

## Homogeneous hydrogenation of 1-hexene by ruthenium(II) carbonyl phosphine complexes of the types $(R_3P)_2Ru(CO)_2Cl_2$ and $(R_3P)_3Ru(CO)Cl_2$ : effects of the nature of the phosphine, of complex geometry and stoichiometry on catalytic efficiency

Daniel W. Krassowski and John H. Nelson\*

*Department of Chemistry, University of Nevada, Reno, Nevada 89557 (U.S.A.)*

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### Abstract

A series of ruthenium(II) complexes of the types  $(R_3P)_2Ru(CO)_2Cl_2$  ( $R_3P = Bzl_3P, Ph_3P, Ph_2MeP, PhMe_2P$  and  $Me_3P$ ) and  $(R_3P)_3Ru(CO)Cl_2$  ( $R_3P = Ph_2MeP, PhMe_2P$  and  $Me_3P$ ) were investigated for their ability to catalyze the homogeneous hydrogenation of 1-hexene at 100 °C and a hydrogen pressure of 100 psi in 50% ethanol/benzene. Each of the complexes catalyzed both the hydrogenation of 1-hexene to hexane and its isomerization to 2- and 3-hexenes, probably by a monohydride pathway. Both the geometry and stoichiometry of the complex effect the rates of hydrogenation and isomerization. For both series of complexes, the catalytic rate decreases with a decrease in the size and an increase in the basicity of the phosphine. For the  $(R_3P)_2Ru(CO)_2Cl_2$  complexes, the *ttt* isomers were more active than the *cct* isomers. However, for the  $(R_3P)_3Ru(CO)Cl_2$  complexes, the complex geometry did not influence the catalytic activity. Hydrogenation reactions using *ttt*-( $Ph_2MeP$ )<sub>2</sub> $Ru(CO)_2Cl_2$  were carried out in the presence of the Lewis acids:  $AlCl_3$ ,  $BCl_3$  and  $SnCl_2 \cdot 2H_2O$  as well as with  $Me_3NO$ . Both  $BCl_3$  and  $AlCl_3$  completely inhibited hydrogenation and reduced the rate of hexene isomerization.  $SnCl_2 \cdot 2H_2O$  slowed the rate of hydrogenation but had little effect on isomerization.  $Me_3NO$  had little effect on hydrogenation but significantly increased the rate of hexene isomerization. The ruthenium species present at the termination of the catalysis experiments were characterized by infrared and NMR spectroscopy. In most cases the thermodynamically stable isomer of these complexes was recovered in high yield.

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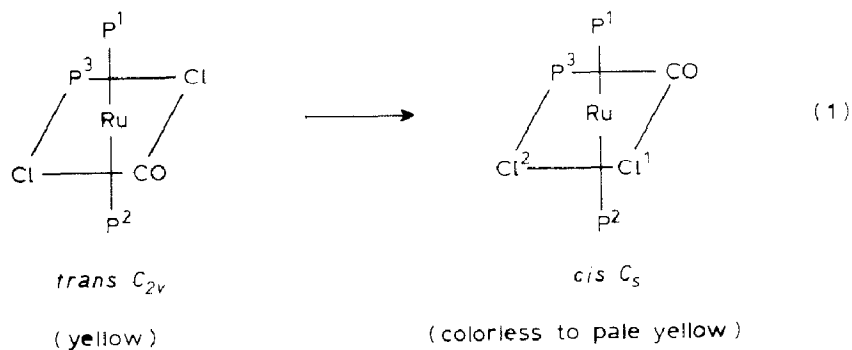
### Introduction

In general, unless hydrogen atom transfer mechanisms are operative, in order for a transition metal complex to act as a homogeneous catalyst, a vacant coordination

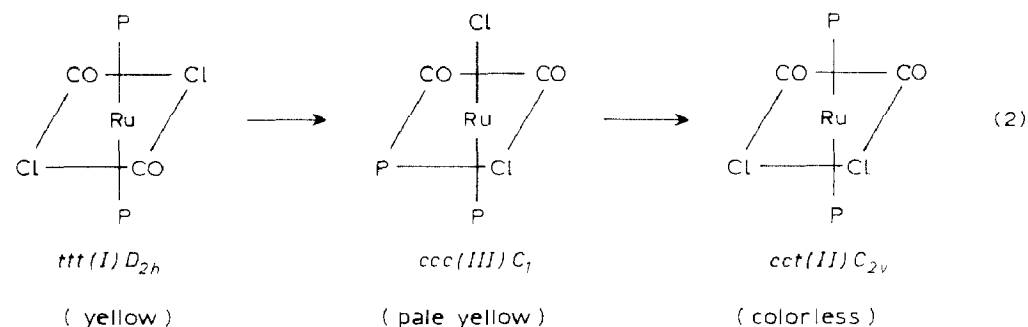
site on the metal is required for binding of the substrate. Thus, coordinatively unsaturated complexes such as  $(\text{Ph}_3\text{P})_3\text{RhCl}$  [1] and  $(\text{Ph}_3\text{P})_3\text{RuCl}_2$  [2-4] are especially good catalysts.

