J. Chem. Sci. Vol. 127, No. 8, August 2015, pp. 1329–1338.
DOI 10.1007/s12039-015-0905-z

Synthesis and unexpected reactivity of [Ru(η^6-cymene)$Cl_2(PPh_2Cl)$], leading to [Ru(η^6-cymene)$Cl_2(PPh_2H)$] and [Ru(η^6-cymene)$Cl_2(PPh_2OH)$] complexes

ARUN KUMAR PANDIAKUMAR and ASHOKA G SAMUELSON*
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India
e-mail: ashoka@ipc.iisc.ernet.in

MS received 4 April 2015; revised 22 May 2015; accepted 30 May 2015

Abstract. The reaction of [Ru(η^6-cymene)Cl_2]$_2$ and PPh_2Cl in the ratio 1:2 gives a stable [Ru(η^6-cymene)$Cl_2(PPh_2Cl)$] complex. Attempts to make the cationic [Ru(η^6-cymene)$Cl(PPh_2Cl)_2$]Cl with excess PPh_2Cl and higher temperatures led to adventitious hydrolysis and formation of [Ru(η^6-cymene)$Cl_2(PPh_2OH)$]. Attempts to make a phosphinite complex by reacting [Ru(η^6-cymene)Cl_2]$_2$ with PPh_2Cl in the presence of an alcohol results in the reduction of PPh_2Cl to give [Ru(η^6-cymene)$Cl_2(PPh_2H)$] and the expected phosphinite. The yield of the hydride complex is highest when the alcohol is 1-phenyl-ethane-1,2-diol. All three half-sandwich complexes are characterized by X-ray crystallography. Surprisingly, the conversion of chlorodiphenylphosphine to diphenylphosphine is mediated by 1-phenyl-ethane-1,2-diol even in the absence of the ruthenium half-sandwich precursor.

Keywords. 1-Phenylethane-1,2-diol; chlorodiphenylphosphine; diphenylphosphine; diphenylphosphinous acid; half sandwich ruthenium complexes.

1. Introduction

Transition metal complexes containing organophosphorus ligands are ubiquitous.[1,2] The primary attraction in using phosphorus donors is the wide range of electronic and steric effects they exert.[3–5] Alkyl, aryl, alkoxy or aryloxy groups have been extensively used to tune the property of metal complexes formed by P(III) ligands.[6–8] However, P(III) ligands with hydrogen, halogen or the hydroxy group are less exploited for making metal complexes. In the case of hydroxy groups, the situation is quite complicated as the free ligand, $PR_2(OH)$, is quite unstable and rearranges to $(O)PR_2H$ and the ligand has to be generated in the coordination sphere of the metal.[9,10] Metal complexes of chlorodiphenylphosphine PPh_2Cl and diphenylphosphine PPh_2H, on the other hand, are readily synthesized by reacting the free ligand with an appropriate metal precursor.[11–14] However, these complexes are quite unstable due to the reactivity of P-Cl and P-H bonds as explained in the following paragraph with some representative examples.

The reaction of $[Fe(C_5H_5)(CO)_2THF]BF_4$ and PPh_2Cl gives the iron-phosphine complex $[Fe(C_5H_5)(CO)_2(PPh_2Cl)]BF_4$.[15] Similarly an iridium catalyst suitable for ring opening metathesis polymerization (ROMP) reactions $[Ir(OCH_3)(COD)(PPh_2Cl)]$, where COD is the labile cyclo-octadiene, is obtained from a reaction of the dimer $[Ir(COD)(OCH_3)]_2$ with PPh_2Cl.[16] However, these complexes are not very stable and undergo hydrolysis of the P-Cl bond or decomposition due to weak M-P bonds. Thus, the iron-PPh_2Cl complex mentioned above underwent hydrolysis in acetone to give a binuclear hydrogen bridged species $[\{Fe(C_5H_5)(CO)_2PPh_2PO\}_2H]$ which behaves as an acid of moderate strength.[15] Similarly, the anticancer activity of [Pd(dipropyldithiocarbamate)(PPh_2Cl)Cl] is lower than expected due to the weak Pd-P bond. Badshah and co-workers argue that it is likely to undergo decomposition before carrying out their expected function inside the cell.[17] Interestingly, PPh_2H complexes exhibit a number of reactions.[18] Coordinated P-H can react with an M-Cl bond and form a PPh_2Cl complex.[19] Such facile substitution reactions observed in the chemistry of PPh_2X ligands, where X is H or a group more electronegative than C, has deterred studies with PPh_2X ligands.

Several studies have exploited the reactivity of the coordinated PPh_2X to generate a desired complex. A series of palladium and platinum bisphosphinite complexes were generated *in situ* using $[M(PPh_2Cl)_2Cl_2]$ M = Pd or Pt. On reaction with chiral diols, they form very useful chiral catalysts.[20,21] In 2005, Bergamini and

*For correspondence

co-workers described the synthesis of a thiophosphinite-aminophosphane complex from a reaction of the complex $[M(PPh_2Cl)_2Cl_2]$ with the hydrochloride salt of the cysteine methyl ester in the presence of triethyl amine.[22] Another interesting example is the reaction of $(\mu\text{-S})_2Fe_2(CO)_6$, where the sulfido ligand in the coordination sphere of the metal reacts with the incoming PPh_2Cl to give an iron complex with the molecular formula $(\eta^1PPh_2PS\eta^1)_2Fe_2(CO)_6$ capable of catalyzing the reduction of a proton to dihydrogen.[23] Thus, the study of complexes formed by PPh_2X can be a rewarding exercise.

