that the catalysis involved both fragment species and cluster species. In Fig. 8(a) the slope is relatively small at the beginning of the reaction, but as time passes (Figs. 8(b), (c)), fragmentation occurs and fragment catalysis becomes more pronounced.

3.3. *The hydrosilylation of acetophenone*

The hydrosilylation of acetophenone, eqn. (5), was conducted under the conditions used for the hydrosilylation of 1-octene.



$$\mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + HSi(OEt)_3 \xrightarrow[\text{dioxane/benzene}\ 70°C]{1} Ph{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle O-Si(OEt)_3}{|}}{C}}{-}CH_3} \qquad (5)$$

(4)

Under similar conditions, the hydrosilylation reaction of acetophenone is faster than that of 1-octene. Turnover numbers of up to 220 were observed within 15 min at 70°C. Plots of the TN *versus* cluster concentration (Fig. 9) indicate that the acetophenone hydrosilylation involves lower nuclearity fragment species. No hydrogen gas or other by-products were detected. Product **4** was the only hydrosilylation product. Studies are now underway on the asymmetric hydrosilylation of prochiral substrates such as acetophenone using various metal and mixed-metal clusters.

4. Discussion

4.1. *The isomerization reaction*

The isomerization of terminal olefins to internal ones catalysed by cluster **1** and its analogues has been reported as a side reaction in hydroformylation [6,16] and other reactions [2]. Isomerization of 1-pentene by cluster **1** in refluxing hexane in the absence of any silane [10] has been reported. Contrary to this report, we observed no detectable 1-octene isomerization reactions in the absence of the silane under the conditions we used.

Plots of isomerization TN *versus* cluster concentration arising from our studies are shown in Figs. 5 and 6 and can be interpreted in terms of proposals by Laine [19] used here. Figures 5 and 6 suggest that at 60–70°C, in the reaction of 1-octene with silane, isomerization involved lower nuclearity fragment catalytic species formed from the mother cluster. The fact that no changes in the spectrum of the mother cluster spectra were observed indicates that only a small fraction of this cluster undergoes fragmentation. Furthermore, intact cluster catalysis cannot be wholly excluded. Thus, cluster catalysis of 1-pentene thermal and photochemical isomerization by $Ru_3(CO)_{12}$, has been reported [10,11] to take place in the absence of tertiary silanes and the catalysis was judged to involve only cluster species, with no fragmentation. On the other hand, it has been reported that cluster **1** undergoes fragmentation when irradiated in the presence of donor ligands [20]. In this work, while cluster catalysis cannot be excluded, catalysis by fragment species is clearly evident.

The fragmentation of **1** is presumably due to the absence of extra stabilizing capping ligands on the triangular cluster framework; the metal atoms of **1** would achieve electronic saturation by forming bonds with reactant molecules on fragmentation [18].

Cluster **1** by itself is known to be somewhat unreactive [18] towards species such as olefins, and this accounts for the non-occurrence of isomerization in the absence of silane in this work. It is known, however, that cluster **1** becomes more reactive to substrates when other activating ligands are added, such as CH_3CN [22], Ph_2PH [1,23] or others [24]. The role of the silane here is to activate the cluster molecules towards the substrate olefin molecules. Oxidative addition of the $\equiv$Si–H species to the metal atom clusters has been proposed for other catalytic systems such as $Co_4(CO)_{10}(PPh)_2$ [5] and $HRu_3(CO)_{11}^-$ [14].

Further investigations on the mechanism of the olefin isomerization are in progress. Activation of cluster **1** by species other than $(EtO)_3SiH$ is also being studied, *e.g.* by H_2, PPh_3 and CH_3CN [25].

4.2. *The olefin hydrosilylation reactions*

Figure 7 shows that the hydrosilylation of 1-octene involves cluster catalysis, and there is no evidence of fragmentation. This is obvious in Fig. 7(a) at the beginning of the reaction. As the reaction progresses, catalysis by lower nuclearity fragment species is evident. Thus a contribution by cluster catalysis throughout the whole course of the reaction cannot be excluded even when fragment catalysis is evident. These conclusions are consistent with those drawn for the olefin isomerizations; the only difference is that in the hydrosilylation there is direct evidence for cluster catalysis from the curve in Fig. 7(a).

The hydrosilylation of 1-octene was accompanied by a dehydrogenative silylation reaction. Hydrogen was progressively evolved. Dehydrogenative silylation of styrene and its derivatives to give vinylsilane derivatives has been reported by Seki *et al.* [28] to take place in benzene at 80°C in the presence of cluster **1**. Suss-Fink reported the dehydrogenative silylation reactions of ethylene and propylene in the presence and absence of CO using $HRu_3(CO)_{12}^-$ [14]. Furthermore, cluster **1** has been reported to be effective in photocatalysis of dehydrogenative silylation of 1-pentene [29]. In the present work, the production of hydrogen indicates the occurrence of dehydrogenative silylation even though the IR band characteristic of compound **3** was not observed. Instead, a band at 2020 cm^{-1} appeared. The product of the side-reaction of 1-octene is apparently the same as the product of hydrosilylation of 1-octyne. Since no hydrogen gas appeared during the 1-octyne hydrosilylation, compound **3** is the only possible product of the consumption of silane and octyne. This is in accordance with earlier reports [30]. We thus, assume that **3** is the product of the side reaction of 1-octene and of hydrosilylation of 1-octyne.

The formation of the by-product **3** involves fragment catalysis, as is evident from Fig. 8. However, the rate of decrease in the TN value with increasing cluster catalysis is different at different reaction times, as can be seen from Figs. 8(a)–(c). The calculated value of turnover frequency (TF) per minute during the first 5 min at each cluster concentration is higher than that at 60 min (Table 1). These results indicate that: (i) at the beginning of the reaction, cluster fragmentation is less pronounced than after 60 min; (ii) especially at the beginning of the reaction, catalysis by both cluster and fragment species is involved.

4.3. *The acetophenone hydrosilylation reactions*

The hydrosilylation of acetophenone with **1** was faster than that of the hydrosilylation of olefin, as is evident from the turnover values. This could be due to

TABLE 1. Values of TF (min^{-1}) for by-product **3** production measured at various reaction times for each cluster concentration used

Plot no.	[Cluster] $\times 10^3$ (M)	TF (after 5 min)	TF (after 11 min)	TF (after 60 min)
8(a)	1.75	2.5	2.4	1.2
8(b)	5.84	1.5	1.4	0.4
8(c)	9.86	0.5	0.5	0.3

Reaction conditions: in benzene (5 ml)/dioxane (0.8 ml), using 1-octene (2.35 ml, 1.5 M) and $(EtO)_3SiH$ (1.85 ml, 1.0 M) at 70°C.

the higher polarity of the carbonyl bond which makes interaction with **1** easier than that of olefins. Furthermore, no side reactions were detected in the acetophenone hydrosilylation. The high selectivity of **1** towards the hydrosilylation reaction is an advantageous feature of the catalytic system described here. With other catalytic systems, side reactions have been reported; thus Pittman *et al.* [5,26,27] observed O-silylation of the enol form of the acetophenone as a side reaction in photochemical hydrosilylation of acetophenone in the presence of $Co_4(CO)_{10}(PPh)_2$.

Plots of TN *versus* the concentration of cluster **1** suggest that fragment catalysis is involved rather than cluster catalysis.

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