On the other hand, coordinatively saturated complexes must first dissociate a ligand in order to gain entry into a catalytic cycle. Tolman [5,6] found that the size of the phosphine was of prime importance in determining the extent of its dissociation from  $(\text{R}_3\text{P})_4\text{Ni}$  complexes. Phosphorus ligand steric effects have been noted in rhodium catalyzed hydrogenation of alkenes [7] and in nickel catalyzed cyclodimerization of butadiene [8]. Furthermore, Head and Nixon [9] found that the tendency for dissociation of a phosphine from six-coordinate ruthenium phosphine complexes increased with increasing size of the ligand, and that an increased tendency toward phosphine dissociation corresponded with an increase in catalytic activity.

We reported [10] that complexes of the type *trans*- $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  isomerize to the thermodynamically preferred *cis* isomer (reaction 1) by a dissociative process



involving phosphine dissociation. Similarly, complexes of the type *ttt*- $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  thermally isomerize (reaction 2), but by way of CO dissociation [10-13]. The rates of these isomerizations [10] decrease with increasing phosphine basicity and decreasing phosphine steric bulk. The same coordinatively unsaturated



species,  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})\text{Cl}_2$ , likely exists during the isomerizations of both these types of complexes [10]. The structure of these species is probably similar to those of  $(\text{C}_y\text{P})_2\text{Ru}(\text{CO})\text{Cl}_2$  [14,15] and  $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})\text{Cl}_2$ . The latter has been reported [16] to be an effective alkene isomerization catalyst and was suggested to be the catalytic species in the  $(\text{Ph}_3\text{P})_3\text{RuCl}_2$  catalyzed isomerization of vinylcyclohexene [17]. Fahey [18-20] has shown that *cct*- $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  is an effective and, in the presence of excess  $\text{Ph}_3\text{P}$ , a selective homogeneous hydrogenation catalyst. This compound is thermodynamically very stable and undergoes ligand substitution

reactions extremely slowly [12]. Because the geometric isomerizations of the *trans*-(R<sub>3</sub>P)<sub>3</sub>Ru(CO)Cl<sub>2</sub> and *ttt*-(R<sub>3</sub>P)<sub>2</sub>Ru(CO)<sub>2</sub>Cl<sub>2</sub> complexes are initiated by ligand dissociation, we thought that some of these complexes might be more effective catalysts than *cct*-(Ph<sub>3</sub>P)<sub>2</sub>Ru(CO)<sub>2</sub>Cl<sub>2</sub> for the homogeneous hydrogenation of alkenes. A study of the relative catalytic activities of these closely related complexes could provide information regarding the effects of complex geometry and the nature of the dissociated ligand on catalysis. It has been demonstrated [21] that in many cases added phosphine acts to poison catalysts by binding to vacant coordination sites.

Consequently, in order to make the aforementioned comparisons, the following complexes were prepared: *cis*- and *trans*-(R<sub>3</sub>P)<sub>3</sub>Ru(CO)Cl<sub>2</sub> (R<sub>3</sub>P = Ph<sub>2</sub>MeP, PhMe<sub>2</sub>P, Me<sub>3</sub>P); *ttt*- and *cct*-(R<sub>3</sub>P)<sub>2</sub>Ru(CO)<sub>2</sub>Cl<sub>2</sub> (R<sub>3</sub>P = Bzl<sub>3</sub>P, Ph<sub>2</sub>MeP, PhMe<sub>2</sub>P and Me<sub>3</sub>P), *cct*-(Ph<sub>3</sub>P)<sub>2</sub>Ru(CO)<sub>2</sub>Cl<sub>2</sub>, RuHCl(CO)(Ph<sub>2</sub>MeP)<sub>3</sub> and [RuCl<sub>2</sub>(CO)(Ph<sub>2</sub>MeP)<sub>2</sub>]<sub>2</sub> and their ability to homogeneously hydrogenate 1-hexene was determined.

