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THE CATALYTIC ACTIVITY OF NEW RUTHENIUM(II) COMPLEXES CONTAINING CHELATING DIPHOSPHINE LIGAND IN THE HOMOGENEOUS HYDROGENATION OF CYCLOHEXENE

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Abstract—A series of new hydridocarbonyl ruthenium(II) complexes containing chelating diphosphine ligands of the type $[RuHCl(CO)(PPh_3)(L\text{-}L)]$ [L-L = $Ph_2PCH_2PPh_2$ **2**, $Ph_2PCH_2CH_2PPh_2$ **3**, $Ph_2PCH_2CH_2CH_2PPh_2$ **4**, *cis*-$Ph_2PCH{=}CHPPh_2$ **5** and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ **6**] has been prepared by the reactions of $[RuHCl(CO)(PPh_3)_3]$ **1** with $Ph_2PCH_2PPh_2$ [dppm, *bis*(diphenylphosphino)methane], $Ph_2PCH_2CH_2PPh_2$ [dppe, 1,2-*bis*(diphenylphosphino)ethane], $Ph_2PCH_2CH_2CH_2PPh_2$ [dppp, 1,3-*bis*(diphenylphosphino)propane], *cis*-$Ph_2PCH{=}CHPPh_2$ [dppv, *cis*-1,2-*bis*(diphenylphosphino)ethylene] and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ [(dppf, 1,1′-*bis*(diphenylphosphino)ferrocene] in boiling PhMe. The compounds **2–6** are moderately stable in solution. The new compounds were characterized by elemental analysis, IR and ^1H NMR spectroscopy. Compounds **1–6** have been shown to catalyse the homogeneous hydrogenation of the C=C bond of cyclohexene; some relations between structures and catalytic activities are described. The Arrhenius activation energy of cyclohexene for compound **4** is 33.0 kJ mol^{-1}.

Homogeneous hydrogenation of unsaturated organic compounds by platinum group metal (Ru, Rh, Pd, Os, Ir, Pt) complexes has played a key role in the fundamental understanding of catalytic reactions.[1] A number of neutral ruthenium complexes of tertiary phosphine, hydride and carbonyl (or halide) ligands, such as $RuHCl(PPh_3)_3$,[2] $[RuHX(CO)(PPh_3)_3]$ (X = Br,Cl),[3] $RuHCl(CO)(PCy_3)_3$,[3] $RuH_2(CO)_2(PPh_3)_2$[4] and $RuH_2(CO)(PPh_3)_3$,[5] are known to be efficient catalyst precursors for homogeneous reduction of organic compounds, such as the hydrogenation of olefins, the oligomerization of ethylene and butadiene, the hydrogenation of aldehydes and ketones and the transfer hydrogenation of conjugated organic functional groups.[6]

An objective of our current research is to synthesize transition metal complexes of bidentate ligands that may be efficient homogeneous catalysts. A bidentate phosphine ligand has several advantages over comparable monodentate ligands: (i) more control on the coordination number, stoichiometry and stereochemistry of the resulting complex; (ii) an increased basicity (or nucleophilicity) at the metal.[7]

Robinson and co-workers have developed the synthesis of creamy white, air-stable ruthenium and

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osmium complexes of the type $[MHCl(CO)(PPh_3)_3]$ [M = Ru **1**, Os] by the reaction of the metal salts with PPh_3 and aqueous formaldehyde in boiling 2-methoxyethanol.[8] $[MHCl(CO)(PPh_3)_3]$ [M = Ru **1**, Os] has been shown to be a good catalyst for the hydrogenation of olefins. Sanchez-Delgado *et al.* reported that complex **1** catalysed the reduction of aldehydes and ketones to their corresponding alcohols.[9] The most interesting result of their experiments is the high turnover number of complex **1**. In the reduction of propionaldehyde to propan-1-ol by complex **1**, the turnover number was up to 32,000.

