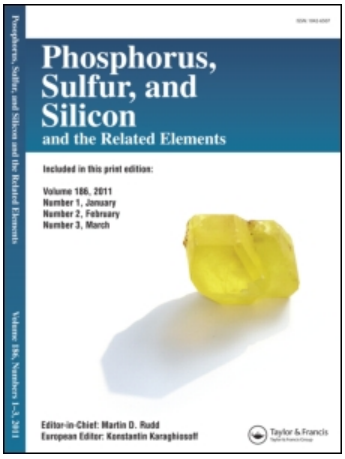

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Hydrogenation of Acetophenone and Its Derivatives with 2-Propanol Using Aminomethylphosphine-Ruthenium Catalysis

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HYDROGENATION OF ACETOPHENONE AND ITS DERIVATIVES WITH 2-PROPANOL USING AMINOMETHYLPHOSPHINE-RUTHENIUM CATALYSIS

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The reaction of 3′-aminopropyltriethoxysilane with the phosphonium salt ($[Ph_2P(CH_2OH)_2]Cl$) gives an aminomethylphosphine-type ligand ($((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$). Reaction of the ligand ($((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$) with silica gives silica supported aminomethylphosphine ligand (SiO_2)-O-$Si(CH_2)_3N(CH_2PPh_2)_2$). The ligands were refluxed with $[RuCl_2$(p-cymene)$]_2$ in toluene to give $[RuCl_2((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)]$ and silica-supported SiO_2)-O-$[RuCl_2((Si(CH_2)_3N(CH_2PPh_2)_2)_2]$ complex, respectively. The catalytic studies show that the complexes $[RuCl_2((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)]$ and SiO_2)-O-$[RuCl_2((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)_2]$ are very active catalysts for the transfer hydrogenation of acetophenone by 2-propanol in basic media. The best yield was observed in hydrogenation of* **m-methoxy acetophenone (95%) with catalyst $[RuCl_2((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)]$.*

Keywords Acetophenone; aminomethylphosphine; hydrogenation; silica

INTRODUCTION

In a homogeneous system, the use of transition metal complexes for catalysis has many advantages in organic synthesis.[1] The problems of homogeneous systems are separation and purification of heavy metals from the product. These problems of homogeneous catalysis systems restrict their application in organic synthesis.[1,2] Recently immobilizations of catalysts to solid supports are able to combine the advantages of homogenous and heterogeneous catalysis to overcome these problems.[3] Solid-supported catalysts are readily separated from the product, can be easily removed from the reaction mixture by filtration, and can be reused in subsequent reactions.[4]

Solid-supported catalysts have been studied by many researchers to compare transition metal complexes in homogeneous systems and heterogeneous systems due to higher catalytic activity under the same reaction parameters.[1,5] Phosphine functionalized Ru(II) complexes have been used as catalysts to generate highly enantioselective products for

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many asymmetric organic process such as the reduction of prochiral ketones to synthesize biologically active compounds.[6,7]

Catalytic transfer hydrogenation with the aid of a stable hydrogen donor is a useful alternative method for catalytic hydrogenation by molecular hydrogen.[8] In transfer hydrogenation, organic molecules such as primary and secondary alcohols[9] or formic acid and its salts[10] have been employed as the hydrogen source. The use of a hydrogen donor has some advantages over the use of molecular hydrogen, since it avoids the risks and the constraints associated with hydrogen gas as well as the necessity for pressure vessels and other equipment. Although metal catalyzed transfer hydrogenation using a stable H-donor has been found to be reliable, the current emphasis on cleaner methods for chemical transformations requires high selectivity, low cost, and minimum waste production.

Transition-metal catalyzed transfer hydrogenation using 2-propanol as a hydrogen source has become an efficient method in organic synthesis as illustrated by several useful applications reported in recent years.[11] The features for this important process are relatively mild conditions and environmentally friendly processes. The most commonly used catalysts for this reaction are ruthenium (II) complexes, but some rhodium and iridium derivatives have also been used.[12]

In this article, we report the synthesis of silica supported and unsupported N′N-bis(diphenylphosphinomethyl)aminopropyltriethoxysilane ligand and its Ru(II) complex. These complexes applied the reduction of derivative ketones as catalyst to compare catalytic activity of homogenized and heterogenized catalysts.

