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Selective isomerization of 1-alkenes by binary metal carbonyl compounds

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ABSTRACT

An efficient and selective isomerization of 1-alkenes to their corresponding 2-alkenes is achieved by using binary metal carbonyls such as $Ru_3(CO)_{12}$ as catalysts. Possible mechanisms are discussed. Substituents on the 1-alkene have a significant effect on the isomerization.

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1. Introduction

1-Alkene isomerization is a key step in many industrial processes, particularly in petrochemical refining, which involves various heterogeneous and homogeneous catalysts [1–3]. Thus, selective olefin isomerization under mild conditions is an important goal. Double bond isomerization has been exploited as a desired reaction in organic synthesis [4,5], SHOP technology [1], polymerization reactions [6], DuPont butadiene to adiponitrile synthesis [1], BASF synthesis of vitamin A[1], asymmetric isomerization [7], etc.

It has been reported that organotitanium [8] or titanocene [9] derivatives are useful catalysts for the selective isomerization of 1-alkenes to their corresponding 2-alkenes. Most of the catalysts reported for alkene isomerization and subsequent hydrogenation are metal carbonyl hydride clusters and their derivatives [10], Ru(I) and Ru(II) phosphine substituted carbonyl derivatives [11] and $Fe_3(CO)_{12}$ [12]. Photochemical catalysis of $Ru_3(CO)_{12}$ was also briefly reported for 1-alkene isomerization reactions [13]. Complexes such as $M(CO)_2(PPh_3)_3$ (M = Fe, Ru) were found [14] to be active, but air-sensitive, catalysts for alkene isomerization. Olefin isomerization was also observed with some metathesis catalysts, sometimes prior to olefin metathesis [15]. Depending upon the particular catalyst involved, the isomerization can occur by either a metal hydride addition–elimination mechanism or by a mechanism involving a π-allyl metal hydride intermediate. These mechanistic pathways have been discussed previously [1,10,16]. Since the isomerization plays an important role in the reactions of alkenes catalyzed by transition metal complexes, we now describe an investigation on this isomerization in the presence of binary metal carbonyl clusters to evaluate the role of these compounds for this alkene transformation.

2. Experimental

2.1. Materials and methods

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques. Commercially available solvents were distilled from Na metal/benzophenone ketyl before use.

2.2. Nuclear magnetic resonance spectroscopy

^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DMX-400 spectrometer and all ^1H chemical shifts are reported relative to the residual proton resonance in deuterated solvents (all at 298 K).

2.3. Elemental analysis

Microanalyses were conducted with a Thermo Flash 1112 Series CHNS-O Elemental Analyzer instrument.

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2.4. GC–MS analysis

GC analyses were carried out using a Varian 3900 gas chromatograph equipped with an FID and a 30 m × 0.32 mm CP-Wax 52 CB column (0.25 μm film thickness). The carrier gas was helium at 5.0 psi. The oven was programmed to hold at 32 °C for 4 min and then to ramp to 200 °C at 10°/min and hold 5 min. GC–MS analyses for peak identification were performed using an Agilent 5973 gas chromatograph equipped with MSD and a 60 m × 0.25 mm Rtx-1 column (0.5 μm film thickness). The carrier gas was helium at 0.9 ml/min. The oven was programmed to hold at 50 °C for 2 min and then ramp to 250 °C at 10°/min and hold for 8 min.

2.5. Infrared spectroscopy

Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer.

2.6. Materials

$Ru_3(CO)_{12}$ (**1**), $Os_3(CO)_{12}$, $Re_2(CO)_{10}$, $Co_2(CO)_8$, $Mo(CO)_6$, and $W(CO)_6$ were purchased from Aldrich and used without further purification. $PPh_2CH_2CH_2CH_2CH{=}CH_2$ [17] was prepared as previously described. The solvents were commercially available and distilled from dark purple solutions of sodium/benzophenone ketyl. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker DMX-400 spectrometer and all ^{1}H chemical shifts are reported relative to the residual proton resonance in the deuterated solvents. The compounds **3**–**6** were prepared by the reported literature procedures [18,19].