The substitution chemistry of complexes of the general formula $RuHCl(CO)(PR_3)_3$ is relatively undeveloped. Garrou *et al.* reported ruthenium(II) dihydride complexes containing diphosphine and arphos ($Ph_2AsCH_2CH_2PPh_2$) were good catalyst precursors for the dehydrogenation of alcohols, as well as for the hydrogenation of aldehydes. $RuH_2(CO)(PPh_3)$(arphos) showed its higher catalytic activities than $RuH_2(CO)(PPh_3)$(dppe).[10] While in our previous results for the hydrogenation of propionaldehyde to propan-1-ol, [RuHCl(CO)(PPh_3)(dppe)] **3** has been shown to be a more effective catalyst precursor than $RuHCl(CO)(PPh_3)$(arphos).[11]

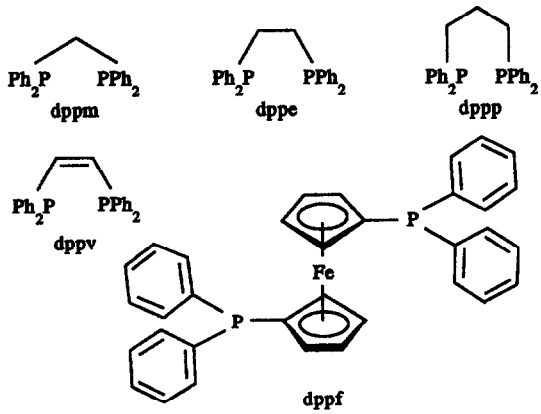
In a previous report we have described the syntheses and some catalytic applications of ruthenium and osmium arsine complexes also containing hydride, carbonyl and carboxylate ligands or arphos.[12]

$$MCl(CO)(OCOMe)(AsPh_3)_2$$

$$MHCl(CO)(AsPh_3)(arphos)$$

M = Ru, Os; arphos = $Ph_2PCH_2CH_2AsPh_2$

We describe here some of our results which indicate that ruthenium(II) complexes containing chelating diphosphine ligands can be rapid and efficient hydrogenation catalysts for cyclic olefins. Chelating diphosphine ligands used in this research are shown in Scheme 1.



Scheme 1.

EXPERIMENTAL

Except where noted, dry cyclohexene and solvents were used. The preparations of all the complexes were necessarily performed in an oxygen-free environment. $RuCl_3 \cdot 3H_2O$, PPh_3 and diphosphine ligands were purchased from Aldrich and used without further purification.

Physical measurements

^1H NMR spectra were recorded on Bruker AMX-500 (500 MHz) or Varian Gemini-300 (300 MHz) instruments. Variable-temperature ^1H NMR spectra were obtained using a Bruker AMX-500, using toluene-d_8. Chemical shifts are expressed in ppm relative to $SiMe_4$. IR spectra were measured with a MIDAC model 101025 FT-IR spectrometer in KBr discs. Elemental analyses were performed at Micro-Tech Analytical Laboratories, Skokie, Illinois, U.S.A. The analyses of the products of the catalytic reactions were performed with a Hewlett–Packard 5890 Series II gas chromatograph using HP-5 (cross-linked 5% PhMe silicone; 25 mm × 0.2 mm × 0.11 μm film thickness) column and internal standard (n-heptane) method. The chromatograph was connected to a HP 3394A integrator.

Preparation of $RuHCl(CO)(PPh_3)(Ph_2PCH_2PPh_2)$ (2)

A suspension of compound **1**[13] (0.48 g, 0.5 mmol) in PhMe (30 cm^3) was treated with $Ph_2PCH_2PPh_2$ (0.289 g, 0.75 mmol) and heated for 30 min under reflux. After the mixture was cooled to room temperature, a yellow solution was obtained, which was concentrated *in vacuo* to *ca* 15 cm^3. After the slow addition of n-pentane (30 cm^3) an off-white precipitate was formed, which was filtered off, washed with small quantities of n-pentane and ethyl ether and dried *in vacuo*: yield 0.401 g (98% based on Ru). IR (KBr disc, cm^{-1}): 1939 vs, 1483 m, 1435 vs, 1188 m, 1119 m, 1096 m, 741 s, 694 vs, 542 m, 517 m. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ −8.1 [dq, ^2J(H—*trans*-P) = 128.3 Hz, ^2J(H—*cis*-P) = 19.1 Hz], −13.6 [dq, ^2J(H—*cis*-P) = 22.4, 17.1, 19.7 Hz].