RESULTS AND DISCUSSION

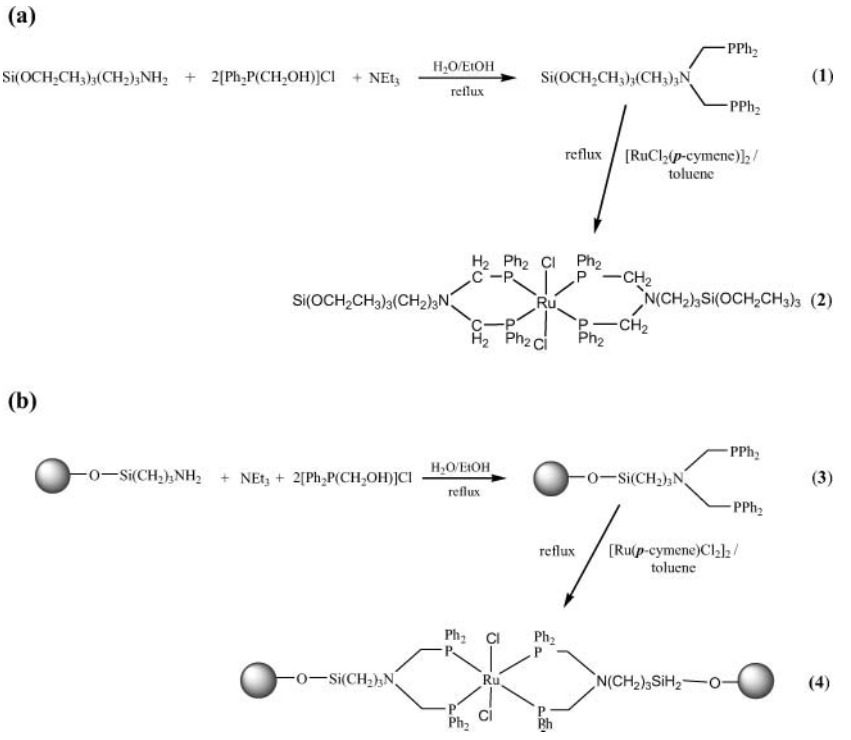
Synthesis and Characterization

Tertiary diphosphine ($(CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$) **(1)** was synthesized using a Mannich reaction by treating ($[Ph_2P(CH_2OH)_2]Cl$) with the appropriate primary amine. The silica-supported (SiO_2)-O-$Si(CH_2)_3N(CH_2PPh_2)_2$ ligand **(3)** was synthesized by modification of the method in the literature.[13] The Ru((II) complexes of the bis(diphenylphosphinomethyl)amino ligands were prepared using $[RuCl_2(p\text{-cymene})]_2$ complex as shown in Scheme 1.

The ^{13}C NMR spectrum of ligand **3** showed that signals appeared at 7.8 ($-Si\underline{C}H_2$), 23.7 ($SiCH_2\underline{C}H_2$),and 60.9 ($CH_2\underline{C}H_2N$) ppm were assigned to $SiCH_2CH_2CH_2N$ group. The carbon atoms of OCH_2CH_3 signals were occurred at 58.1 and 19.0 ppm, respectively. The signal at 62.9 ppm was assigned to $P-\underline{C}H_2-N$ carbon atom. All these spectra were consistent as reported in the literature.[14,15]

Complex **2** was obtained by reacting 2 equivalents of **1** with 1 equivalent of $[Ru(p\text{-cymene})Cl_2]_2$ under reflux for 6 h in toluene. The product was purified with acetone. The ^{31}P NMR signal of **1** was observed at -28.2 ppm and shifted to 27.1 ppm when it reacted with $[Ru(p\text{-cymene})Cl_2]_2$. Silica-supported complex **4** was synthesized by reacting ligand **3** with $[Ru(p\text{-cymene})Cl_2]_2$ in toluene and refluxing for 12 h. The product was purified with toluene and acetone. ^{31}P NMR signal of **3** shifted from -27.0 to 26.3 when reacted with $[RuCl_2(p\text{-cymene})]_2$.

It was found that ^{31}P NMR signals of two complexes showed more shielded signals compared with the uncoordinated aminomethylphosphine ligands. The coordination shift values of the complexes (Δ), as varied depending on the metal centers and the chemical structures of the ligands, showed that the ligands were bound to Ru(II) via a P-P bidentate to

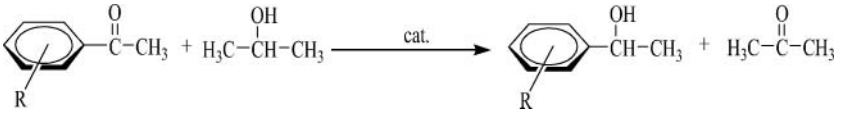


Scheme 1

give chelated complexes rather than Ru-N interaction.[16,17] Based on the elemental analysis of complex **2**, the ligand to metal ratio was found to be 2:1 having chlorides placed in the coordination sphere (Scheme 1).