Among complexes containing phosphorus(III) ligands, half-sandwich ruthenium complexes are of special interest due to their versatility.[24] They are valuable in catalysis,[25–28] have marked anticancer activity[29] and their non-linear optical properties are tunable.[30,31] In this paper we report the synthesis, structure and reactivity of $[Ru(\eta^6\text{-cymene})Cl_2(PPh_2Cl)]$, $[Ru(\eta^6\text{-cymene})Cl_2(PPh_2H)]$ and $[Ru(\eta^6\text{-cymene})Cl_2(PPh_2OH)]$. Interestingly it is observed that the 1-phenylethane-1,2-diol mediates the transformation of PPh_2Cl to PPh_2H even in the absence of the half-sandwich precursor although in poorer yields. The source of hydrogen is not unambiguously identified due to the exchangeable nature of the P-H bond.

2. Experimental

2.1 *Materials and methods*

All reactions and manipulations were routinely performed under nitrogen atmosphere using standard Schlenk techniques in oven-dried glassware. Tetrahydrofuran and diethyl ether were distilled over sodium/benzophenone. Triethylamine was distilled over KOH followed by $LiAlH_4$. Diphenylphosphine chloride was purified by distillation under nitrogen atmosphere. Nuclear magnetic resonance spectra were recorded on a Bruker AMX 400 spectrometer operating at 400 MHz for ^1H, 100 MHz for ^{13}C, 162.02 MHz for ^{31}P ($CDCl_3$ as solvent). Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Phosphorus nuclear magnetic resonance spectra (^{31}P NMR) are reported in δ units, parts per million (ppm) relative to external H_3PO_4 (δ 0.0).

2.2 *X-ray Structure Determination of **2, 4** and **5***

Crystals of complexes **2, 4** and **5** suitable for X-ray diffraction study were carefully chosen and mounted on the Goniometer head. The unit cell parameters and intensity data were collected at room temperature employing a Bruker SMART APEX CCD diffractometer equipped with a $Mo_{K\alpha}$ X-ray source (50 KV, 40 mA). Data acquisition was carried out using SMART software and data reduction was carried out using SAINT software.[32] The empirical absorption corrections were carried out using the SADABS program.[33] The structure was solved and refined using the SHELXL-97 program.[34] Hydrogen atoms were fixed in idealized positions and refined in a riding model.

2.3 *Preparation of 1-phenylethane-1,2-diol*

To a suspension of lithium aluminium hydride (0.745 g, 19.71 mmol) in diethyl ether (20 mL) kept in an ice bath was added a solution of mandelic acid (0.5 g, 3.284 mmol) in dry diethyl ether (20 mL) over a period of 10 minutes. Once the addition was complete, the reaction mixture was refluxed for 3 h and cooled in an ice bath. Dilute HCl was added carefully to the stirred solution till the pH was between 4 and 5. The resulting suspension was passed through a celite pad and washed with diethyl ether (50 mL). The diethyl ether solution was dried over anhydrous sodium sulphate and concentrated to give the solid product. Recrystallization from toluene-hexane (1:2) gave colorless crystals. Yield: 72%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.38 (m, 5H, H_{arom}), 4.81 (t, 1H, J = 4 Hz, C*H*OH), 3.63-3.75 (m, 2H, CH_2OH), 2.94 (s, 1H, CHO*H*), 2.52(s, 1H, CH_2OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 129.0, 128.5, 126.6, 75.2, 68.5.

2.4 *Preparation of $[Ru(\eta^6\text{-cymene})Cl_2(PPh_2Cl)]$ (**2**)*

To a solution of $[Ru(\eta^6\text{-cymene})Cl_2]_2$ **1** (0.1 g, 0.163 mmol) in THF (5 mL) was added a solution of PPh_2Cl (0.12 mL, 0.652 mmol) in THF(1 mL) resulting in a blood red colored solution which was allowed to stir for 7 h at room temperature. The reaction mixture was then concentrated to 1/3 of the original volume and dry ether (10 mL) was added. It was stirred for two hours to give a dark red precipitate was obtained which upon recrystallization from chloroform-hexane mixture gave dark red crystals. Yield: 82%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (m, 4H), 7.39 (m, 6H), 5.36 (d, J = 6.4 Hz, 2H, *H*cym), 5.32 (d, J = 6.4 Hz, 2H, *H*cym), 2.88 (sept, 1H, C*H*Me_2), 1.99 (s, 3H, CH_3), 1.18 (d, 3H, J = 6.8 Hz, CH(CH_3)$_2$). $^{31}P\{^1H\}$NMR (162.02 MHz, $CDCl_3$): δ 95.9 (s). Anal.Calcd for $C_{22}H_{24}Cl_3PRu$: C 50.1927; H 4.5987. Found: C 50.6434; H 4.6817.

2.5 *Preparation of $[Ru(\eta^6\text{-cymene})Cl_2(PPh_2OH)]$ (**4**)*

$[Ru(\eta^6\text{-cymene})Cl_2]_2$ (0.1 g, 0.163 mmol) was dissolved in THF (5 mL) followed by addition of PPh_2Cl

(0.12 mL, 0.652 mmol) solution in THF (1 mL) that a gave a blood red colored solution which was refluxed for 10 h. The reaction mixture was then concentrated to 1/3 of the original volume and dry ether (10 mL) was added and stirred for two hours. A dark red precipitate obtained was filtered and dried in air. It was recrystallized from chloroform-hexane mixture to give dark red crystals. Yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.72 (m, 4H), 7.44-7.49 (m, 6H), 5.38 (d, J = 5.2 Hz, 2H, *H*cym), 5.24 (d, J = 6.0 Hz, 2H, *H*cym), 2.50 (sept, 1H, C*H*Me$_2$), 2.0 (s, 3H, CH_3), 0.98 (d, J = 6.8 Hz, 3H, CH(CH_3)$_2$). ^{31}P {^{1}H}NMR (162.02 MHz, $CDCl_3$): δ 107 (s) Anal.Calcd for $C_{22}H_{25}Cl_2OPRu$: C 51.9679; H 4.9597. Found: C 51.5800; H 5.0516.