Preparation of $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$ **(3)**

This complex was prepared analogously by a previous method.[11]

Preparation of $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ **(4)**

This complex was prepared according to a similar method as that used to prepare compound **2**, with compound **1** (0.96 g, 1.0 mmol) and $Ph_2PCH_2CH_2CH_2PPh_2$ (0.619 g, 1.5 mmol): white precipitate: yield 0.668 g (80% based on Ru) IR (KBr disc, cm^{-1}): 1927 vs, 1483 m, 1435 vs, 1190 m, 1096 m, 743 s, 696 vs, 540 m, 513 m. ^1H NMR (500 MHz, toluene-d_8, 25°C): δ −6.1 (m), −15.5 (m).

Preparation of $RuHCl(CO)(PPh_3)(cis\text{-}Ph_2PCH{=}CHPPh_2)$ **(5)**

This complex was prepared according to a similar method as that used to prepare compound **2**, with compound **1** (0.48 g, 0.5 mmol) and *cis*-$Ph_2PCH{=}CHPPh_2$ (0.297 g, 0.75 mmol): white precipitate: yield 0.259 g (63% based on Ru) IR (KBr disc, cm^{-1}): 1946 vs, 1699 m, 1649 m, 1539 s, 1435 s, 1186 m, 1098 m, 742 s, 696 vs, 546 m, 519 m. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ −5.5 [dq, ^2J(H—*trans*-P) = 118.0 Hz, ^2J(H—*cis*-P) = 20.7, 17.4 Hz].

Preparation of $RuHCl(CO)(PPh_3)(Fe(\eta^5\text{-}C_5H_4PPh_2)_2)$ **(6)**

This complex was prepared according to a similar method as that used to prepare compound **2**, with compound **1** (0.48 g, 0.5 mmol) and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (0.416 g, 0.75 mmol): yellow precipitate: yield 0.416 g (85% based on Ru) IR (KBr disc, cm^{-1}): 1923 vs, 1479 m, 1433 s, 1186 m, 1163 m, 1088 s, 1028 m, 743 s, 694 vs, 592 m, 513 m, 494 m. ^1H NMR (300 MHz, $CDCl_3$, 25°C): δ −7.9 [dq, ^2J(H—*trans*-P) = 108.6 Hz, ^2J(H—*cis*-P) = 27.8, 27.8 Hz].

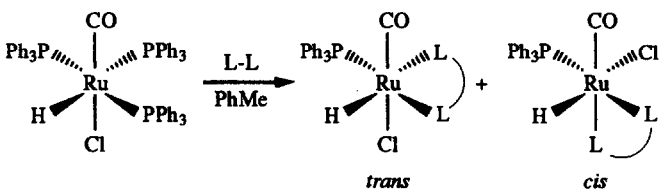
Hydrogenation reactions

A 60 cm^3 PhMe solution containing catalyst (2.0×10^{-2} mmol), substrate (2.0 mmol) and n-heptane (internal standard material; *ca* 0.2 g) was introduced into an autoclave[14] fitted with a sampling valve. It was flushed three times by 5 atm. hydrogen gas and was filled to *ca* 15 atm. with hydrogen gas. The temperature was raised to 150°C (taking *ca* 40 min), and then the hydrogen gas pressure was modified at 20 atm. and maintained constant throughout the reaction by a continuous supply from a high-pressure reservoir. At this time, stirring commenced. Then (*zero time*), samples of the reaction mixture were obtained in an aluminium capped vial (2 cm^3) through a needle attached to the autoclave every 20 min and quenched at −20°C to keep further reaction from proceeding, and quantitatively analysed immediately by a gas chromatograph equipped with an FID detector.

