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Research Article

SYNTHESIS OF NOVEL BIS(PHOSPHINO)AMINE-RU^{II}(ACAC)$_2$ COMPLEXES, AND INVESTIGATION OF CATALYTIC ACTIVITY IN TRANSFER HYDROGENATION

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Abstract: *In this study, reactions of $(PPh_2)_2NCH_2CH_2N(PPh_2)_2$ **(L_1)** and $\{(PPh_2)_2NCH_2CH_2\}_3N$ **(L_2)** with $[Ru^{II}(acac)_2(CH_3CN)_2]$ led to the production of new dinuclear complex $[Ru(acac)_2]_2(L_1)$ **(1)** and trinuclear complex $[Ru(acac)_2]_3(L_2)$ **(2)**. Complex 1 and 2 are excellent candidates for the role of catalyst precursors in the transfer hydrogenation (TH) of acetophenone and its derivatives. Compared to complex **(1)**, the trinuclear complex **(2)** is an exceptional catalyst, producing the corresponding alcohols in 98–99% yields in 20 minutes at 80 °C (TOF≤300 h^{-1}) for the TH process. A comparison of the catalytic properties of the complexes is also briefly discussed. Complex structures have also been characterized by combining nuclear magnetic resonance (NMR), Fourier Transform Infrared (FT-IR), and elemental analysis.*

Keywords*: Transfer Hydrogenation; Ruthenium Complex; Aminophosphine; Homogeneous Catalysis.*

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1. Introduction

One of the most crucial processes for creating high-value alcohols for academic research and commercial uses, notably in organic synthesis and the pharmaceutical sector, is TH catalysis. Catalytic TH is a valuable alternative approach for catalytic hydrogenation by molecular hydrogen. This method involves catalytic hydrogenation being carried out with the assistance of a stable hydrogen donor. The TH technique, in which formic acid and its salts or secondary alcohols have been utilized as hydrogen sources, is more desirable and safer than the direct hydrogenation method[1-4]. The catalytic transfer hydrogenation process results in the generation of minimal by-products eliminates the use of potentially dangerous chemicals and makes use of easily accessible and nonhazardous starting ingredients such as carbonyl compounds[2, 5]. The transfer hydrogenation process, which began with the use of main-group metals such as aluminum, has given way to complexes including transition metals such as ruthenium, rhodium, and iridium[6, 7].

The synthesis and coordination chemistry of bis(phosphino)amines $RN(PR_2)_2$ have gained much interest in recent years because of their varied donor-acceptor characteristics when a substituent is added to the ligand backbone[8-11]. The use of preparative pathways gives access to several structural alterations via the production of a straightforward P-N bond[12, 13]. P-N-P skeletons are more versatile

than P-C-P skeletons, and tiny modifications in substituents result in dramatic alterations in the P-N-P angle and structure around the whole P-centers[14-16]. As a result, by modifying the substituents, their coordination characteristics and structural features may be drastically altered. This property permits the synthesis of an extensive variety of novel transition metal complexes[17-19]. The synthesis of extremely effective transition metal-based catalysts derived from aminophosphines, which can be used in several catalytic processes, including the TH reaction, has lately attracted more attention[20].

In this study, new binuclear complex (**1**) and trinuclear complex (**2**) were obtained as a result of the reaction of $(PPh_2)_2NCH_2CH_2N(PPh_2)_2$ (**L_1**) and $\{(PPh_2)_2NCH_2CH_2\}_3N$ (**L_2**) aminophosphine ligands with $[Ru^{II}(acac)_2(CH_3CN)_2]$. The structures of the (**1**) and (**2**) complexes were characterized by ^{31}P, ^{1}H NMR, ^{13}C NMR, and FT-IR. Then, the applications of (**1**) and (**2**) complexes as catalysts in the TH of acetophenone derivatives to their respective 1-phenylethanol derivatives using isopropanol as a hydrogen source were investigated.