2.6 *Preparation of [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **(5)***

To a solution of [Ru(η^6-cymene)Cl_2]$_2$ **1** (0.1 g, 0.163 mmol) in THF (5 mL) was added a solution of PPh_2Cl (0.12 mL, 0.652 mmol) in THF(1 mL) resulting in a blood red coloration, a THF solution of 1-Phenylethane-1,2-diol (0.045 g, 0.326 mmol) was added to this solution and stirred for 7 h. The reaction mixture was concentrated to 1/3 of the original volume and dry ether (10 mL) was added and stirred for two hours. A red precipitate was obtained that gave deep red crystals upon recrystallization from chloroform/hexane. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.75 (m, 10H, *Ph*), 6.44 (d, 1H, J_{P-H} = 416 Hz, PPh_2H), 5.40 (q, 4H, J = 4.0 Hz, *H*cym), 2.56 (sept, 1H, C*H*Me$_2$), 1.99 (s, 3H, CH_3), 0.97 (d, 6H, J = 8.0 Hz, CH(CH_3)$_2$)^{31}P{^{1}H}NMR (162.02 MHz, $CDCl_3$): δ 21.1 (s). ^{31}P NMR (162.02 MHz, $CDCl_3$): δ 21.2 (doublet of quintet, J_{P-H} = 414 Hz, $^3J_{P-Harom}$ = 10.4 Hz) Anal.Calcd for $C_{22}H_{25}Cl_2PRu$: C 53.6573, H 5.1209. Found C 53.1555, H 5.0060.

2.7 *Reaction of [Ru(η^6-cymene)Cl_2]$_2$ with PPh_2 Cl and isopropyl alcohol*

To a solution of [Ru(η^6-cymene)Cl_2]$_2$ (0.1 g, 0.163 mmol) in THF (5 mL) was added a solution of PPh_2Cl (0.06 mL, 0.326 mmol) in THF (1 mL) resulting in the characteristic red color, a THF solution of isopropyl alcohol (0.024 mL, 0.326 mmol) was added to this solution and stirred for 7 h. The reaction mixture was concentrated to 1/3 of the original volume and dry ether (10 mL) was added and stirred for a further period of two hours. The red precipitate obtained was filtered and dried in air. ^{1}H NMR spectrum recorded in $CDCl_3$ showed the presence of two complexes. *[Ru(η^6-cymene)$Cl_2(PPh_2H)$]* (28%) ^{1}*H* NMR (400 MHz, $CDCl_3$): 7.40-7.75 (m, 10H, *Ph*), 6.44 (d, 1H, J_{P-H} = 416 Hz, PPh_2H), 5.40 (q, 4H, J = 4.0 Hz, *H*cym), 2.56 (sept, 1H, C*H*Me$_2$), 1.99 (s, 3H, CH_3), 0.97 (d, 6H, J = 8.0 Hz, CH(CH_3)$_2$). ^{31}P{^{1}H}NMR (162.02 MHz, $CDCl_3$): δ 21.1 (s) and *[Ru(η^6-cymene)$Cl_2(PPh_2OCH(CH_3)_2)$]* (72%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (m, 4H), 7.46 (m, 6H), 5.22 (d, J = 6.12 Hz, 2H), 5.11 (d, J = 5.3 Hz, 2H), 4.58 (sept, 1H, OC*H*(CH$_3$)$_2$), 2.69 (sept, 1H, C*H*Me$_2$), 1.84 (s, 3H), 1.10 (dd, J = 7.0, 6.2 Hz, 12H, OCH(CH_3)$_2$, -CH(CH_3)$_2$). ^{31}P{^{1}H}NMR (162.02 MHz, $CDCl_3$): δ 107.9 (s).

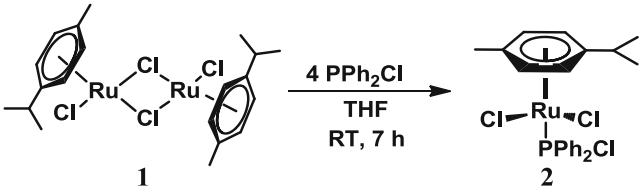
3. Results and Discussion

3.1 *Synthesis and characterization of [Ru(η^6-cymene)$Cl_2(PPh_2Cl)$]*

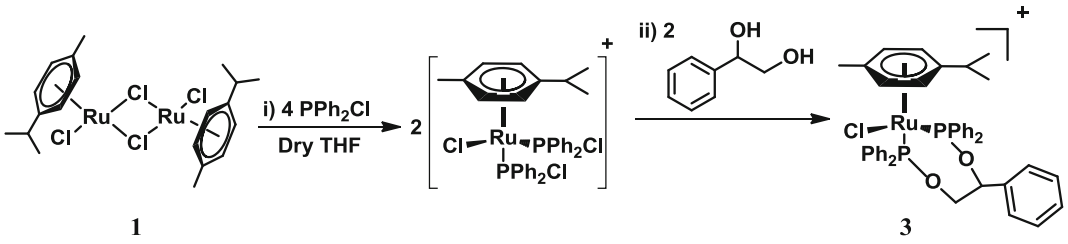
Reacting the dinuclear [Ru(η^6-cymene)Cl_2]$_2$ **1** with PPh_2Cl in THF at room temperature led to the formation of complex **2** in nearly quantitative yields as shown in scheme 1. Formation of the half sandwich complex [Ru(η^6-cymene)$Cl_2(PPh_2Cl)$] **2** was inferred from the ^{1}H and ^{31}P NMR spectra. The proton decoupled ^{31}P NMR spectrum exhibited a singlet at 95.9 ppm consistent with a coordinated PPh_2Cl. After work up and crystallization from a mixture of chloroform and hexane, the product was obtained as dark red crystals and was characterized further by single crystal X-ray crystallography.