RESULTS AND DISCUSSION

Ruthenium(II) diphosphine complexes

Compound **1** reacted readily with an excess of the bidentate ligands $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), *cis*-$Ph_2PCH{=}CHPPh_2$ (dppv) and $Fe(\eta^5\text{-}C_5H_4PPh_2)_2$ (dppf) to yield the corresponding diphosphine complexes $[RuHCl(CO)(PPh_3)(L\text{-}L)]$ **2**: L-L = dppm; **3**: L-L = dppe; **4**: L-L = dppp; **5**: L-L = dppv; **6**: L-L = dppf), according to eq. (1).



(1)

$$RuHCl(CO)(PPh_3)_3 + L\text{-}L \rightarrow \underset{\mathbf{1}}{} \quad RuHCl(CO)(PPh_3)(L\text{-}L) \quad (1)$$
$$\underset{\mathbf{2\text{–}6}}{}$$

L-L	*trans* isomer	*cis* isomer
dppm **2**	40%	60%
dppe **3**	90%	10%
dppp **4**	≃100%	Trace
dppv **5**	100%	.....
dppf **6**	100%	.....

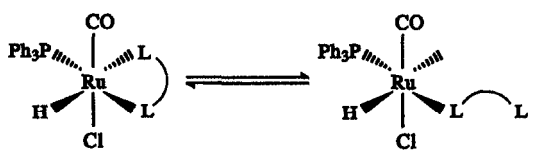
Analytical data of these complexes are shown in Table 1. In the ^1H NMR spectrum of **2**, the metal

Table 1. Elemental analysis

Compound	Found (Calc.)% C	H
2 $RuHCl(CO)(PPh_3)(Ph_2PCH_2PPh_2)$	64.9(65.0)	4.7(4.7)
4 $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$	66.0(65.7)	5.1(5.0)
5 $RuHCl(CO)(PPh_3)(cis\text{-}Ph_2PCH{=}CHPPh_2)$	65.4(65.5)	4.6(4.6)
6 $RuHCl(CO)(PPh_3)(Fe(\eta^5\text{-}C_5H_4PPh_2)_2)$	64.8(64.8)	4.5(4.5)

hydride signal was detected at −8.1 ppm as a doublet of quartet [(i) *trans* isomer; ^2J(H—*trans*-P) = 128.3 Hz, ^2J(H—*cis*-P) = 19.1, 11.7 Hz] and −13.4 ppm as a doublet of quartets [(ii) *cis* isomer; ^2J(*H*—*cis*-P) = 22.4, 19.7, 17.1 Hz] to be consistent with a chelating phosphorus atom being *trans* to the hydride and *cis* to PPh_3 in the *trans* isomer and two chelating phosphorus atoms being *cis* to the hydride, respectively, in the *cis* isomer, as represented in eq. (1). It was based upon the observations that the metal hydride ligand *trans* to the π-accepting ligands [$P(OR)_3$, PR_3, AsR_3 etc.] shows less high-field chemical shift than −10 ppm in the ^1H NMR spectrum, while that *trans* to the non-π-accepting ligands shows more high-field chemical shift than −10 ppm in the ^1H NMR spectrum.[15] Garrou *et al.* also reported the presence of stereoisomers in the substitution reactions of chelate ligands.[10] Further spectroscopic data for **3–6** are shown in Table 2. To our surprise, the isomer ratio was slightly different in each complex and in each synthesis under the same reflux conditions.[11]

The dissociation step may occur by the dissociation of the phosphorus atom of the dppe ligand which is *trans* to the hydride ligand, as illustrated in eq. (2). Certainly, all of these transformations



(2)

may be reversible at elevated temperatures, e.g. during the hydrogenation reaction.

It is interesting to note that the coordination of *cis*-1,2-bis(diphenylphosphino)ethylene (dppv) **5** and 1,1′-bis(diphenylphosphino)ferrocene (dppf) **6** exclusively yield the *trans* isomer only, while $OsHCl(CO)(PPh_3)_3$ also reacts with dppm, dppe, dppp, dppv and dppf in boiling PhMe to yield the *trans* isomer as a unique product according to the ^1H NMR spectra of these compounds.[17] At any rate, these different isomer ratios in compounds **2–6** strongly depend upon the geometrical structure and the electronic character of the entering diphosphine ligands.