## Experimental

The preparation and characterization of the complexes is reported elsewhere [10]. Hydrogenations were carried out in three ounce, thick-walled glass vessels fitted with a stainless steel cap and sealed by a neoprene O-ring. The bottles are available from the Fischer-Porter Company, and are referred to as aerosol compatibility tubes. The pressure cap was fitted with a pressure gauge, a hydrogen inlet and a dip tube through which aliquots of the reaction mixture could be withdrawn as shown in Fig. 1. Absolute ethanol (10.0 ml), benzene (10.0 ml) and 1-hexene (5.0 ml) were added to 0.05 mmole of the complex in the glass pressure vessel. A small Teflon stirring bar was placed in the solution before sealing the system. After bubbling H<sub>2</sub> through the solution for three minutes, the system was pressurized with H<sub>2</sub> to 100 psi. The vessel was then lowered into a constant temperature (100 ± 0.25 °C) oil bath supported by a magnetic stirrer. After an initial increase due to the temperature change, the pressure began to drop as the hydrogenation progressed and was held constant at 100 psi throughout the reaction. Aliquots were periodically withdrawn from the system using the dip tube. These were analyzed with a Hewlett-Packard model 5700A gas chromatograph equipped with a thermal conductivity detector. The 10 foot × 1/8 inch stainless steel column contained 10% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 Chromosorb P (acid washed). Maximum separation of the hexene isomers and hexane was achieved using a constant column temperature of 70 °C and a helium carrier gas flow rate of 25 ml/min. The products were identified by comparing their retention times with those of authentic samples (Aldrich): hexane, 144 s; 1-hexene, 180 s; *cis*-2-hexene, 210 s; *trans*-2-hexene, 186 s; *trans*-3-hexene, 178 s. Peak areas were determined using a Hewlett-Packard 3390 reporting integrator. All results are the average of at least three measurements.

## Results

The ability of each complex to catalyze the homogeneous hydrogenation of 1-hexene was investigated. The hydrogenations were carried out in a glass pressure vessel using 0.05 millimole of complex dissolved in 20 ml of a 50% benzene/ethanol solution to which 5 ml of 1-hexene was added (1-hexene/catalyst molar ratios of

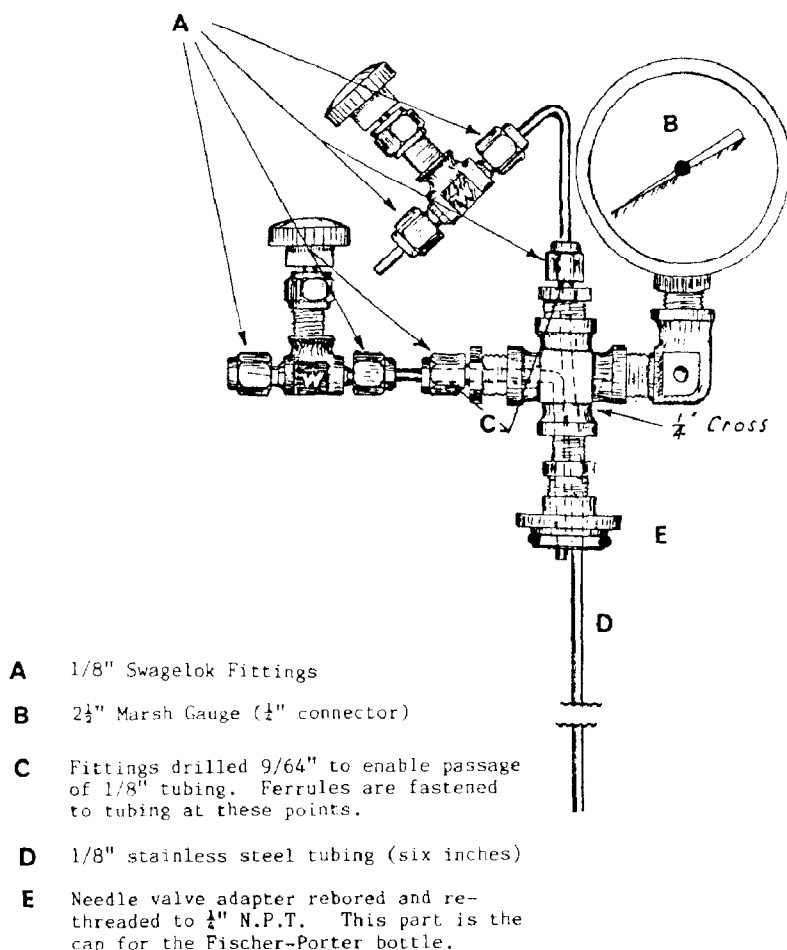


Fig. 1. Stainless steel cap for above-ambient pressure hydrogenations. Dip tube (D) allowed for withdrawal of aliquots during the hydrogenation reactions.

about 800). The pressure (100 psi) and temperature (100°C) were held constant during the experiments. Aliquots of the solutions were withdrawn periodically, and the amounts of the various hydrocarbons were measured by gas chromatography.