2. Materials and Methods

2.1. Materials

$Ru(acac)_3$, Ethylenediamine, Tris(2-aminoethyl) amine, PPh_2Cl and Et_3N were purchased from Sigma-Aldrich. $[Ru^{II}(acac)_2(CH_3CN)_2]$[21], N,N,N',N'-Tetrakis(diphenylphosphino)ethylenediamine ($(PPh_2)_2NCH_2CH_2N(PPh_2)_2$ **(L_1))**[22, 23] and Tris[2-(N,N-bis(diphenylphosphino)aminoethyl)amine] ($\{(PPh_2)_2NCH_2CH_2\}_3N$ **(L_2))** [24] were synthesized according to the literature procedures. Since the substances used in all reactions are sensitive to air and humidity, the glass materials and solvents were dried and the reactions were carried out using the standard Schlenk technique in a high-purity argon or nitrogen atmosphere. The solvents used (THF, diethyl ether, toluene, etc.) were dried by distillation with sodium-benzophenone, dichloromethane with di-phosphoruspentaoxide, and 2-propanol with calcium hydride (CaH_2). Triethylamine is distilled with CaH_2 and dried with metallic sodium before use. Reaction monitoring of aminophosphine compounds was performed with $^{31}P-\{^{1}H\}$ NMR. All synthesized complexes have their structures elucidated by ^{1}H (at 400.1 MHz), ^{13}C (at 100.6 MHz), and $^{31}P-^{1}H$ NMR (at 162.0 MHz) as well as elemental analysis. To conduct the GC analyses, a Shimadzu GC 2010 Plus Gas Chromatograph fitted with a capillary column was used.

2.2. The general hydrogen transfer procedure

Below is a sample procedure for TH of ketones: A degassed (5 mL) solution of catalysts (**1** and **2**) (0.005 mmol), potassium hydroxide (0.025 mmol), and corresponding ketone (0.5 mmol) in isopropanol was heated to reflux until the reactions were complete. Then, a specimen was taken from this medium, followed by dilution with acetone, and analyzed immediately by GC. The conversions are calculated depending on the remaining ketone. ^{1}H NMR spectra of the resulting products were as anticipated.

2.3. Synthesis and characterization of complexes

2.3.1 Preparation of complex (1)

Under a nitrogen atmosphere, 36 mg of $[Ru^{II}(acac)_2(CH_3CN)_2]$ (0.045 mmol), 36 mg of $(PPh_2)_2NCH_2CH_2N(PPh_2)_2$ **(L_1)**) (0.045 mmol), and 20 mL of dry toluene were combined in a 100 mL two-neck flask and refluxed at 110 °C for 12 hours. The reaction was terminated after the samples taken at certain intervals during the reaction period were checked with ^{31}P $\{^1H\}$ NMR and the $(PPh_2)_2NCH_2CH_2N(PPh_2)_2$ **(L_1)** was depleted and the complex formation was observed. At the end of the reaction, the solvent was removed under vacuum until approximately 1-2 mL remained, petroleum ether was added to it and the crude products were precipitated. Next, the product was desiccated after being washed in a (1:1) mixture of diethyl ether-hexane. A dark red solid product was obtained. (yield: 0.05 g, 79 %); **^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ:** 7.25-7.36 (m, 40 H, $C_6\underline{\mathbf{H}}_5P$), 4.98 (s, 4H, acac-C**H**), 3.78 (s, 4H, C$\mathbf{H}_2$N), 1.58 (s, 24H, acac-C$\mathbf{H}_3$); **^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ:** 187.30, 185.65 (acac-**C**=O), (126.85, 128.65, 128.95, 131.50, 133.24, 138.52 (-$\underline{\mathbf{C}}_6H_5P$); 98.95 (acac-**C**H), 47.78 (**C**H_2N), 25.98 (acac-**C**H_3); **^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$,ppm) δ:** 87.02 (s, N**P**$(Ph)_2$); **IR (KBr pellet cm^{-1}) υ:** (P-N-P): 805, (P-Ph): 1438, (C-O) 1574; **For element analysis $C_{70}H_{76}N_2P_4O_8Ru_2$ (1399.36gr/mol) calculated:** C 60.08, N 2.00, H 5.47; **found:** C 59.70, N 1.95, H 5.08.