3.2 *Attempted synthesis of of [Ru(η^6-cymene)Cl $(PPh_2Cl)_2$]Cl and formation of [Ru(η^6-cymene)$Cl_2(PPh_2OH)$]*

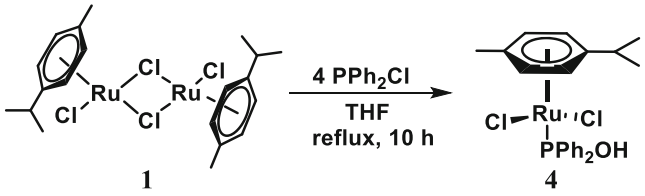
An attempt was made to generate the complex [Ru(η^6-cymene)Cl($PPh_2Cl)_2$]Cl a proposed intermediate as shown in scheme 2, en-route to the ruthenium bisphosphinite complex **3**. Since a room temperature reaction of [Ru(η^6-cymene)Cl_2]$_2$ **1** and PPh_2Cl in the appropriate ratio only resulted in the formation of **2**, the reaction mixture was refluxed for 10 h to force the formation of [Ru(η^6-cymene)Cl($PPh_2Cl)_2$]Cl. In the ^{1}H NMR spectrum of the product isolated from this reaction mixture, the ratio of the cymene isopropyl -C**H**(CH$_3$)$_2$ proton at 2.50 ppm, to the aromatic protons from the phenyl



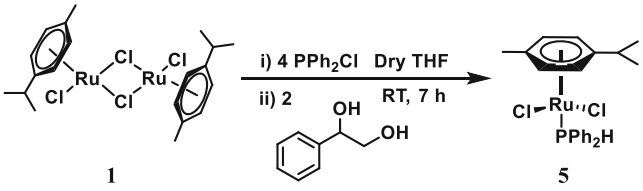
Scheme 1. [Ru(η^6-cymene)$Cl_2(PPh_2Cl)$] **2** using [Ru(η^6-cymene)Cl_2]$_2$ and chlorodiphenylphosphine.



Scheme 2. Proposed pathway for the synthesis of ruthenium bisphosphinite complex **3** using PPh_2Cl and 1-phenylethane1,2-diol.



Scheme 3. Formation of [Ru(η^6-cymene)$Cl_2(PPh_2OH)$] **4** in the reaction of **1** and PPh_2Cl.



Scheme 4. Formation of [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **5** employing 1-phenylethane1,2-diol and PPh_2Cl.

group at 7.46-7.74 ppm remained 1:10 suggesting that the expected complex was not formed. The ^1H decoupled ^{31}P NMR spectrum with a singlet at 107.2 ppm suggested that the phosphorus atom was now attached to an oxygen atom. A tentative assignment of structure **4,** (scheme 3) to the complex due to hydrolysis of the P-Cl bond in the starting material by the adventitious moisture present to form [Ru(η^6-cymene)Cl_2PPh_2OH], was confirmed by the X-ray crystal structure analysis (*vide infra*). This also suggested that the formation of [Ru(η^6-cymene)$Cl(PPh_2Cl)_2$]Cl was unfavourable compared to hydrolysis.

3.3 *Synthesis and characterization of [Ru(η^6-cymene)$Cl_2(PPh_2H)$]*

Previous reports on the facile formation of palladium and platinum bisphosphinite complexes employing [M(COD)Cl_2] M=Pd and Pt, chlorodiphenylphosphine and chiral diols encouraged us to attempt an *in situ* reaction.[20,21] Attempts to prepare ruthenium bisphosphinite complex using chlorodiphenylphosphine and 1-phenylethane-1,2-diol were made employing the dimer [Ru(η^6-cymene)$Cl_2]_2$ **1** as a metal precursor as depicted in scheme 2.

The reaction was carried out at room temperature for 7 h in THF. After workup and crystallization from chloroform-hexane solutions, the formation of red crystals was observed. It was analyzed in a similar way as mentioned earlier for the isolation of complex **2**. Instead of the expected product, the unusual formation of [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **5** in 93% yield (scheme 4) was inferred from spectroscopic studies and later confirmed by X-ray crystallography.

In the ^1H NMR spectrum of [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **5**, the proton attached to the phosphorus atom appeared as a doublet at 6.44 ppm due to coupling with the phosphorus atom. The $^1J_{P-H}$ value was found to be 412 Hz. The proton coupled ^{31}P NMR spectrum showed the phosphorus atom attached to the proton appeared as a doublet of a quintet at 21.2 ppm with a coupling constant of 413 Hz. This suggested that the phosphorus atom and the proton are directly connected to each other. To confirm the $^1J_{P-H}$ coupling between ^{31}P and ^1H, 2D heteronuclear single quantum coherence experiment was carried out. It showed a correlation peak between ^{31}P NMR at 21.2 ppm and the doublet at 6.44 ppm in ^1H NMR and confirmed the formation of [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **4**. Reactions in the absence of an alcohol only led to hydrolysis clearly demonstrating that 1-phenylethane-1,2-diol promotes the formation of [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **4** by acting as a good hydrogen donor.