2.6.1. $Ru_3(CO)_{11}[PPh_2(CH_2CH_2CH{=}CHCH_3)]$ (**2**)

In a Schlenk flask, $PPh_2CH_2CH_2CH_2CH{=}CH_2$ (248 mg, 0.975 mmol) was added to $Ru_3(CO)_{12}$ (750 mg, 1.173 mmol) in 50 ml acetonitrile. Slowly, the colour of the solution changed to intense red. The solution was heated 80 °C for 72 h under constant stirring to yield **2** as a product and the reaction was monitored by ^{31}P NMR. The product was isolated by using preparative TLC using dichloromethane as eluent. The major red band was extracted using dichloromethane. After removing the solvent, the product was dried under high vacuum for 6 h to give red crystals of **2**; m.p. 156–158 °C (with decomposition); yield 47%; ^{1}H NMR δ 7.28–7.46 (m, 10H, Ph); 5.34–5.39 (m, 2H, =CH); 2.41–2.54 (m, 2H, P–CH_2); 1.81–1.99 (m, 2H, CH_2); 2.17 (s, 3H, CH_3); $^{31}P\{^1H\}$ 26.70 (s) and 27.36 (s); *Anal.* Calc. for $C_{28}H_{19}O_{11}PRu_3$: C, 38.85; H, 2.21. Found: C, 38.69; H, 2.32%. IR data in CH_2Cl_2: ν (cm^{-1}) 2060 (s), 2045 (s), 2028 (broad), 2012 (broad), 1966 (broad). $Ru_3(CO)_9[PPh_2CH_2\text{-}CH_2CH{=}CHCH_3]_3$ was also isolated as a secondary product (12%) from the orange yellow band on preparative TLC. *Anal.* Calc. for $C_{60}H_{57}O_9P_3Ru_3$: C, 54.67; H, 4.36. Found: C, 55.04; H, 4.21%.

Table 1
Various substrates tested for the isomerization with $Ru_3(CO)_{12}$

Substrate	Experimental conditions	Product	% Conversion (a mixture of *cis* and *trans* isomers)[a]
1-Pentene	3 h, 80 °C	2-pentene	100
1-Hexene	3 h, 80 °C	2-hexene	100
1-Heptene	3 h, 80 °C	2-heptene	100
1-Octene	3 h, 80 °C	2-octene	100
1-Decene	3 h, 80 °C	2-decene	100
5-Bromo-1-pentene	10 d, 80 °C	5-bromo-2-pentene	84
6-Chloro-1-hexene	16 d, 80 °C	6-chloro-2-hexene	93
1,5-Hexadiene	3 h, 80 °C	2,4-hexadiene	100
5-Hexen-1-ol	6 h, 80 °C	4-hexene-1-ol	100
7-Hexene-1,2-diol	6 h, 80 °C	6-hexene-1,2-diol	100

[a] Analyzed by GC–MS.

Table 2
Various catalysts tested for the isomerization of 1-pentene to 2-pentene

Catalyst used	Experimental conditions: 80 °C, toluene	% Conversion (a mixture of *cis* and *trans* isomers)
1	3 h	100
2	8 h	100[a]
3	10 d	66
4	5 d	100
5	10 d	35
6	10 d	0
$Os_3(CO)_{12}$	10 d	100
$Re_2(CO)_{10}$	10 d	4
$Co_2(CO)_8$	3 d	100[a]
$W(CO)_6$	10 d	0
$Mo(CO)_6$	10 d	80[a]

[a] Catalyst decomposed under these experimental conditions.

2.6.2. General procedure for 1-alkene isomerization reactions

All the isomerization reactions were carried out in sealed John-Young NMR tubes (Aldrich). The reaction mixture containing solvent, catalyst and olefin was cooled, evacuated and heated in an oil bath thermostated at the prescribed temperature (±1 °C). The reaction progress was monitored by ^{1}H NMR and then the products analyzed by GC and GC–MS to identify and quantify the final organic products. The results of these catalytic experiments are reported in Tables 1 and 2.