The progress of a typical experiment is shown in Fig. 2, where the percent composition is plotted as a function of reaction time. In the early stages of each reaction, isomerization of 1-hexene occurred to a greater extent than hydrogenation. Fahey [18–20] observed similar behavior for  $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$ . *cis*-2-Hexene was the primary isomerization product, although a small amount of another internal alkene (probably *trans*-2-hexene) was also detected. Table 1 lists the maximum amounts of *cis*-2-hexene formed with each catalyst and the time required to reach that level. The *ttt*- $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes promote hexene isomerization more rapidly than do their *cct* isomers. The nature of the phosphine also effects the isomerization rate, with the rate decreasing in the order:  $\text{Bzl}_3\text{P} > \text{Ph}_2\text{MeP} > \text{PhMe}_2\text{P} > \text{Me}_3\text{P}$ . In contrast, the geometry of the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes had little influence on the rate of 1-hexene isomerization. However, as with the  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes, the nature of the phosphine in  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$

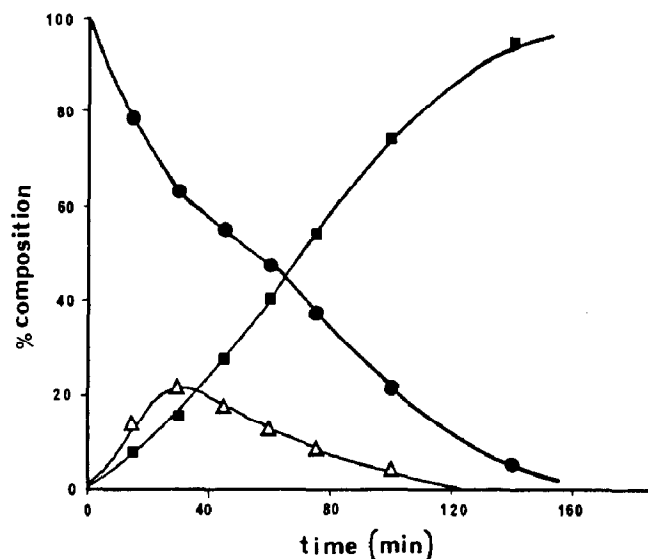


Fig. 2. Percent composition of  $C_6$  hydrocarbons during the hydrogenation of 1-hexene. Catalyst was  $ttt\text{-}(\text{Bzl}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  (■) hexane, (●) 1-hexene, (Δ) *cis*-2-hexene; the small apparent increase in 1-hexene at 50 minutes is probably due to some *trans*-2-hexene or -3-hexene that is formed.

Table 1

Isomerization and hydrogenation of 1-hexene by some ruthenium(II) complexes

Phosphine	Geometry <sup>a</sup>	Turnover number <sup>b</sup>	Maximum 2-hexane(%) <sup>c</sup>	Hexene produced(%) <sup>c</sup>	$t_{1/2}$ (s) for Geometric isomerization at 100 °C <sup>d</sup>
<i>(R_3P)_2Ru(CO)_2Cl_2</i>					
Bzl <sub>3</sub> P	<i>ttt</i>	315	21 (40)	94 (175)	47
	<i>cct</i>	170	17 (85)	91 (270)	
Ph <sub>3</sub> P	<i>cct</i>	200	22 (50)	94 (255)	
Ph <sub>2</sub> MeP	<i>ttt</i>	120	27 (40)	86 (420)	42 (960)
	<i>cct</i>	37	24 (100)	73 (1360)	
PhMe <sub>2</sub> P	<i>ttt</i>	27	22 (150)	57 (1220)	440 (40 600)
	<i>cct</i>	7	23 (450)	11 (1110)	
Me <sub>3</sub> P	<i>ttt</i>	5	22 (275)	8 (390)	2300
	<i>cct</i>	<1	13 (> 500) <sup>e</sup>	1 (411)	
<i>(R_3P)_3Ru(CO)Cl_2</i>					
Ph <sub>2</sub> MeP	<i>trans</i>	44	30 (50)	82 (1380)	3.4
	<i>cis</i>	36	30 (70)	84 (1480)	
PhMe <sub>2</sub> P	<i>trans</i>	34	22 (225)	56 (1290)	74
	<i>cis</i>	39	22 (225)	56 (1220)	
Me <sub>3</sub> P	<i>trans</i>	24	20 (400)	23 (410)	2770
	<i>cis</i>	24	20 (400)	18 (370)	
RuHCl(CO)(Ph <sub>2</sub> MeP) <sub>3</sub>		160	> 25 (<10)	87 (250)	
[RuCl <sub>2</sub> (CO)(Ph <sub>2</sub> MeP) <sub>2</sub> ] <sub>2</sub>		40	28 (40)	78 (1470)	

<sup>a</sup> See reactions 1 and 2. <sup>b</sup> Moles hexane produced/moles catalyst  $\times$  hour. <sup>c</sup> As percent of all  $C_6$  hydrocarbons present in the mixture at the time indicated in parentheses (in minutes). <sup>d</sup> Ref. 10. Isomerization is *trans* to *cis*, or *ttt* to *ccc* (with *ccc* to *cct* in parentheses). <sup>e</sup> Still slowly increasing at 500 minutes.

effects the rate of hexene hydrogenation, which decreases in the order:  $\text{Ph}_2\text{MeP} > \text{PhMe}_2\text{P} > \text{Me}_3\text{P}$ . The hydride complex,  $\text{RuHCl}(\text{CO})(\text{Ph}_2\text{MeP})_3$  had the highest activity for hexene isomerization and the activity of the one dimer studied  $[\text{RuCl}_2(\text{CO})(\text{Ph}_2\text{MeP})_2]_2$  was also quite high.