Catalytic hydrogenation of cyclohexene

All the complexes **1–6** are efficient catalyst precursors for the homogeneous hydrogenation of cyclohexene to cyclohexane under moderate reaction conditions.

Observed reaction rates (expressed as k_{obs}) from plots of time (min) vs ln[cyclohexene] are shown in Table 3. Rate constants (k_{obs}) and relative rates for the hydrogenation process have been obtained from the slopes of such plots and are collected in Table 3, together with data for the starting complex $RuHCl(CO)(PPh_3)_3$, which is included for comparison. The catalytic activity of the compound decreases in the order **4** > **3** > **1** > **6** > **5** > **2**. Except compounds **3** and **4**, complexes containing bidentate phosphine ligands have shown lower catalytic activities than compound **1**, which has monodentate PPh_3 ligands only. However, compared with our earlier observations in the homogeneous reduction of propionaldehyde to propan-1-ol, the catalytic activity of compound **3** was higher than that of $RuHCl(CO)(PPh_3)_3$.[11] This order of the catalytic activities might be caused by the result of combined effects, such as different steric hindrance of the incoming substrates, different ligand structures,[17] different type of organic functional groups, different isomer ratios of stereoisomers for compound **3**, and so on.

Several important relationships between structures and catalytic activities can be revealed. In compounds **2**, **3**, **4**, and **5**, their catalytic activities [expressed as $\ln(k_{obs} \times 10^3)$] have shown to be directly correlated to their chelate ring size in Fig. 1. (Correlation coefficient = 0.988) Chelate effects on reactions of this kind have recently been discussed in detail by Milstein *et al.*[18] The catalytic

Table 2. Spectroscopic data

Compound	^{1}H NMR Ru—H (ppm)[a]	
2 $RuHCl(CO)(PPh_3)(Ph_2PCH_2PPh_2)$	−8.1(dq)[b]	−13.4(dq)
3 $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$	−5.8(dq)	−15.5(dq)
4 $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$[c]	−6.1(dq)	−14.9(dq)
5 $RuHCl(CO)(PPh_3)(cis\text{-}Ph_2PCH{=}CHPPh_2)$	−5.5(dq)	[d]
6 $RuHCl(CO)(PPh_3)(Fe(\eta^5\text{-}C_5H_4PPh_2)_2)$	−7.9(dq)	[d]

[a] In $CDCl_3$.
[b] dq = doublet of quartet.
[c] In toluene-d_8.
[d] Not observed.

Table 3. Hydrogenation of cyclohexene catalyzed by Ru complexes[a]

Complex	$k_{obs} \times 10^3$ (min^{-1})[b]	Rel. Act.[c]
1 $RuHCl(CO)(PPh_3)_3$	17.67 ± 0.07	1.00
2 $RuHCl(CO)(PPh_3)(Ph_2PCH_2PPh_2)$	1.56 ± 0.04	0.09
3 $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$	22.08 ± 0.11	1.26
4 $RuHCl(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$	73.49 ± 0.22	4.16
5 $RuHCl(CO)(PPh_3)(cis\text{-}Ph_2PCH{=}CHPPh_2)$	6.82 ± 0.03	0.39
6 $RuHCl(CO)(PPh_3)(Fe(\eta^5\text{-}C_5H_4PPh_2)_2)$	7.03 ± 0.05	0.40

[a] In PhMe, 150°C, 20 atm. hydrogen [cyclohexene] = 2.0 mmol, [catalyst] = 2.0×10^{-2} mmol.
[b] k_{obs} in $-d[\text{cyclohexene}]/dt = k_{obs}$ [cyclohexene].
[c] k_{obs}/k_{obs} for $RuHCl(CO)(PPh_3)_3$.

activity will increase when their chelate ring size increases, which may be attributed to the increased fluxionalities of the ligand. In complex **2**, the four-membered rings are so strained that they do not readily open to give a vacant site. The slight difference of the catalytic activities of compounds **3** and **5** (their chelate ring size are the same as for **5**) may be the result of the different geometrical structure of the chelating ligands and the different electronic nature of the chelating ligands; in compound **3**, sp^3 C—C bond, while sp^2 C=C bond in compound **5**.