3. Results and discussion

$Ru_3(CO)_{12}$ (**1**), $Ru_3(CO)_{11}L$ [L = (2-pentenyl)diphenylphosphine] (**2**), $[Ru(CO)_2(MeCO_2)_2]_n$ (**3**), $[Ru_2(CO)_4(\mu\text{-}MeCO_2)_2(CH_3CN)_2]$ (**4**), $[Ru_2(CO)_4(\mu\text{-}MeCO_2)(\mu\text{-}dppm)_2][PF_6]$ (**5**) [where dppm = bis(diphenylphosphino)methane], $[Os_2(CO)_6(\mu\text{-}MeCO_2)_2]$ (**6**), $Os_3(CO)_{12}$, $Re_2(CO)_{10}$, $Co_2(CO)_8$, $Mo(CO)_6$, and $W(CO)_6$ were all tested as homogeneous catalysts for the 1-alkene isomerization reactions (see Tables 1 and 2). Complexes **1** and **2** are catalytically active for olefin isomerization in a broad range of solvents (see below) and at temperatures above 60 °C. Our attempts to carry out the isomerization reaction of (1-pentenyl)diphenylphosphine with **1** on heating in order to examine the effect of the bulky phosphine group on the alkenyl chain, yielded **2** ($Ru_3(CO)_{11}L$) (Chart 1). Compound **2** was obtained as an intense red solid in good yield after the reaction of $Ru_3(CO)_{12}$with (1-pentenyl)diphenylphosphine [17] [L] as ligand in a molar ratio of 1:1. It was recrystallized from CH_2Cl_2/diethylether and was characterized spectroscopically and analytically. The studies with the phosphine derivative $Ru_3(CO)_{11}L$ (**2**) were carried out in order to explore the influence of this functionalized phosphine ligand on the catalytic activity in the isomerization reactions. The other compounds (**3**–**5**) were synthesized from $Ru_3(CO)_{12}$ (**1**) using literature procedures [19] to explore the catalytic activity towards 1-alkene isomerization reactions. In a similar way, compound **6** was obtained from the reaction of acetic acid with $Os_3(CO)_{12}$ [20]. Various 1-alkenes were tested for the isomerization reactions to give their corresponding 2-alkenes as shown in Eq. (1). In a similar way, the isomerization of 1,5-hexadiene yielded 2,4-hexadiene quantitatively (Eq. (2)).

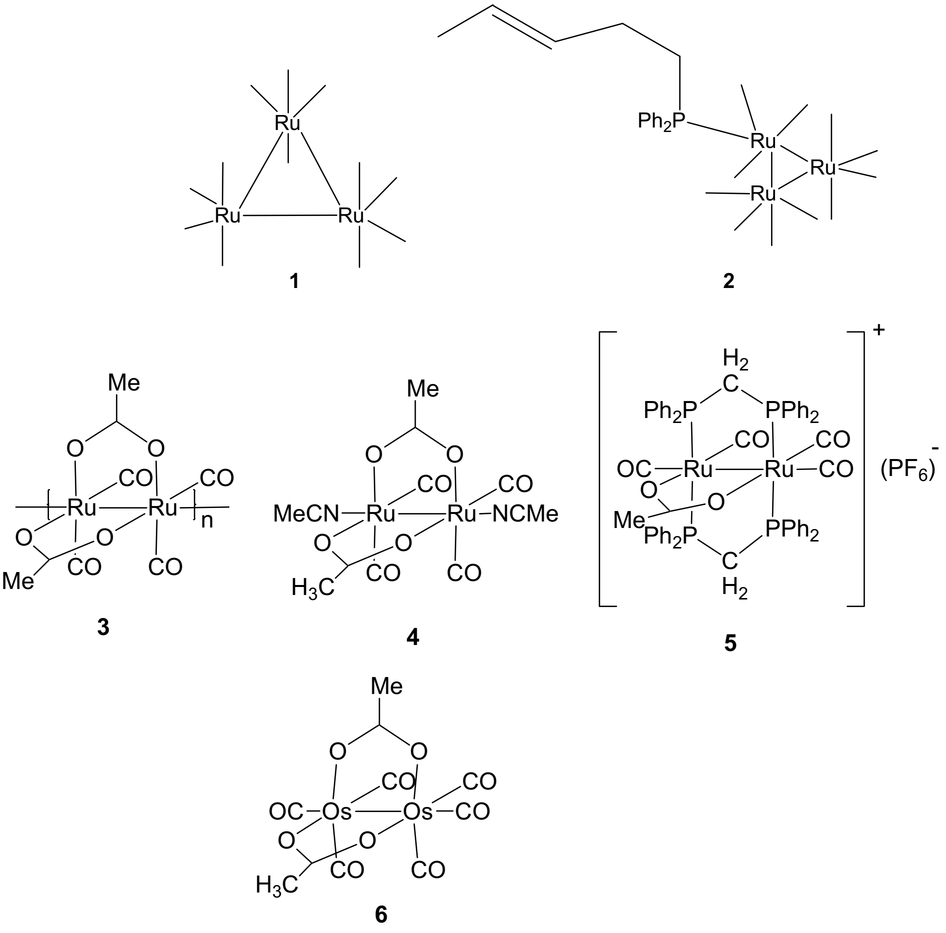
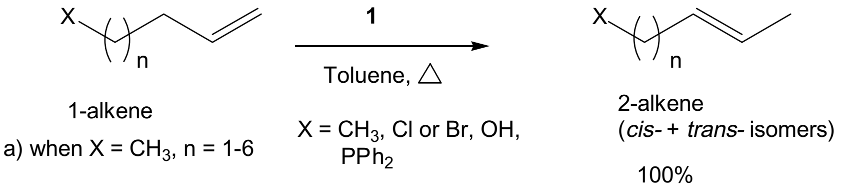
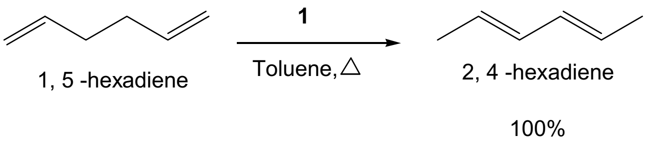