All the complexes studied also catalyzed the reduction of 1-hexene and 2-hexene to hexane. The internal alkene was usually hydrogenated at a lower rate, although the difference was often less than a factor of two. The effectiveness of the  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes toward hexene reduction varied in the same manner as that observed for 1-hexene isomerization. The *ttt*- $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes were more effective than their *cct* isomers and the hydrogenation rates decreased as the phosphines became smaller and more basic. For the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes, the hydrogenation rate was essentially independent of the complex geometry. However, small differences were apparent based on the phosphine ligands. Hydrogenations with the  $\text{Ph}_2\text{MeP}$  complexes were slightly faster than with the  $\text{PhMe}_2\text{P}$  complexes, which in turn were faster than with the  $\text{Me}_3\text{P}$  complexes. The dimer was no more active than any of the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes, while the hydride was at least four times as effective as any of the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes and roughly equal in activity to  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  ( $\text{R}_3\text{P} = \text{Bzl}_3\text{P}, \text{Ph}_3\text{P}$ ) complexes as a hydrogenation catalyst.

Fahey has shown [19] that for *cct*- $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  the hydrogenation rate law is of the form shown in eq. 3 where  $k$  contains terms for  $\text{H}_2$  and  $\text{Ph}_3\text{P}$

$$\text{rate} = k[\text{Ru}][\text{alkene}] \quad (3)$$

concentrations [20]. Assuming that this same rate law holds for the complexes studied herein, the relative catalytic activities may be evaluated by comparing the turnover numbers, since all reactant concentrations and conditions were the same for each experiment. For each of the hydrogenations studied herein a linear relationship between  $\ln[1\text{-hexene}]_0/[1\text{-hexene}]$  and time exists in support of this rate law [18]. The turnover numbers (Table 1) were calculated by determining the moles of hexane produced per hour for the initial stages of the reaction and dividing this quantity by the moles of catalyst used. Although replicate trials were carried out under the same conditions using catalysts from the same preparation, a range of  $\pm 10\%$  in the reproducibility of the individual turnover numbers was not uncommon. The data in Table 1 represent averages of three replicate measurements.

During the course of the hydrogenations, aliquots of the reaction mixture were withdrawn for infrared analysis. Inspection of the carbonyl region allowed an identification of the major metal carbonyl species in solution. In no case, except for  $\text{RuHCl}(\text{CO})(\text{Ph}_2\text{MeP})_3$ , was a hydride species detected by IR or  $^1\text{H}$  NMR indicating that appreciable concentrations of hydride species were not present though they are surely involved in catalysis [20]. The spectroscopic studies showed that for the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes ( $\text{R}_3\text{P} = \text{Ph}_2\text{MeP}$  and  $\text{PhMe}_2\text{P}$ ), isomerization to the *cis* isomer was complete in less than ten minutes. For the  $\text{Me}_3\text{P}$  complexes some of the *trans* isomer could still be detected after 50 minutes. No subsequent change was observed in the infrared spectra of the *cis* complexes during catalysis and when the *cis* complex was the initial catalyst, it was the only carbonyl species that could be detected by infrared spectroscopy.

The *ttt* complexes isomerized to the *cct* isomers during catalysis with no infrared evidence of the formation of other products. The clean isomerization of the *ttt*

isomers is also supported by  $^{31}\text{P}$  NMR data. Each *ttt* complex was treated under catalysis conditions for 5 h, except that no aliquots of the solution were withdrawn. The solid residue that remained after the solvent was removed at low pressure was dissolved in  $\text{CDCl}_3$  and the  $^{31}\text{P}$  NMR spectra showed that only the *cct* isomer was present in each case. Only the *cct* isomer was found if it was the initial catalyst, a single exception being *cct*- $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$ . In this case the  $^{31}\text{P}$  NMR showed that, while the major component was *cct*- $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$ , *ccc*- $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  ( $\delta$  45.9, 26.8 ppm;  $^2J(\text{PP})$  24.4 Hz) accounted for 5% of the phosphorus and an unidentified species ( $\delta$  28.8 ppm), which may be  $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})\text{Cl}_2]_2$ , accounted for 30% of the total phosphorus.

Similar experiments with the *trans*- $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes demonstrated that for these complexes considerable decomposition occurred during catalysis. For the  $\text{Ph}_2\text{MeP}$  complex, the *cis* isomer accounts for 36% of the phosphorus, *cct*- $(\text{Ph}_2\text{MeP})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  for 3% and the remainder are unidentified species. For the  $\text{PhMe}_2\text{P}$  and  $\text{Me}_3\text{P}$  complexes, *cis*- $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  accounts for 61 and 14% of the total phosphorus respectively; a substantial amount of the dimers  $[(\text{R}_3\text{P})_2\text{Ru}(\text{CO})\text{Cl}_2]_2$  [10] along with other unidentified species were formed. Thus, the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes underwent considerably more decomposition than the  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes.