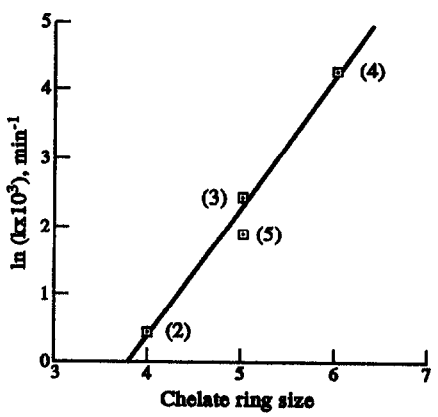


Fig. 1. Plots of the chelate ring size vs ln ($k_{obs} \times 10^3$).

The variable-temperature ^{1}H NMR spectra for compounds **4** and **5** are shown in Fig. 2. Compound **4** exhibits very complicated metal hydride signals above 47°C and the unambiguous assignment of peaks is impossible. However, compared with that of compound **5**, whose metal hydride signals do not change greatly within the observed temperature range (303–363 K), the bidentate–monodentate transformation of the bidentate phosphine ligand [*trans* to the hydride for the *trans* isomer, as shown in eq. (2)] of compound **4** may be easy relative to that of compound **5**. Compound **1** loses *trans*-positioned PPh_3 in the presence of MeCN at 65°C, to yield $RuHCl(CO)(NCMe)(PPh_3)_2$.[19] Therefore, the initial stage of the catalytic cycle for compound **4** must be faster than those of others. This initial equilibrium stage may be the most important factor influencing the catalytic activities of compounds **2**–**6**.

This opening of the bidentate phosphine ligand is in turn influenced by the labilizing influence of

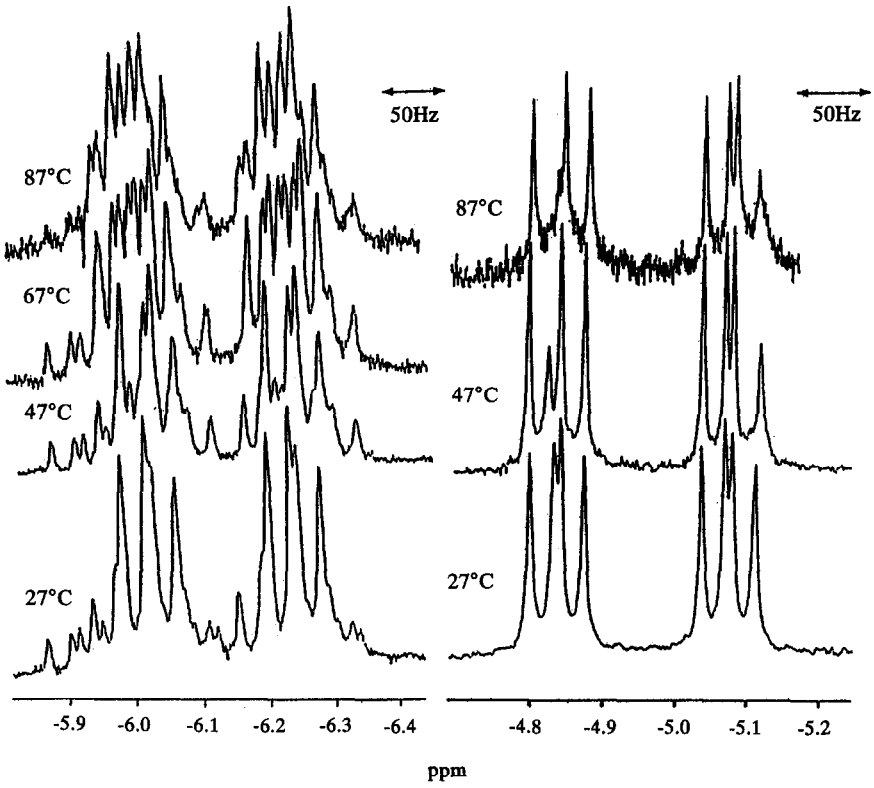


Fig. 2. ^{1}H NMR spectra recorded at different temperatures for complexes **4** and **5** in toluene-d_8 (hydrido region only).