Chart 1. Catalysts used in olefin isomerization reactions.



(1)



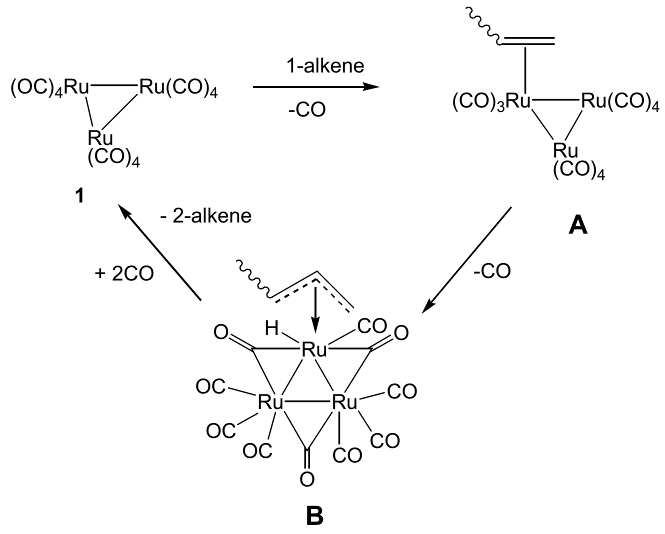
(2)

Although we find that many mononuclear, binuclear and trinuclear metal carbonyl compounds can, in fact, isomerize olefins, significant differences in the activity of the various complexes are formed (see Table 2): $W(CO)_6$ and **6** are mainly inactive in isomerization reactions of aliphatic alkenes and dienes. In case of $Re_2(CO)_{10}$, the catalytic activity was extremely low. The activity of **5** was decreased relative to **4** due to the steric as well as chelating nature of diphosphine ligands. The catalytic activity of the polymeric compound **3** is decreased considerably relative to **4**, which might be due to the insoluble nature of the compound in aromatic solvents. In contrast, the compound **4**, which was derived from **3** by reaction with acetonitrile, catalyzes the isomerization of 1-pentene to 2-pentene quantitatively. The other metal carbonyl compounds such as $Os_3(CO)_{12}$, $Mo(CO)_6$ and $Co_2(CO)_8$ showed significant activity under similar experimental conditions. $Ru_3(CO)_{12}$ however showed the best results (the turnover number for $Ru_3(CO)_{12}$ was found to be 10000 h^{-1}) among the other catalysts, while the activity is quite dependent on the nature of the metal at 80 °C. The rate of the isomerization reaction decreases along the series: $Ru_3(CO)_{12} > Os_3(CO)_{12} > Mo(CO)_6 > Re_2(CO)_{10} > W(CO)_6$ (see Table 2). It was also found that the di-ruthenium compounds $L_2PtRu_2(CO)_8$ [20] and $[Cp^*Ru(CO)_2]_2$ were inactive towards the olefin isomerization reactions, which could be due to the steric, and electronic properties of these compounds. At high temperatures, the isomerization of 1-alkenes to their internal alkenes is feasible with the other metal carbonyl compounds but the catalyst recovery is difficult. In all of these isomerizations of 1-olefins, the *trans*-2-olefin is the major product. Tables 1 and 2 summarize the results of the isomerization of aliphatic olefins. We find that the order of activity of the various catalysts we tested is as follows: $Ru_3(CO)_{12} > Ru_3(CO)_{11}L > Co_2(CO)_8 > Os_3(CO)_{12} > Mo(CO)_6 \gg Re_2(CO)_{10} \gg W(CO)_6$.