2.3.2 Preparation of complex (2)

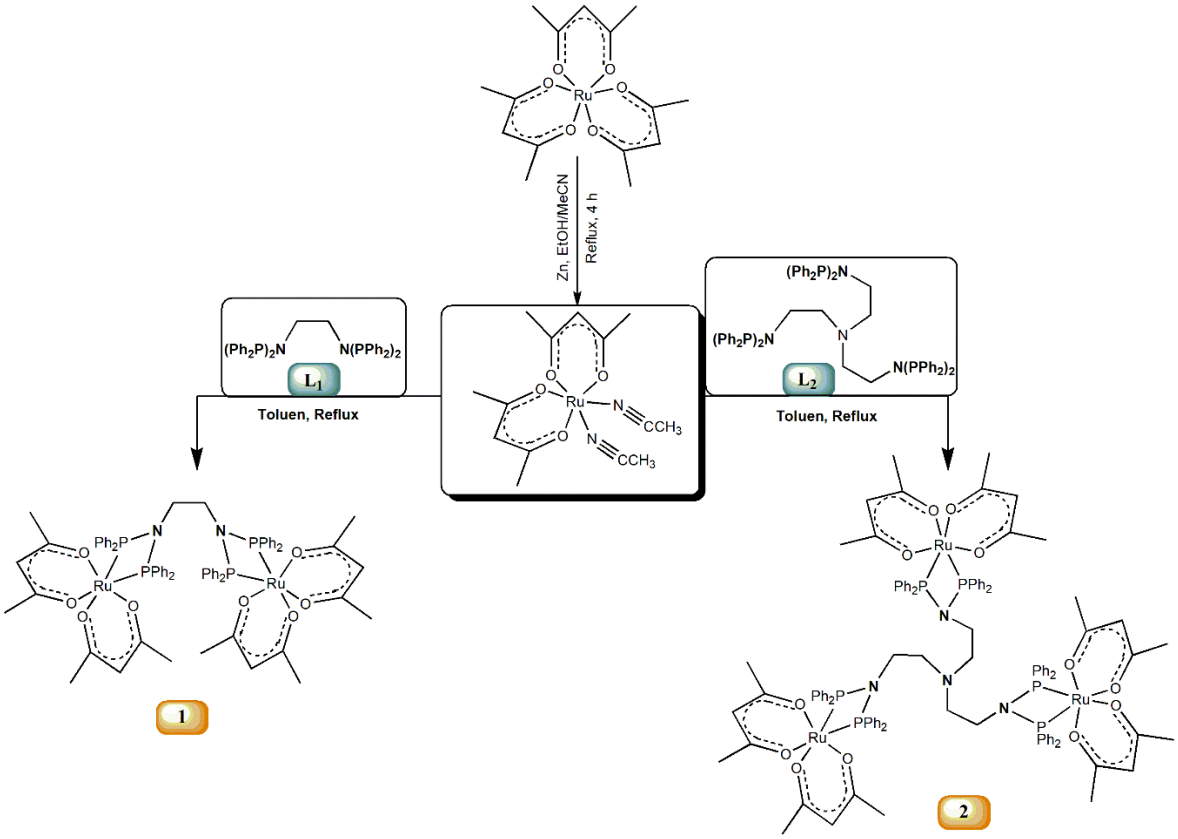
Under a nitrogen atmosphere, 400 mg of $[Ru^{II}(acac)_2(CH_3CN)_2]$ (1.06 mmol), 440 mg of $\{(PPh_2)_2NCH_2CH_2\}_3N$ (**L_2**) (0.35 mmol), and 20 mL of dry toluene were combined in a 100 mL two-neck flask and refluxed at 110 °C for 12 hours. The reaction was terminated after the samples taken at certain intervals during the reaction period were checked with ^{31}P $\{^1H\}$ NMR and the $\{(PPh_2)_2NCH_2CH_2\}_3N$ (**L_2**) ligand was depleted and the complex formation was observed. At the end of the reaction, the solvent was removed under vacuum until approximately 1-2 mL remained, petroleum ether was added to it, and the crude products were precipitated. Next, the product was desiccated after being washed in a (1:1) mixture of diethyl ether-hexane. A dark red solid product was obtained. (yield: 0.65 g, 86 %); **^{1}H NMR (400.1 MHz, $CDCl_3$, ppm) δ:** 7.94- 6.94 (m, 60H, -$C_6\underline{\mathbf{H}}_5P$), 4.81 (s, 6H, acac-C**H**), 5.22-5.53 (m, 12H, NC$\mathbf{H}_2$-), 1.83 (s, 18H, acac-C$\mathbf{H}_3$) 1.44 (s, 18H, acac-C$\mathbf{H}_3$) ; **^{13}C NMR (100.6 MHz, $CDCl_3$, ppm) δ:** 186.29, 185.07 (acac-**C**=O), 134.32, 131.64, 130.71, 127.82 (aromatik karbonlar), 98.62 (acac-**C**H), 54.3 (N**C**H_2-), 53.48 (NCH_2-), 27.84 (acac-**C**H_3), 27.72 (acac-**C**H_3); **^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) δ:** 88.43 (s, N**P**$(Ph)_2$); **IR (KBr pellet cm^{-1}) υ:** (P-N-P): 843, (P-Ph): 1435, (C-O) 1575; **For element analysis $C_{108}H_{120}N_4P_6O_{12}Ru_3$ (2153.9 gr/mol) calculated:** C 60.22, N 2.60, H 5.62; **found:** % C 59.78, N 2.45, H 5.36.