## Discussion

Every catalysis mechanism proposed for the homogeneous hydrogenation of alkenes involves the intermediacy of metal-hydride species. In general, the two types of hydrides that are postulated [22] are a dihydride and a monohydride intermediate. These are often distinguished by the extent of alkene isomerization which accompanies hydrogenation. The monohydride pathways shows considerable alkene isomerization, whereas with the dihydride pathway, usually little alkene isomerization occurs [22].

Each of the complexes tested (Table 1) not only hydrogenated 1-hexene, but also promoted considerable isomerization. Therefore, a monohydride as also proposed by Fahey [18–20] seems likely during catalysis with each of these complexes. This assumption appears justified, since the one preformed hydride,  $\text{RuHCl}(\text{CO})(\text{Ph}_2\text{MeP})_3$ , showed the most rapid isomerization of the alkene. The fact that hydrogenation is also relatively fast with this complex suggests the importance of a hydride species for this process as well.

### *(R<sub>3</sub>P)<sub>3</sub>Ru(CO)Cl<sub>2</sub> complexes*

The formation of a vacant coordination site from *trans*- $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  has been shown to occur [10] by phosphine dissociation. The half-lives for complex isomerization (Table 1) indicate that geometric isomerization of the complex should be rapid under catalytic conditions at least for the  $\text{Ph}_2\text{MeP}$  and  $\text{PhMe}_2\text{P}$  complexes. Infrared monitoring of the catalysis solutions shows this to be the case. Not unexpectedly then, there is, within experimental error (Fig. 3), no difference in the catalytic activity based upon the geometry of the catalyst precursor.

The rate and extent of alkene hydrogenation and isomerization do exhibit a dependence on the phosphine ligand. As the phosphine becomes smaller and more basic, a decrease in the hydrogenation turnover number is observed. This can be

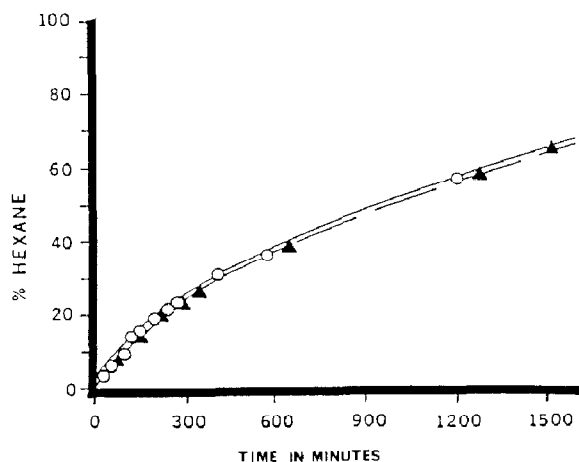


Fig. 3. Hydrogenation of 1-hexene using *cis*- ( $\Delta$ ) and *trans*- $(\text{PhMe}_2\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  ( $\circ$ ) as catalysts. Catalyst concentration 2.0 millimolar;  $100^\circ\text{C}$ , 100 psi of  $\text{H}_2$ .

rationalized by the relative ease of phosphine dissociation. Similar variations in the extent of ligand dissociation with the phosphine size have been noted in other systems [5–9].

A more dramatic change is seen in the time required for alkene isomerization as the phosphine becomes smaller and more basic. The  $\text{Me}_3\text{P}$  complex produces less 2-hexene (20%) than does the  $\text{Ph}_2\text{MeP}$  complex (30%) and requires about six times as long to bring about the maximum amount of isomerization.

#### $(R_3P)_2\text{Ru}(\text{CO})_2\text{Cl}_2$ complexes

The half-lives of geometric isomerization of the *ttt*- $(R_3P)_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes and, in parentheses, of the *ccc*- $(R_3P)_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes are given in Table 1. Although the geometric isomerization of the *ttt* complexes to *ccc* may be fast at the temperature of catalysis, that of the *ccc* isomer (except for  $\text{Bzl}_3\text{P}$  and  $\text{Ph}_3\text{P}$  [23]) is not. Surprisingly though, none of the *ccc* isomers were observed by infrared monitoring of the catalysis solutions, though 5% of *ccc*- $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  was found in the catalyst residue. Only the *cct* isomers were observed by infrared spectroscopy and these were formed from the *ttt* complexes much faster than expected from the values of  $t_{1/2}$ . This change is not merely due to the higher pressure of catalysis, since the rates of complex isomerization determined under 100 psi of nitrogen were found to be identical (within experimental error) to those at atmospheric pressure. In addition, when the complex isomerization was carried out under very high pressure, a decrease in the isomerization rate was observed, not an increase [10]. Thus, it appears that the presence of  $\text{H}_2$  and/or alkene effects the mechanism of geometric isomerization.