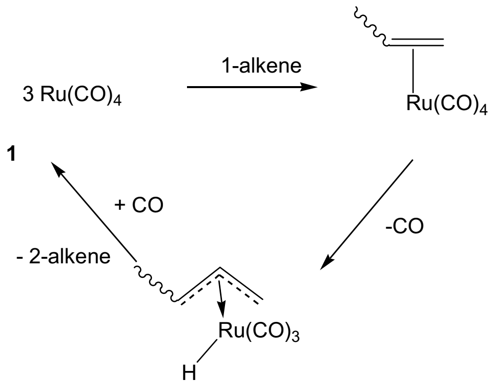
3.1. Mechanistic pathways

We have carried out a number of experiments to try and shed light on the mechanism of these isomerization reactions. Thus, we have carried out IR and NMR spectral studies of the reaction of $Ru_3(CO)_{12}$ with 1-octene in $CDCl_3$. We have made attempts using ^1H NMR to observe an η^3-allyl ruthenium hydride intermediate **B** in Scheme 1a, which is an established mechanism for other metal complexes [10,16]. However, these attempts were unsuccessful. We also used IR to obtain new information thus after heating the reaction mixture for 20 min at 80 °C, the reaction mixture was cooled and the IR spectrum was recorded [bands were now seen at 2100 (vw), 2061 (vs), 2028 (vs), 1985 (vw), 1825 (m), 1795 (m), 1652 (vs) cm^{-1}] (Fig. 1). Thus, new bands are seen which are not present in $Ru_3(CO)_{12}$ [the bands of $Ru_3(CO)_{12}$ are: ν(CO) 2061 (vs), 2028 (vs) and 1985 (vw) cm^{-1}]. Most striking bands are at 1825 (m) and 1795 (m) which could be due to bridging carbonyls of a ruthenium intermediate such as **B** in Scheme 1a.

(a) Involving Ru_3 cluster



(b) Involving mononuclear Ru fragment



Scheme 1. Two possible reaction mechanisms for the catalytic 1-alkene isomerization. (a) Involving Ru_3 cluster. (b) Involving mononuclear Ru fragment.

A key step in the alkene isomerization reaction could be the dissociation of a CO ligand and olefin coordination to give the intermediate species **A**. That CO dissociation occurs during the isomerization reaction was supported by the observation that 1-alkene isomerization is inhibited when the reaction was carried out under a CO atmosphere. The oxidative addition of a C–H bond to the metal centre could lead to the formation of η^3-allyl metal hydride complex **B** which then decomposes to give the 2-alkene product and **1** as shown in Scheme 1. An alternative mechanism could involve mononuclear ruthenium species as shown in Scheme 1b. Both the mechanisms could be expected to be inhibited by CO, as is found.

We could not detect any ruthenium hydride species in the ^1H NMR spectra of the reaction mixtures even at temperatures up to 90 °C in $CD_3C_6D_5$. After heating at 80 °C for 3 h, the reaction was complete as the IR showed the disappearance of the new bands of the intermediate and indicated that the trinuclear ruthenium catalyst is restored (see Fig. 1). The GC analyses of the solution at the end of reaction showed mainly, the presence of *cis*-oct-2-ene (14%) and *trans*-oct-2-ene (86%). As the isomerization activity is high at high temperatures (>120 °C), there is a significant increase in the formation of oct-3-ene (>5%). The reactions of olefins in the presence of other catalysts showed similar trends in the isomerization reactions and analogous behaviour was noticed with **2**, which could go via a similar mechanism. These suggestions are also in agreement with previous studies reported where $Fe_3(CO)_{12}$ was used as catalyst [12].