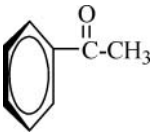
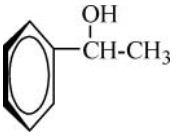
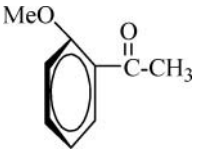
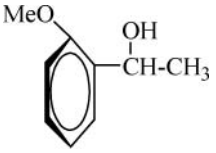
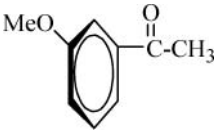
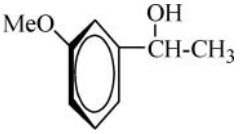
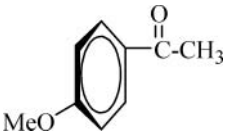
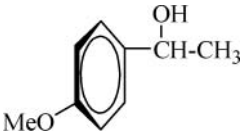
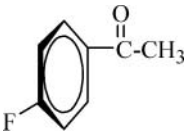
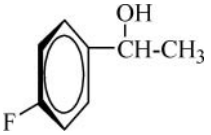
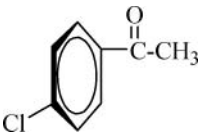
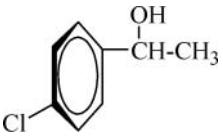
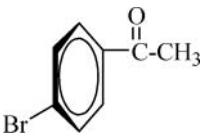
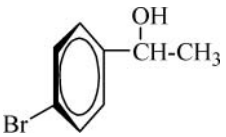
Hydrogenation of Acetophenone and Its Derivatives

The catalytic activity of the Ru(II) complexes was tested on the hydrogenation of aromatic ketones giving secondary alcohols (Scheme 2). Complexes **2** or **4** (0.01 mmol), 2-propanol (10 mmol), *t*-BuOK (5 mmol%), and the ketones (1 mmol) each were introduced into a Schlenk tube under an argon atmosphere. The resulting solution was heated at 80°C for 12 h. The hydrogenation results of acetophenone and its derivatives with the catalysts **2** or **4** are listed in Table I. The yield was affected by the reaction conditions as well as properties of the substituents of the ketones. With catalyst **2**, the ketones were hydrogenated in very high yield. The *m*-methoxy acetophenone was reduced in a 95% yield, and *o*-methoxy and *p*-methoxy acetophenone were reduced to secondary alcohols with 90% and 85% yield,



Scheme 2

Table I Hydrogenation of acetophenone and its derivatives with Ru(II) complexes with 2-propanol

Entry	Substrate	Product	Catalyst	Yield (%)[a,b]	TOF[c]
1			**2**	86	717
2			**4**	82	683
3			**2**	90	750
4			**4**	92	767
5			**2**	95	791
6			**4**	93	775
7			**2**	85	708
8			**4**	83	692
9			**2**	75	625
10			**4**	73	608
11			**2**	72	600
12			**4**	63	525
13			**2**	72	600
14			**4**	65	542

[a]Catalyst (0.01 mmol), substrate (1 mmol), ^{i}PrOH (10 mL), KOBu^{t} (5 mmol %), 80°C, 12 h.
[b]Purity of compounds is checked by NMR and GC; yields are based on methyl aryl ketone.
[c]TOF: (mol substrate/mol cat.)x percent/h.

respectively (Table I). The ketones having electron-withdrawing groups such as 2-fluoro, 2-chloro, and 2-bromo acetophenone reduced to secondary alcohols with 75%, 72%, and 72% yields, respectively.

All the ketones shown above were also investigated with the silica-supported Ru(II) complex **4**. By reducing the acetophenone and its derivatives to secondary alcohols, catalyst **4** exhibited small differences compared to the catalyst **2**. With catalyst **4**, *m*-methoxy acetophenone was reduced in high yield (93%) compared with *o*-methoxy acetophenone (92%) and *p*-methoxy acetophenone (85%) as catalyst **2**. All these results, as described in Table I, showed that ketones having electron-donating or electron-withdrawing groups

influenced the catalytic reaction.[18,19] Ketones that have methoxy group were reduced in high yields in the presence of catalysts **2** or **4** compared with electron-withdrawing substituted ketones (e.g., fluoro, chloro, or bromo). The results are consistent with the reported data.[20]

It is notable that solid-supported Ru(II) complex **4** exhibits small differences when compared to unsupported Ru(II) complex **2** as catalyst. However based on the TOF, the solid-supported complex **4** could have reuse potential to the same catalytic reaction without losing its activity.

CONCLUSIONS

Two complexes of Ru(II) with bidentate tertiary bis(diphenylphosphinomethyl)amino ligands have been synthesized and characterized using spectroscopic techniques. The ^{31}P NMR spectra of the complexes indicate that coordination of the aminomethylphosphine ligand occurs via two phosphorus atoms. The complexes have been tested as catalysts for hydrogenation of acetophenone. The results show that the homogeneous catalyst show higher catalytic activity than silica supported catalyst.