3.4 *X-ray structural studies of **2**, **4** and **5***

Molecular structures of **2, 4** and **5** have been confirmed by X-ray crystallographic studies and their molecular structures are depicted in figures 1, 2 and 3 respectively. The crystallographic details, selected bond distances and angles have been summarized in tables 1 and 2. The three complexes adopt the three-legged piano stool structure and are quite similar to one another. The ruthenium center thus has a pseudo-octahedral geometry.

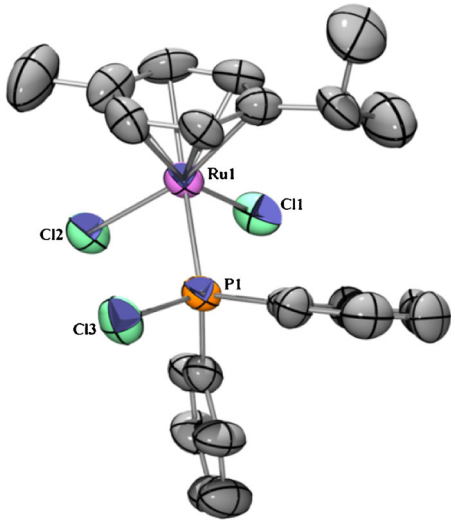


Figure 1. ORTEP view of [Ru(η^6-cymene)Cl_2(PPh_2Cl)] **2** at the 50% probability level showing selected atom labeling. Hydrogen atoms are omitted for clarity.

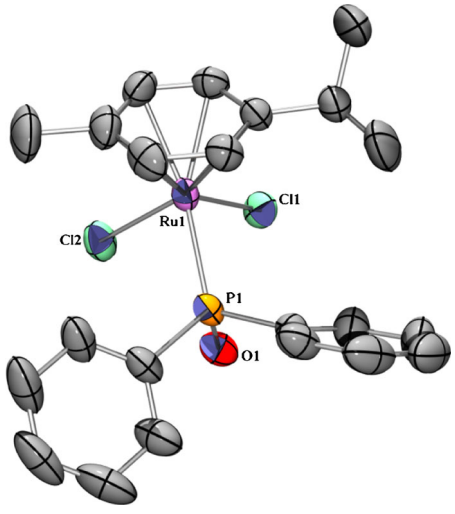


Figure 2. ORTEP view of [Ru(η^6-cymene)Cl_2(PPh_2OH)], **4** at the 50% probability level showing selected atom labeling. Hydrogen atoms are omitted for clarity.

3.5 *Reaction of [Ru(η^6-cymene)Cl_2]$_2$ with PPh_2 Cl and isopropanol*

The formation of the ruthenium phosphine complex **5** was then attempted with isopropanol a well established hydrogen donor in transfer hydrogenation reactions[35,36] to see if it can mediate the reduction of PPh_2Cl to generate PPh_2H more effectively than 1-phenylethane-1,2-diol. The reaction was carried out with the ruthenium cymene dimer **1**, chlorodiphenylphosphine and isopropanol in THF at room temperature for 7 h (scheme 5).

The reaction mixture was concentrated to one-third of its volume and dry diethyl ether was added to get a red precipitate. It was filtered, dried and analyzed by

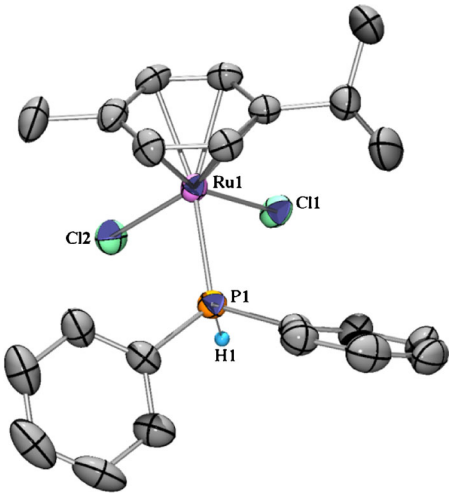


Figure 3. ORTEP view of [Ru(η^6-cymene)Cl_2(PPh_2H)] **5** at the 50% probability level showing selected atom labeling. Hydrogen atoms are omitted for clarity.

multinuclear NMR spectroscopic techniques. In the ^{1}H NMR spectrum, apart from the presence of cymene isopropyl group protons, resonances for additional isopropyl groups were observed from the isopropoxy moiety attached to the phosphorus atom. In the $^{31}P\{^1H\}$NMR spectrum two peaks were observed. A peak at 21.8 ppm was assigned for the ruthenium-PPh_2H complex **5,** and a peak at 107.9 ppm was assigned to the complex [Ru(η^6-cymene)Cl_2($PPh_2OCH(CH_3)_2$)] **6**. So even in the case of isopropanol, a good hydrogen donor, a mixture of ruthenium-PPh_2H **5**, and a ruthenium monophosphite complex **6** were observed in the ratio 28:72. The ratio of products was calculated from the ^{1}H NMR spectrum as the separation and purification of these products could not be carried out. Studies with a variety of other alcohols showed that 1-phenylethane1,2-diol was indeed unique as it led to exclusive formation of complex **5**.

3.6 *Reaction of 1-phenylethane-1,2-diol with PPh_2 Cl*

It was evident that the diol promotes the reduction of PPh_2Cl to PPh_2H. However it was not clear if the reaction was happening in the coordination sphere of the Ru or if the free ligand could be reduced by the diol resulting in PPh_2H independant of ruthenium. To verify this possibility, a stoichiometric reaction was carried out using 1-phenylethane-1,2-diol and PPh_2Cl in THF for 7 h at room temperature (scheme 6). After removal of the solvent, THF, dry $CDCl_3$ was added and ^{1}H and ^{31}P NMR spectra recorded.