the ligands *trans* to the metal–phosphorus bonds and the steric strain imposed by the chelate ring size, which is reasonable by considering the results of the additive effect, as shown in Figs 3 and 4 for compound **4**. In Fig. 3, when the ratio of free PPh_3 added was increased up to 3, the catalytic activities for compound **4** decreased rapidly. These results agree well with the results of Sanchez-Delgado *et al.*[3] In Fig. 4, additives of different steric factors (expressed as different Tolman's cone angles)[17] influence the catalytic activity of compound **4** differently. Relatively small free ligands decreased the catalytic activities greatly. This can be interpreted as the result of blocking the vacant site of the 16-electron intermediate by small free ligands added to form relatively stable 18-electron species for compound **4**. A similar decreased conversion (%) in the hydroformylations of hex-1-ene by $[RuH(CO)(NCMe)_2(PPh_3)_2]BF_4$ in the presence of

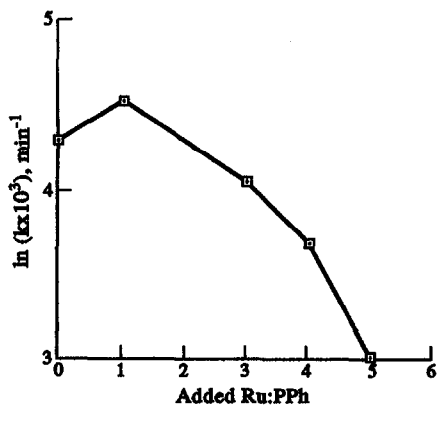


Fig. 3. Hydrogenation of cyclohexene for compound **4**.

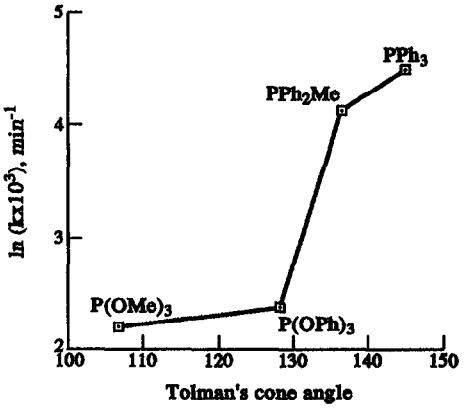


Fig. 4. Hydrogenation of cyclohexene for compound **4**. Every addition is an equimolar amount of compound **4**.

$P(OPh)_3$, PPh_3 and PCy_3 was reported.[20] In the case of PPh_2Me, the Tolman's cone angle of PPh_2Me (136°) is slightly larger than that of the dppp ligand (127°), the difference between the catalytic activities is not great.

Hydrogenation of cyclohexene by compounds **2–6** has shown first-order rate dependence on substrate concentration under the pseudo-first-order reaction condition. After hydrogenation, each reaction mixture of compounds **4–6** was characterized by ^1H NMR spectroscopy.[20] Compounds **4–6** existed in their original form. No metallic impurities were obtained after hydrogenation. Therefore, the compounds are very stable catalysts for the homogeneous hydrogenation of cyclohexene.

Compound **4** was shown to be the most efficient catalyst precursor. To determine the Arrhenius activation energy for the reduction of cyclohexene by compound **4**, its catalytic activities at four different temperatures were obtained.

Figure 5 shows the Arrhenius plot for the hydrogenation of cyclohexene by compound **4**. There is good linearity (correlation coefficient = 0.991) within the temperature range. Ignoring the difference of solubility of hydrogen within the temperature range, the reaction showed simple kinetics. The Arrhenius activation energy, calculated from the slope of Fig. 5, is 33.0 kJ/mol^{-1}. Wilkinson *et al.* reported the Arrhenius activation energy for the hydrogenation of cyclohexene by Wilkinson's catalyst to be 77.8 kJ mol^{-1}.[9]