The most striking aspect of catalysis with the *ttt*- and *cct*- $(R_3P)_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes is the markedly different rates exhibited as a function of complex geometry, for both alkene hydrogenation and isomerization. In each case the *ttt* isomer was a better catalyst than the *cct* isomer. This is in spite of the seemingly rapid and complete isomerization of the *ttt* complexes to the *cct* isomer. Figure 4 shows the difference in catalytic activity (two replicate trials) for the isomeric pair of  $(\text{PhMe}_2\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes. The rates of hydrogenation using the *ttt* com-



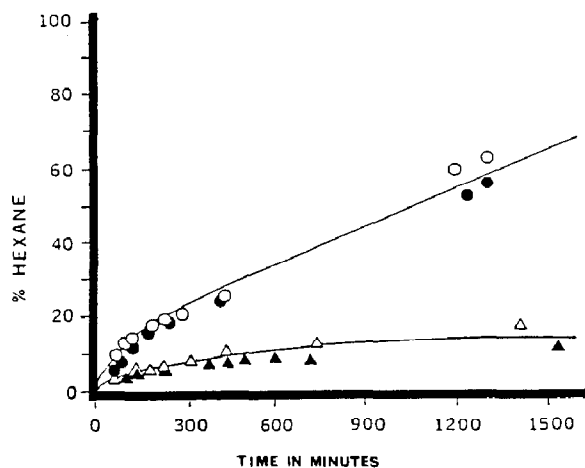


Fig. 4. Hydrogenation of 1-hexene using *cct*- ( $\Delta$ ,  $\blacktriangle$ ) and *ttt*-( $\text{PhMe}_2\text{P}$ ) $_2\text{Ru}(\text{CO})_2\text{Cl}_2$  ( $\circ$ ,  $\bullet$ ) as catalysts. Catalyst concentration 2.0 millimolar; 100 °C, 100 psi  $\text{H}_2$ . Open and closed symbols represent two replicate experiments.

plexes are higher throughout catalysis than those of the corresponding *cct* complexes. This suggests that the catalytically active species though perhaps present in small amount, is long lived. Such species usually cannot be detected [22], so it is not unexpected that only the *cct* isomer was typically found by IR and NMR spectroscopy in either the catalysis solution or the catalytic residues.

The greater catalytic activity of the *ttt* complexes can be attributed to the geometry of the complex, specifically to the *trans* orientation of the carbonyl ligands. The large *trans* effect of coordinated CO causes a weakening of the *trans* M–CO bond and facilitates CO dissociation. The *cct* isomers are also likely to enter the catalytic cycle by CO dissociation, but at a much lower rate than the corresponding *ttt* isomer. In the *cct* isomer the chloride ligand *trans* to CO has only a small *trans* effect and thus does not labilize the *trans* CO.

In addition to the difference in catalytic activity as a function of complex geometry, there is an even more dramatic effect due to the nature of the phosphine. An increase in catalytic activity is observed which corresponds to a decrease in the basicity and an increase in the steric bulk of the phosphine. The turnover number increases by more than 200 times when comparing the *cct* complexes of  $\text{Me}_3\text{P}$  and  $\text{Bzl}_3\text{P}$  and 63 times for the *ttt* isomers of  $\text{Me}_3\text{P}$  and  $\text{Bzl}_3\text{P}$ . The similar trends in the rates of alkene hydrogenation and isomerization for the two isomers suggests that a common pathway occurs for these two processes.

The relative activity of the *ttt*- and *cct*-( $\text{R}_3\text{P}$ ) $_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes increases with increasing phosphine basicity. This relative activity may be expressed by the ratio of the turnover number of the *ttt* isomer to the turnover number for the *cct* isomer. This ratio increases in the sequence  $\text{Bzl}_3\text{P}(1.8) < \text{Ph}_2\text{MeP}(3.2) < \text{PhMe}_2\text{P}(3.9) < \text{Me}_3\text{P}(> 5)$ .

The difference in the catalytic activities of the *ttt*- and *cct*-( $\text{R}_3\text{P}$ ) $_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes is in stark contrast to what was observed for the ( $\text{R}_3\text{P}$ ) $_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes, where the initial complex geometry had little or no effect on catalytic activity. This difference seems to be associated with the donor ability of the ligand that dissociates during the isomerization of the complex. Phosphine from

$(R_3P)_3Ru(CO)Cl_2$  is a better donor than CO from  $(R_3P)_2Ru(CO)_2Cl_2$  and competes more effectively with  $H_2$  or alkene than does CO for the vacant coordination site on  $(R_3P)_2Ru(CO)Cl_2$ . Basolo and Pearson [24] have shown that  $Ni(CO)_4$  also discriminates between these two donors. Displacement of CO by  $Ph_3P$  occurs five times more rapidly than ligand exchange with  $C^{18}O$ .