3. Results and Discussion

3.1. Synthesis and characterization of complex 1 and 2

For the manufacture of phosphinoamines and bis(phosphino)amines, many different methods have been established, however, aminolysis seems to be the one that is used the most often. The synthesis as well as the characterisation of the ligands (L_1) and (L_2) were discussed elsewhere[22, 24]. The coordination chemistry of these aminophosphines with $[Ru^{II}(acac)_2(CH_3CN)_2]$ precusor was investigated. Crystalline dark red powders (1) and (2) were obtained by reacting (L_1) and (L_2) with $[Ru^{II}(acac)_2(CH_3CN)_2]$ in molar ratios of 1:2 and 1:3, respectively, at room temperature for 1 hour

(Scheme 1). Singlet peaks at 61.33 and 62.20 ppm in the ^{31}P-{^{1}H} NMR spectra of aminophosphine L_1 and L_2 ligands, respectively, show that the ligands were successfully separated by giving rise to singlets at 87.20 and 88.43 ppm in the formation of complexes 1 and 2, as shown in Figure 1. In addition, when the ^{1}H and ^{13}C-NMR spectra of complexes are examined, the disappearance of the CH_3CN-peak of 2.49 ppm in ^{1}H-NMR and 27.66 ppm in ^{13}C-NMR of $[Ru^{II}(acac)_2(CH_3CN)_2]$ indicates that the structure was formed. In their ^{1}H-NMR spectra, compounds 1 and 2 are characterized by CH resonances of *acac* at δ ~ 4.90 ppm, whereas in the ^{13}C-{^{1}H} NMR spectra, resonance at δ ~ 98 ppm correspond to CH resonances of *acac*. ^{1}H-NMR spectra of compounds 1 and 2 display the anticipated multiplets at ~ 8.00-7.00 ppm for protons of phenyls. Furthermore, other ^{1}H and ^{13}C-NMR data are in agreement with the proposed structures (for details see Experiment Section). The infrared spectrum of 1 and 2 exhibits the bands at 1574 and 1438 cm^{-1} due to υ(C-O) and υ(P-Ph), respectively[25]. Characterization of the complexes by infrared spectroscopy and elemental analysis revealed values that were in excellent accord with theoretical.