In the proton decoupled ^{31}P NMR spectrum, a peak at –39.8 ppm was observed close to the reported value of free diphenylphosphine (–37.12 ppm)[42] in addition

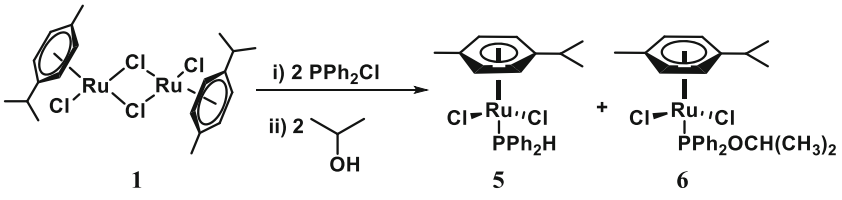
Table 1. Crystal data and refinement details for **2, 4** and **5**.

	2	**4**	**5**
Formula	$C_{22}H_{24}Cl_3PRu$	$C_{22}H_{25}Cl_2OPRu$	$C_{22}H_{25}Cl_2PRu$
Formula weight	527.81	507.35	492.36
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P21/C	P21/C	P21/C
T (K)	293(2)	293(2)	293(2)
a, Å	12.581(12)	10.3643(10)	10.4231(2)
b, Å	10.599(10)	12.2350(12)	11.7729(3)
c, Å	17.415(17)	17.5312(17)	17.5265(4)
α, deg	90.00	90.00	90.00
B	106.073(16)	99.185(2)	97.0820(10)
Γ	90.00	90.00	90.00
V, Å	2231(4)	2194.6(4)	2134.27(8)
Z	4	4	4
d_{calc}, g cm^{-3}	1.571	1.536	1.529
μ (mm^{-1})	1.139	1.040	1.063
λ(Å)	0.71073	0.71073	0.71073
R^a	0.0957	0.0438	0.0274
R_w	0.1913	0.0861	0.0567

[a] $R = \sum(|F_o|-|Fc|)/\sum|F_o|$, $Rw = [\sum w(|F_o|-|Fc|)^2/\sum w|F_o|^2]^{1/2}$ (based on reflections with $I > 2\sigma(I)$).

Table 2. Selected bond distances (Å) and bond angles (°) for complexes **2, 4** and **5.**

2		**4**		**5**	
Ru1-P1	2.311(3)	Ru1-P1	2.3115(10)	Ru1-P1	2.3226(5)
Ru1-Cl1	2.399(3)	Ru1-Cl1	2.4144(10)	Ru1-Cl1	2.4124(6)
Ru1-Cl2	2.406(3)	Ru1-Cl2	2.4152(10)	Ru1-Cl2	2.4214(6)
P1-Cl3	2.053(4)	P1-O1	1.601(3)	P1-H1	1.35(2)
Cl2-Ru1-Cl1	89.62(12)	Cl2-Ru1-Cl1	87.32(4)	Cl2-Ru1-Cl1	87.56(2)
P1-Ru1-Cl1	87.33(11)	P1-Ru1-Cl1	84.37(4)	P1-Ru1-Cl1	82.800(19)
P1-Ru1-Cl2	84.38(9)	P1-Ru1-Cl2	82.94(4)	P1-Ru1-Cl2	81.43(2)
Cl3-P1-Ru1	110.36(16)	O1-P1-Ru1	112.62(10)	H1-P1-Ru1	110.6(8)



1 5 6

Scheme 5. Ruthenium-PPh_2H **5** and monophosphite complex **6** with ruthenium cymene dimer **1**, PPh_2Cl and isopropanol.

to a number of other peaks (figure 4). A proton coupled ^{31}P NMR spectrum was recorded to verify P-H coupling. Unexpectedly, no coupling of the phosphorus with the hydrogen atom could be detected. As the reaction involves formation of HCl, it was suspected that the metal free reaction results in the formation of PPh_2H as an adduct coordinated to HCl. As the H in PPh_2H would exchange rapidly with an external proton it would not exhibit ^{31}P-^{1}H coupling. Two experiments described below suggested that this was indeed the case.

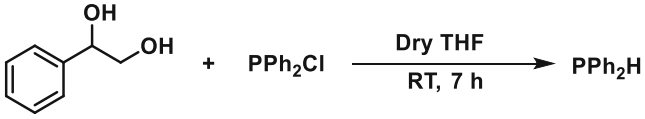
3.7 *Arresting PPh_2H exchange*

To verify if the exhange of H on the phosphorus atom with HCl could be slowed down, variable temperature NMR studies were carried out. The proton coupled ^{31}P NMR spectrum of the reaction mixture obtained by the stoichiometric reaction of PPh_2Cl and 1-phenylethnae-1,2-diol was recorded at different temperatures. At –30°C a peak at –39.8 ppm which was assigned for the free diphenylphosphine started splitting and at –50°C

a clear doublet was observed at –40.8 ppm due to coupling with the hydrogen atom. The observed coupling constant is 222 Hz, close to the reported coupling constant 218 Hz[42] (figure 5).

To further ascertain the coupling with the hydrogen atom, both proton coupled and proton decoupled ^{31}P NMR spectra were recorded at –50°C. In the proton coupled ^{31}P NMR spectrum, a doublet was observed and in the case of proton decoupled NMR spectrum a singlet was observed (figure 6). This study clearly suggests that the formation of free diphenylphopshine is possible even in the absence of the ruthenium complex. A subsequent reaction with **1** would result in the formation of the ruthenium-PPh_2H complex **5**.