*Homogeneous hydrogenation in the presence of Lewis acids and trimethylamine oxide as cocatalysts*

Lewis acids have been used in conjunction with transition metal complexes in order to increase the activity or selectivity of the original catalyst. Since entry into the catalytic cycle for the complexes studied herein is probably a dissociative process, species that could facilitate ligand dissociation might promote catalysis. Aluminum chloride [25–30] and  $BCl_3$  [31] could promote  $Cl^-$  abstraction. Aluminum chloride has been shown to increase the catalytic activity of rhodium [29] and cobalt [30] based hydrogenation catalysts. Boron trichloride is also known to aid in phosphine dissociation [32]. The Lewis acid  $SnCl_2$  has been suggested to influence catalytic activity by insertion into the metal–chloride bond. The resulting  $SnCl_3^-$  ligand has a large *trans* effect and is an excellent  $\pi$ -acceptor [33,34], properties which labilize the transition metal center [35]. Several catalytic systems involving  $SnCl_3^-$  are known [36–38] but  $SnCl_2$  is also known to inhibit catalysis [39,40].

The use of trimethylamine oxide as a cocatalyst might also improve catalytic activity by removing a CO as  $CO_2$  [41–44]. This reaction is generally limited to complexes with  $\nu(CO)$  greater than  $2000\text{ cm}^{-1}$  and CO force constants greater than  $16.0\text{ millidynes/cm}^{-1}$  [43]. The *ttt*- $(R_3P)_2Ru(CO)_2Cl_2$  complexes fulfill both of these requirements [10].

The *ttt*- $(Ph_2MeP)_2Ru(CO)_2Cl_2$  complex was employed for the hydrogenation of 1-hexene in the presence of these Lewis acids and  $Me_3NO$ . The ratio of cocatalyst to complex was based roughly on the requirements for activity seen in other systems, with  $AlCl_3$ ,  $BCl_3$ ,  $SnCl_2 \cdot 2H_2O$  and  $Me_3NO$  present in 6/1, 4/1, 1/1 and 8/1 molar ratios. The conditions were otherwise identical to those employed without the cocatalysts.

The results of these experiments are summarized in Table 2. The hydrogenation of 1-hexene was completely inhibited by  $BCl_3$  and  $AlCl_3$ . The isomerization of 1-hexene was also much slower than with *ttt*- $(Ph_2MeP)_2Ru(CO)_2Cl_2$  alone. Added  $SnCl_2 \cdot 2H_2O$  slowed hexene hydrogenation by 71% compared to catalysis in its

Table 2

Isomerization and hydrogenation of 1-hexene with *ttt*- $(Ph_2MeP)_2Ru(CO)_2Cl_2$

Cocatalyst	Cocatalyst/ Catalyst <sup>a</sup>	Maximum turnover number <sup>b</sup>	2-hexene (%) (time, in minutes)
–	–	120	27 (40)
$AlCl_3$	6/1	<sup>c</sup>	4 (245) <sup>d</sup>
$BCl_3$	4/1	<sup>c</sup>	6 (245) <sup>d</sup>
$SnCl_2 \cdot 2H_2O$	1/1	35	29 (35)
$Me_3N \rightarrow O$	8/1	115	> 27 (< 15)

<sup>a</sup> Mole ratio. <sup>b</sup> In moles hexane/moles catalyst/hour. <sup>c</sup> No hexane produced. <sup>d</sup> 2-Hexene still slowly increasing.

absence but had little effect on the rate of hexene isomerization. The  $\text{Me}_3\text{NO}$  had little effect on hydrogenation, but caused a large increase in the rate of alkene isomerization. Except for  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , all these cocatalysts caused extensive decomposition of  $\text{t}t\text{t}-(\text{Ph}_2\text{MeP})_2\text{Ru}(\text{CO})_2\text{Cl}_2$ . With  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$   $\text{c}c\text{t}-(\text{Ph}_2\text{MeP})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  was recovered in greater than 98% yield after catalysis.

## Conclusions

Each of the complexes catalyzed the homogeneous hydrogenation and isomerization of 1-hexene to 2- and 3-hexenes. The extent of hydrogenation suggests that a monohydride pathway is probably operative. The geometry of the  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes has a large influence on the catalytic activity, with the *t*t*t* isomer showing greater activity than the *c*c*t* isomer. In contrast, the geometry of the  $(\text{R}_3\text{P})_3\text{Ru}(\text{CO})\text{Cl}_2$  complexes had very little influence on the catalytic activity. For both series of complexes, the nature of the phosphine influences the catalytic activity, which decreased with a decrease in the size and an increase in the basicity of the phosphine. With most of the  $(\text{R}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  complexes, the *c*c*t* isomer may be recovered in high yield and recycled numerous times. It appears that the  $(\text{BzI}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  and  $(\text{Ph}_3\text{P})_2\text{Ru}(\text{CO})_2\text{Cl}_2$  [18–20] complexes could be of general synthetic utility for the hydrogenation of alkenes.

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