Scheme 1. Synthesis of complex (**1**) and (**2**).

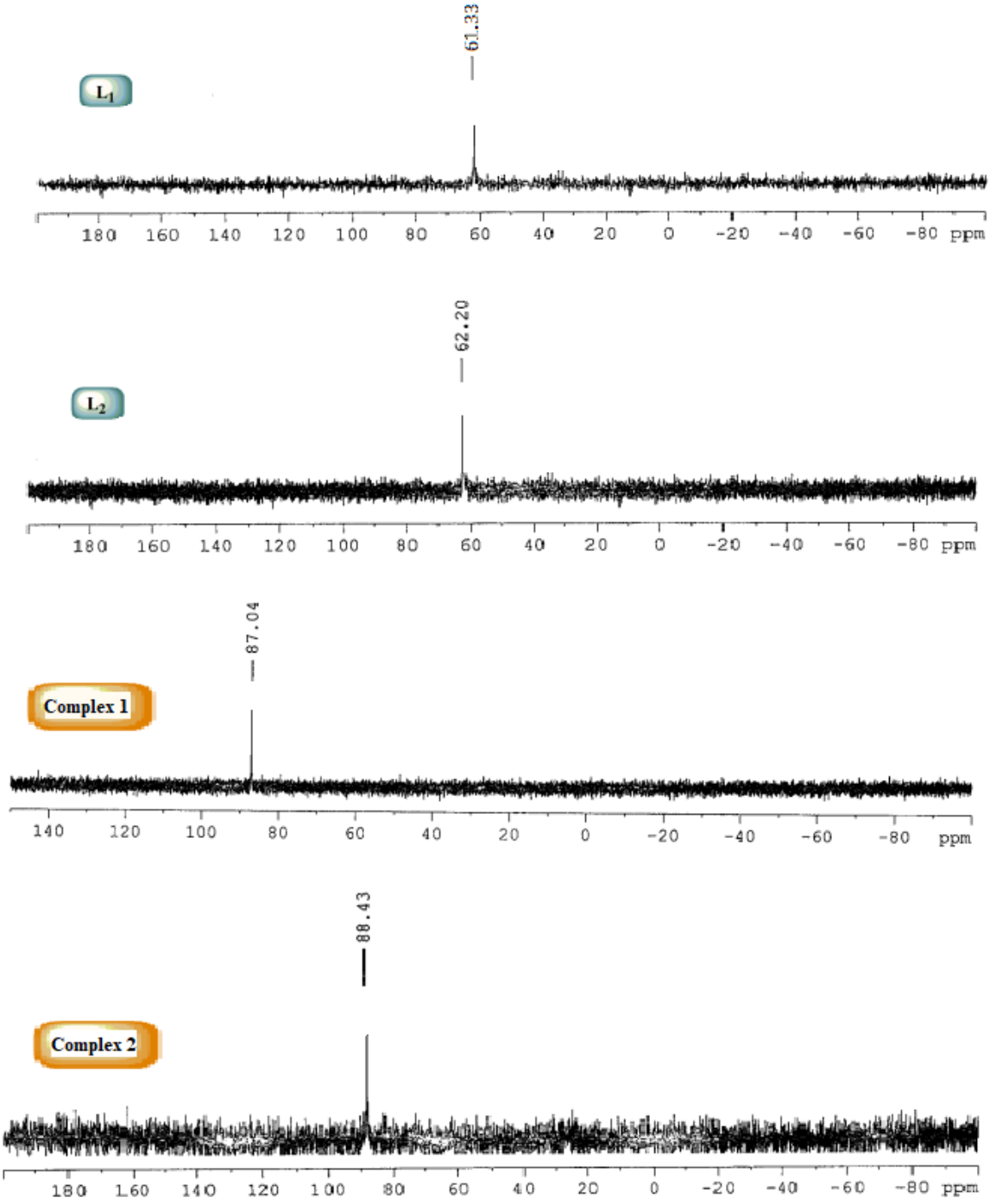


Figure 1. The ^{31}P-{^{1}H} NMR spectra of ligands (L1 and L2) and complexes (1 and 2).