4. Factors affecting the isomerization reaction

4.1. Solvent effects

The factors influencing the rate of the alkene isomerization reactions are the solvent system, temperature, remote substituent on the alkene, and nature of catalyst used. The polarity of the solvent using either methanol or hexane did not affect the isomerization reaction. However, catalyst recovery was not possible when halogenated solvents were used as these solvents make the catalyst inactive. In the other solvent systems, the catalyst recovery was more than 60% in case of $Ru_3(CO)_{12}$. The absence of solvent increased the rate of reaction significantly, for example the isomerization of 1-octene to 2-octene occurred quantitatively within 60 s at 80 °C, in the presence of $Ru_3(CO)_{12}$. It was also found that these reactions do not involve heterogeneous catalysts as the dilute solutions (where catalytic amount of catalysts used) also perform the isomerization reaction in a similar way to concentrated solutions.

4.2. Effect of temperature

A series of experiments on the alkene isomerization reactions, using $Ru_3(CO)_{12}$, as a function of temperature were carried out. The ideal temperature range was found to be 80–100 °C. When the temperature was >120 °C, the catalyst recovery was not possible even though the rate of reaction was increased dramatically. With compound **2**, the recovery of the catalyst was not successful. It was observed however that this monosubstituted phosphine derivative at high temperatures was converted to the stable tris(phosphine) derivative, i.e. $Ru_3(CO)_9(PPh_2R)_3$. Also at high temperatures (>150 °C), the formation of traces of 3-alkenes is observed with the longer alkenyl chain, i.e. $\geqslant C_7$.