If the loss in coupling between ^{31}P and ^{1}H was due to exchange between the two hydrogen atoms (P-**H** and **H**-Cl), addition of a base to remove HCl would also regenerate the coupling. The ^{1}H coupled ^{31}P NMR spectrum of the reaction mixture obtained by the reaction of PPh_2Cl and 1-phenylethane-1,2-diol was recorded at room temperature after adding a stoichiometric amount of triethylamine (figure 7). The coupling between ^{31}P and ^{1}H was observed at room temperature under these conditions. This suggests that in the absence of Et_3N,



Scheme 6. Stoichiometric reaction of PPh_2Cl with 1-phenylethane-1,2-diol.

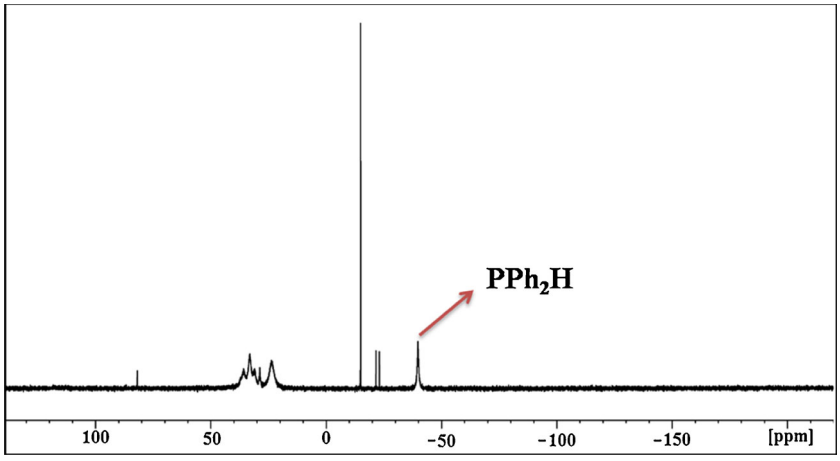


Figure 4. Proton coupled ^{31}PNMR spectrum obtained by the reaction 1-phenylethane-1,2-diol with PPh_2Cl.

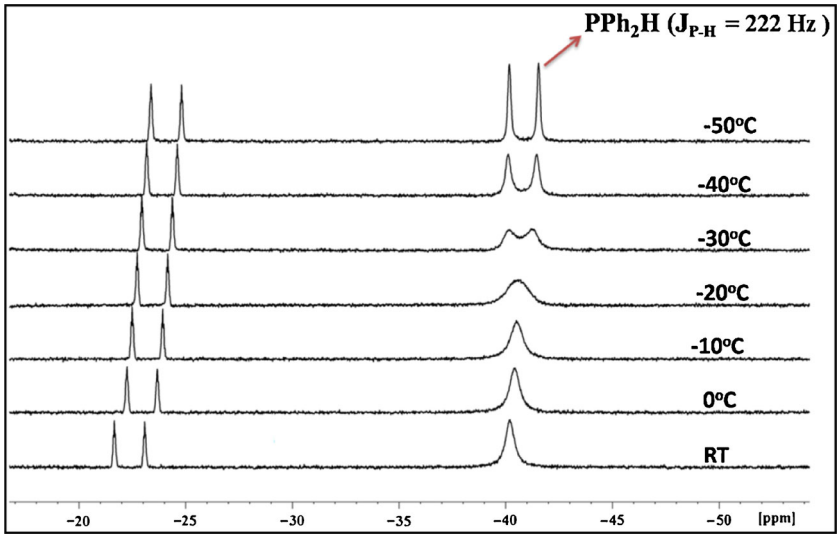


Figure 5. The proton coupled ^{31}P NMR spectra of the reaction mixture obtained by the reaction of 1-phenylethane-1,2-diol with PPh_2Cl at different temperatures.

PPh_2H probably exists in equilibrium with the HCl adduct in solution leading to rapid exchange of the two hydrogen atoms.

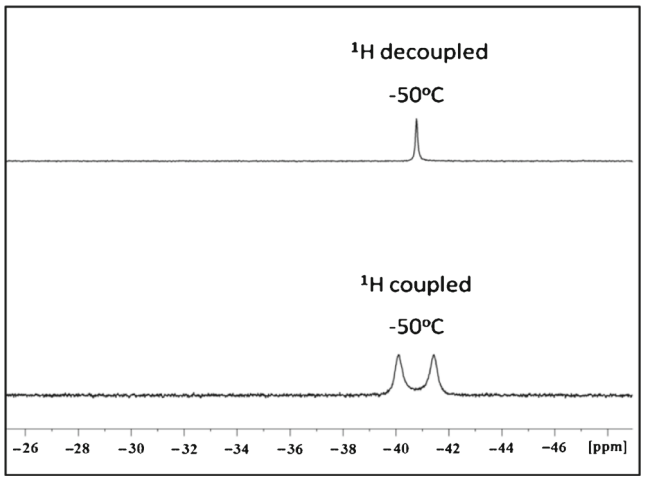


Figure 6. ^{1}H coupled (bottom) and decoupled (top) ^{31}P NMR spectra at –50°C.

Finally, the uniqueness of 1-phenylethane-1,2-diol in promoting the formation of the ruthenium-PPh_2H complex **5** was probed by carrying out this reaction with a variety of alcohols and diols. It was found that 1-phenylethane-1,2-diol gave excellent yields of **5**. Surprisingly it was better than benzyl alcohol, hydrobenzoin and isopropanol in effecting this reaction.