3.2. Transfer hydrogenation studies

After complexes **1** and **2** had been well described, we examined their catalytic potential as a catalyst in the TH reaction that converts ketones to alcohols using the standard heating method. When selecting the beginning conditions, we took into account any past reports. Initially, acetophenone was hydrogenated in isopropanol with KOH as the base in the presence of a catalyst. Isopropanol is employed as a hydrogen source in the TH, and under these conditions, the process is governed by thermodynamics: when isopropanol releases hydrogen, acetone develops, and acetone may act as a hydrogen acceptor, so

equilibrium is achieved. Due to the fact that the boiling point of 2-propanol is only 82 °C, the procedure may be successfully carried out at reflux temperature as well[26, 27]. The outcomes of the transfer hydrogenation are listed in Table 1. In Table 1, entries 2 and 6 clearly demonstrated that the procedure is impossible without a base. Consequently, it follows that a base is required for this reaction. In most cases, the quantity of base is approximately 5 equivalents with regard to the catalyst[28-30]. Therefore, complexes **1** and **2** are effective catalysts in the TH reaction of acetophenone when isopropanol is employed as a hydrogen donor at 82 °C, in the presence of a base, and after a specified amount of time (1 hour and 1/3 hour for complexes **1** and **2**, respectively) (Table 1 entry 1, entry 5). Accordingly, complex **2** effectively converts acetophenone to 1-phenyl-ethanol in high yields, as shown by GC monitoring of the reaction, which revealed a TOF of 294 h^{-1} (Table 2, entry 5). The conversion of complex **1** was likewise satisfactory, with TOF values of 97 h^{-1} (Table 2, entry 1). In addition, an increase in substrate quantity causes an increase in the reaction time, which in turn results in a decrease in TOF (Table 1 entries 3-4, entries 7-8).

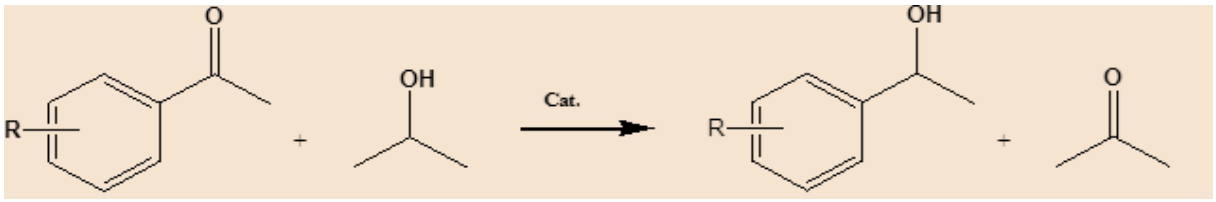
Table 1. TH of acetophenone with isopropanol catalyzed by 1 and 2.

Entry	Catalyst	S/C/KOH	Time	Conversion(%)[e]	TOF(h^{-1})[f]
1	1 [a]	100:1:5	1 h	97	97
2	1 [b]	100:1	24 h	.....	.....
3	1 [c]	500:1:5	6 h	92	15
4	1 [d]	1000:1:5	15 h	98	7
5	2 [a]	100:1:5	1/3 h	98	294
6	2 [b]	100:1	24 h	.....	.....
7	2 [c]	500:1:5	2 h	97	49
8	2 [d]	1000:1:5	5 h	95	19
9	$[Ru(acac)_2(CH_3CN)_2]$	100:2:5	7 h	98	14

Reaction conditions:
[a] Refluxing in 2-propanol; acetophenone/Ru/KOH, (100:1:5); [b] Refluxing in 2-propanol; acetophenone/Ru, in the absence of base; [c] Refluxing in 2-propanol; acetophenone/Ru/KOH, (500:1:5); [d] Refluxing in 2-propanol; acetophenone/Ru/KOH, (1000:1:5); [e] Determined by GC (three independent catalytic experiments); [f] Referred at the reaction time indicated in column; TOF= (mol product/mol Ru(II)Cat.)x h^{-1}.