A possible reaction pathway (olefin route[22]) for the *trans* isomer in the catalytic activity of the compound **4** is shown in Scheme 2, which closely

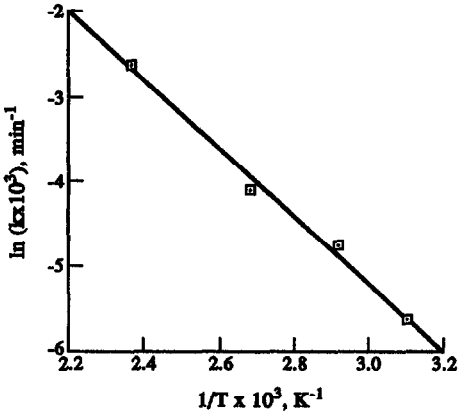
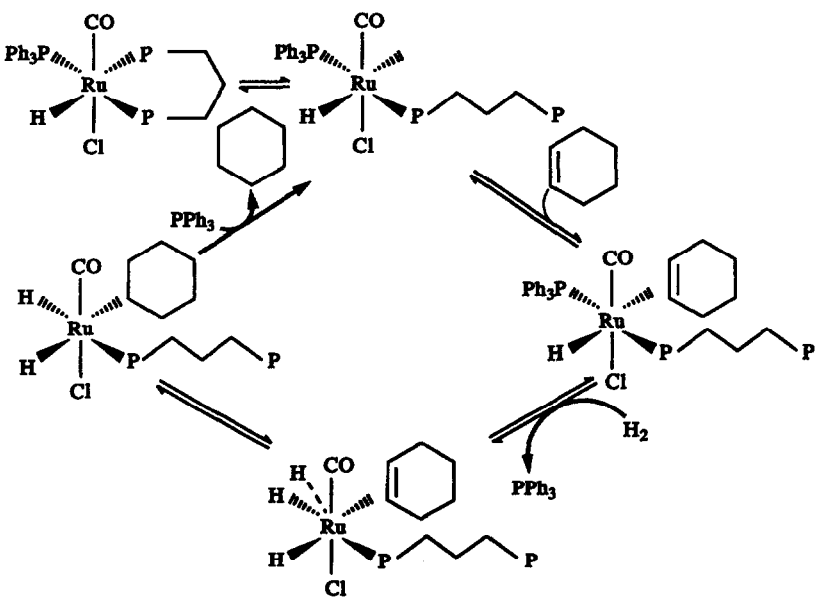


Fig. 5. Arrhenius plot for the hydrogenation of cyclohexene by compound **4**.

resembles the previously reported results by Sanchez-Delgado *et al.*[3(a)] However, it should be emphasized that other reaction routes may be possible for the *cis* isomer.

In Scheme 2, for the *trans* isomer of compound **4**, the chelating phosphorus atom *trans* to the hydride ligand may be dissociated to make a vacant site to accommodate the cyclohexene in the first step. Once cyclohexene is coordinated to the 16-electron intermediate, the oxidative addition of hydrogen and the transfer of hydride yield a nithenium-alkoxy intermediate. Cyclohexane is then separated by a reductive elimination process.

From Table 3, it is noted that the catalytic activities of compounds **2–6** (except compounds **3** and **4**) are much lower relative than $RuHCl(CO)(PPh_3)_3$.



Scheme 2.

However, compounds **3** and **4** can be dissociated much easier in the first equilibrium stage as a result of combined effects such as the ring strain, chelate effects, and the increased basicity (or nucleophilicity) at the metal.

The newly synthesized ruthenium(II) complexes catalyse the homogeneous reduction of cyclohexene. Due to the increased stabilities of these complexes with chelate ligands, the rate of the reduction of cyclohexene has been relatively slower than for that not containing a chelate ligand. Compounds **3** and **4**, however, have higher catalytic activity than compound **1**. The presence of stereoisomers in compounds **2–4** results in an obscure reaction mechanism. However, these catalytic systems offer valuable information about the chelate effect on the catalytic cycle. The presence of free ligands in the reaction mixture do influence the catalytic activity of compound **4**, which reasonably supports the proposed mechanism as shown in Scheme 2.

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