3.8 *A Plausible mechanism for the formation of PPh_2H from PPh_2Cl and 1-phenylethane-1,2-diol*

Till date very few examples are there in the literature where transfer hydrogenation has been carried out in the absence of metals.[37–41] A plausible path for the formation of diphenylphosphine using 1-phenylethane-1,2-diol is given in scheme 7. The mechanism involves the coordination of 1-phenylethane-1,2-diol through its oxygen atoms to P of PPh_2Cl forming adduct **7**. Transfer of a hydride occurs to the phosphorus atom to form a cyclic intermediate **9** which then decomposes to give free diphenylphosphine and 2-hydroxy-1-

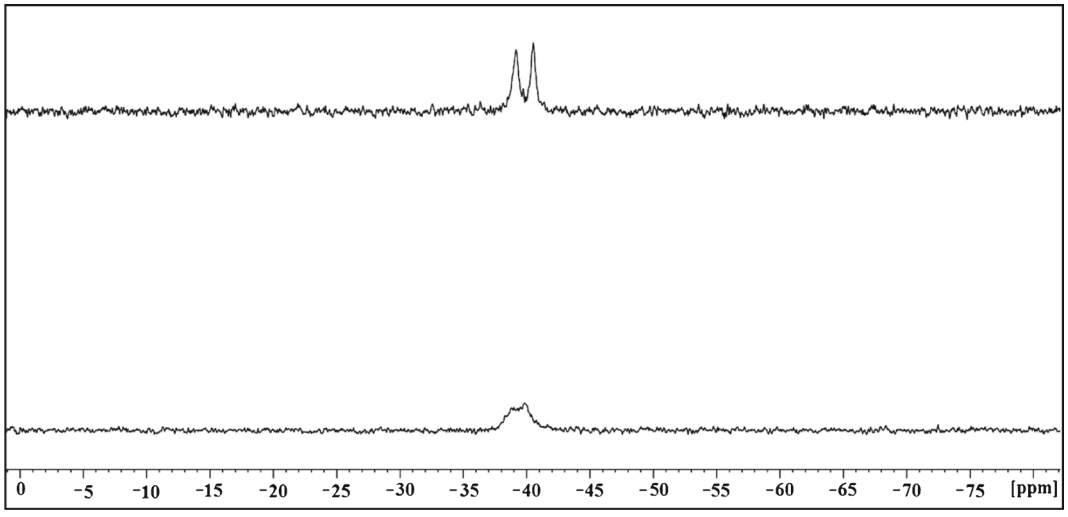
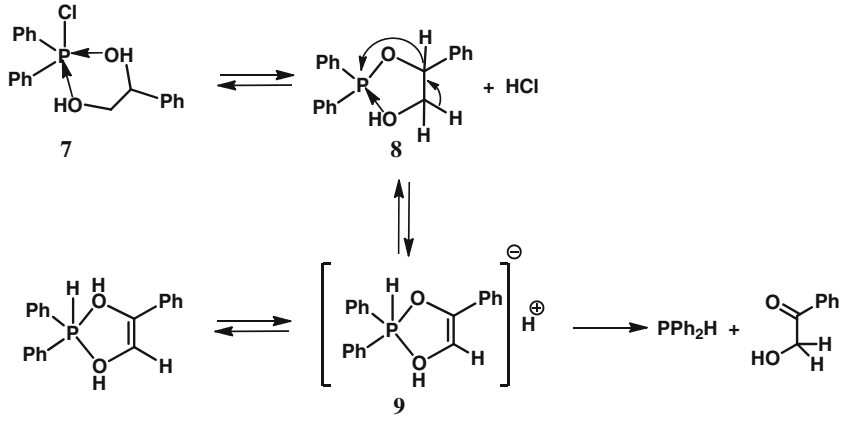


Figure 7. ^{1}H coupled and ^{31}P NMR spectrum before (bottom) and after (top) adding triethylamine.



Scheme 7. Plausible pathway for the formation of PPh_2H from 1-phenylethane-1,2-diol and PPh_2Cl.

phenylethanone. Reactions carried out with deuterium labelled 1-phenylethane-1,2-diol were not useful in identifying the H/D which was transferred as the D exchanged with HCl very rapidly leading to non-deuterated products.

4. Conclusions

The reaction of ruthenium-cymene dimer **1** with PPh_2Cl resulted in the formation of (**2**), a ruthenium-PPh_2Cl complex as expected. However, the expected transformation of this complex to a disubstituted analog was not observed. Instead, hydrolysis of the P-Cl bond occurred, leading to the formation of a ruthenium-$PPh_2(OH)$ complex (**4**). Further, phosphinite complexes are formed along with a reduced ruthenium-PPh_2H (**5**) complex when complex **1** was reacted with PPh_2Cl and alcohols. Surprisingly the reduction could be brought about even in the absence of the metal. Maximum reduction was observed when 1-phenylethane-1,2-diol was used as the reducing agent. The ability of this 1,2-diol was significantly greater than the traditional isopropanol or hydrobenzoin.

Supplementary Information

CCDC 884833, 884834 and 880813 contain the supplementary crystallographic data for [Ru(η^6-cymene)$Cl_2(PPh_2Cl)$] **2** [Ru(η^6-cymene)$Cl_2(PPh_2OH)$] **4** and [Ru(η^6-cymene)$Cl_2(PPh_2H)$] **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. NMR spectra of complexes (figures S1-S15) are available at www.ias.ac.in/chemsci.

Acknowledgements

Financial support from the Department of Science and Technology, New Delhi vide Project number, SR/S5/MBD-02/2007, is gratefully acknowledged. AKP acknowledges CSIR, New Delhi for a SRF Fellowship.

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