In this TH reaction, the catalytic effects of acetophenone derivatives were investigated under the optimal circumstances that could be identified. When utilizing an acetophenone derivative containing an electron-withdrawing moiety, such as F, Cl, Br, or NO_2, the corresponding alcohol is found to form in a shorter amount of time (Table 2, entry 1-6, entry 9-14). Due to the fact that electron-withdrawing groups diminish the electron density of the ketone's C=O bond, the ketone is more readily hydrogenated[31, 32]. Second, the reaction time for TH of acetophenone derivatives containing o- and p-OCH_3 groups is longer, and the TOF values are lower. Also, it was seen that the TOF value is lower when there is an electron-donating substituent on the o-position (-OCH_3) than on the p-position. In fact, when 4-MeO was used in place of 2-MeO catalyzed by **2**, the reaction duration decreased from 3 h to 2 h (Table 2, entries 15-16).

Table 2. TH findings for substituted acetophenones with the catalyst systems, **1** and **2**. [a]



Entry	R	Time	Conversion(%)[b]	TOF(h^{-1})[c]
***Cat.* 1**				
1	2-F	1/2 h	99	198
2	4-F	1/3 h	98	294
3	4-Cl	1/3 h	94	282
4	2-Br	3/4 h	96	77
5	4-Br	1/3 h	97	194
6	4-NO_2	1/2 h	95	190
7	2-MeO	4 h	98	25
8	4-MeO	3 h	99	33
***Cat.* 2**				
9	2-F	1/4 h	98	392
10	4-F	1/6 h	99	594
11	4-Cl	1/4 h	95	380
12	2-Br	1/3 h	98	294
13	4-Br	1/4 h	94	376
14	4-NO_2	1/4 h	96	384
15	2-MeO	3 h	95	32
16	4-MeO	2 h	98	49

[a] Catalyst (0.0025 mmol), substrate (0.5 mmol), 2-propanol(5 mL), KOH (0.025 mmol %), 82 °C, the concentration of acetophenone derivatives is 0.1 M; [b] Purity of compounds is checked by ^{1}H NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone; [c] TOF = (mol product/mol Cat.)xh^{-1}.

4. Conclusions

This study reports the synthesis of a novel series of Ru(II)(acac) compounds based on aminophosphine using amine precursors. The obtained results demonstrate that complexes 1 and 2 are effective catalysts for the TH reaction of aromatic ketones, indicating that desired alcohols can be produced in high yield. Trinuclear complex Catalyst 2 showed better catalytic activity for TH than dinuclear catalyst 1. These catalysts are attractive because of their modular design and versatility in terms of transfer hydrogenation, and future reports will focus on the use of the complexes that we have synthesized in TH of other activated aryl and alkyl ketones.

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Authors' Contributions:

D.E.K.: Investigation, Conceptualization, Methodology, Resources, Writing (30 %)

U. I: Conceptualization, Writing - Original draft preparation (15 %)

M. A: Conceptualization, Formal analysis - Original draft preparation (15 %)

F.D: Methodology, Conceptualization, supervision, and review. (25 %)
A.B.: Supervision and Review. (15 %)
All authors read and approved the final manuscript.

Conflict of Interest

The author declares no conflict of interest.

Compliance with Research and Publication Ethics

This work was carried out by obeying research and ethics rules.

The Declaration of Ethics Committee Approval

The authors declare that this document does not require ethics committee approval or any special permission. Our study does not cause any harm to the environment.

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