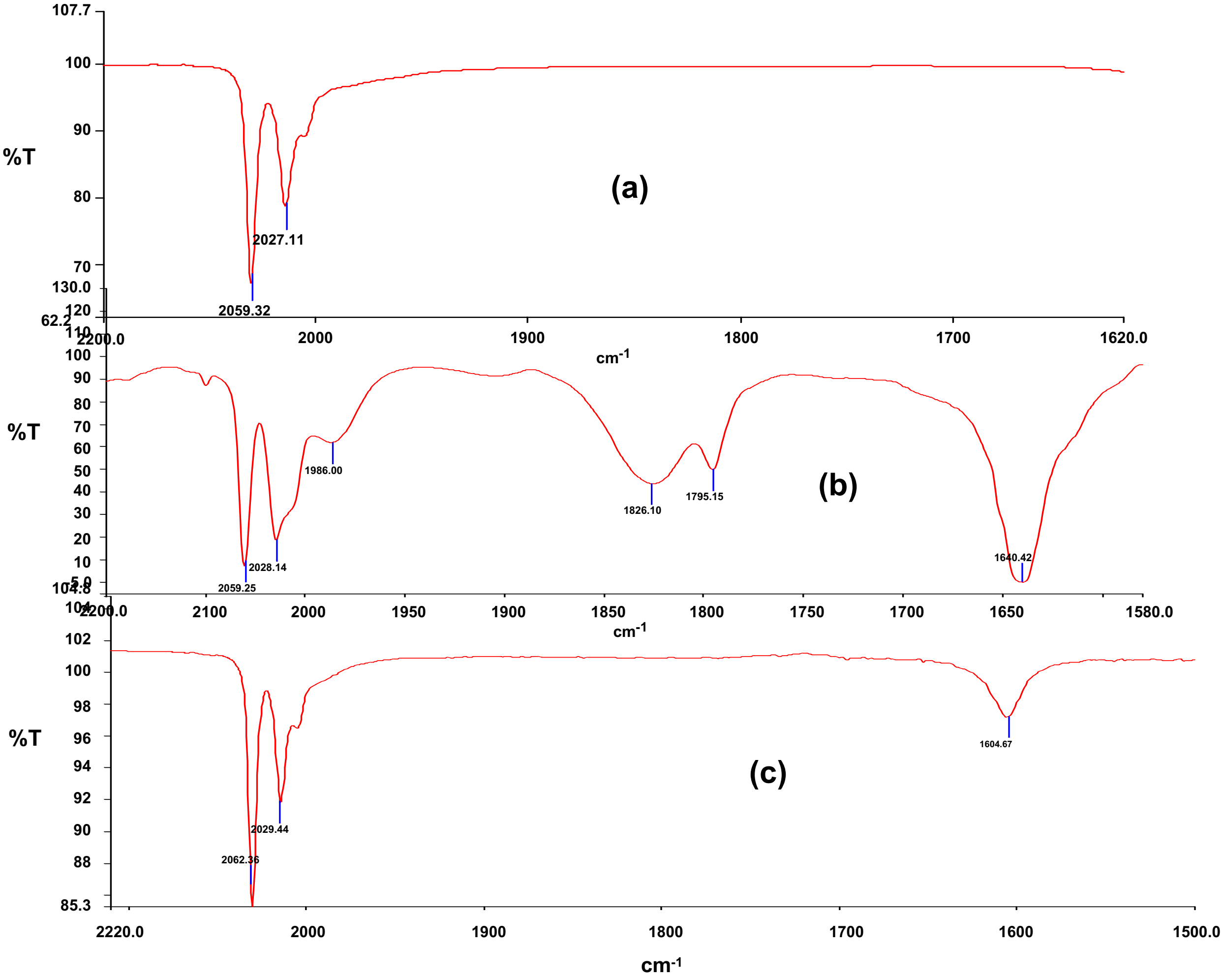


Fig. 1. IR spectra showing the intermediate formed during the olefin isomerization (spectra recorded in $CHCl_3$). (a) $Ru_3(CO)_{12}$. (b) The reaction mixture; after heating with 1-pentene for 20 min at 80 °C. (c) After the complete isomerization reaction after 3 h at 80 °C.

4.3. Substituent effect

Substituents on the alkenyl chains show a significant effect on the isomerization reaction (see Table 1). When X = Cl, Br, the rate of reaction decreases drastically and the formation of different isomeric species was also observed. This could be due to the electron withdrawing effect of the halogens in the alkenyl chain and competing reactions of catalysts with the haloalkenes. Mass spectral studies of the reaction of **1** with 6-chloro-1-hexene indicated the formation of $[Ru(CO)_3Cl]_2$ as one of the products. The presence of hydroxyl groups (X = OH or $(OH)_2$) did not have any significant effect on the isomerization (Eq. (1)). When X = PPh_2, the rate of reaction decreased sharply, which may be due to the steric bulk of the phosphine as well as the phosphine coordinating to the metal and positioning the alkenyl chain away from the cluster. However, on long heating at 80 °C, in acetonitrile for 72 h the corresponding complex **2** was formed. The ^{31}P NMR spectrum showed two singlets close together at δ 26.70 and 27.36 for this compound which could be due to the presence of possible alkene isomers of the compound.

4.4. Effect of catalyst

While $Ru_3(CO)_{12}$ was found to be the most active catalyst (see Table 2), some mononuclear carbonyls, notably $Mo(CO)_6$, were also found to be active. This may suggest that the first step in the mechanistic pathway can be CO loss (as for $Mo(CO)_6$ or $Ru_3(CO)_{12}$). It is also possible that both pathways involving either CO loss or metal–metal bond cleavage could operate for the cluster compounds (see Scheme 1a and b).

4.5. Addition of excess ligands

As expected, the addition of excess ligands such as (diphenylphosphino)methane (dppm) or acetonitrile to the reaction mixture ($Ru_3(CO)_{12}$ and 1-pentene in toulene) resulted in a dramatic decrease in isomerization activity. There was no isomerization observed in the presence of excess of dppm ligand even after the long heating at 80 °C. This is probably due to the phosphine ligand blocking the coordinating sites at ruthenium. Similarly, the isomerization was also retarded when the experiment was carried out under an atmosphere of CO. This suggests that the dissociation of CO from the metal carbonyls is a key step in these catalytic reactions.

5. Conclusions

Some ruthenium carbonyl cluster complexes are efficient and selective catalysts for the isomerization of 1-alkenes to their corresponding 2-alkenes under the mild conditions. The turnover number for the $Ru_3(CO)_{12}$ was found to be 10000 h^{-1} and possible mechanistic pathways for these isomerization reactions are discussed. Other metal carbonyl compounds also show some activity for this reaction.

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