EXPERIMENTAL

Apparatus

Elemental analysis was performed on a LECO CHNS 932. FT-IR spectra were recorded in 4000–450 cm^{-1} range using a Perkin-Elmer RX1 FT-IR system as KBr pellets. The ^{13}C NMR and ^{31}P NMR spectra were recorded at 25°C in DMSO-d_6 and $CDCl_3$ using a Varian Mercury 200 MHz NMR spectrometer. ^{31}P NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H_3PO_4 as external standard. Solid NMR spectra were recorded using a solid NMR Bruker superconducting FTNMR spectrometer, model Avance TN 300 MHz WB.

General Procedures

All reactions were carried out under nitrogen atmosphere using conventional Schlenk glassware. The solvents were dried using established procedures and then were immediately distilled under nitrogen atmosphere prior to use.

$(CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$ (1). $[Ph_2P(CH_2OH)_2]Cl$ (0.6 g, 2.0 mmol) was dissolved in degassed 2:1 H_2O MeOH (20 mL) solvent system, and triethylamine (NEt_3) (0.5 mL, 1.7 mmol) was added to this solution and then 3′-aminopropyltriethoxysilane (1.0 mmol) and acetone 5 mL were added and refluxed for 4 h. The product was extracted with dichloromethane and crystallized at −20°C over 24 h. The solvent was removed in vacuum. Yield 0.50 g (78%). Calc. for $(CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$: C, 68.1; H, 7.3; N, 2.3%; Anal. Found: C, 67.9; H, 7.4; N, 2.2%. FT-IR (KBr, cm^{-1}) 2974, 1640, 1433, 1164, 1078, 749–695. ^{31}P NMR ($CDCI_3$, 25°C): δ −28.2 [$\underline{P}Ph_2$] ppm.

$[Ru((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)Cl_2]$ (2). Ligand **1** (1.0 g, 1.6 mmol) was added to a stirred solution of $[RuCl_2(p\text{-cymene})]$ (0.2 g, 0.65 mmol) in toluene (5 mL). The mixture was stirred under reflux for a further 6 h. Addition of diethylether (15 mL) gave the red solid, which was then filtered and dried in vacuum. Yield 0.37 g (72%). Calc. for $[Ru((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)Cl_2]$: C, 53.2; H, 5.8; N, 1.7%; Anal. Found: C, 53.1; H, 5.6; N, 1.2%. FT-IR (KBr, cm^{-1}) 3051, 2924, 1651, 1435, 1096, 738–695. ^{31}P NMR ($CDCI_3$, 25°C): δ 27.1 [Ru-$\underline{P}Ph_2$] ppm.

Silica-Aupported $(CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2$ (3). $[Ph_2P(CH_2OH)_2]Cl$ (0.57 g, 2 mmol) was dissolved in degassed 2:1 H_2O MeOH (20 mL) solvent system, and triethylamine (NEt_3) (0.5 mL, 1.75 mmol) was added to this solution. Silica-supported 3′-aminopropyltriethoxysilane (2g) and CH_2Cl_2 (10 mL) were added and refluxed for 6 h. The product was purified with acetone and dried in vacuum. Yield 2.3 g (75%). FT-IR (KBr, cm^{-1}) 3035, 2945, 1579, 1483, 1161, 1078, 797–690. ^{13}C NMR (25°C): 7.5–7.7, 18.6–18.7, 23.7, 55.4, 56.5, 58.1–59.8, 60.9–60.6, 128.3–133.7. ^{31}P NMR ($CDCI_3$, 25°C): δ −27.0 [$\underline{P}Ph_2$] ppm.

Solid-Supported $[Ru((CH_3CH_2O)_3Si(CH_2)_3N(CH_2PPh_2)_2)Cl_2]$ (4). Ligand **3** (2.0 g) was added to a stirred solution of $[RuCl_2(p\text{-cymene})]$ (1.2 g, 1.96 mmol) in toluene (5 mL). The mixture was stirred and refluxed further 12 h. The product was purified with CH_2Cl_2 (10 mL) and dried in vacuum. Yield 2.24 g (75%). FT-IR (KBr, cm^{-1}) 3053, 2919, 1664, 1436, 1120, 1098, 743–695. ^{31}P-NMR ($CDCI_3$, 25°C): δ 26.2 ppm.

Typical Procedure for the Transfer Hydrogenation of Ketones

The complexes (**2–4**) (0.01 mmol), 2-propanol (10 mL), *t*-BuOK (5 mmol%), and the substrate (1 mmol) were introduced into a Schlenk tube under argon. The resulting solution was heated at 80°C for 12 h. The solvent was then removed under reduced pressure and purified by flash chromatography (hexane:ethyl acetate, 10:1). Product distribution was determined by ^1H NMR spectroscopy and GC.

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