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SYNTHESIS AND CHARACTERIZATION OF Pd(II) AND Ru(II) COMPLEXES OF TETRADENTATE *N,N,N,N*-(DIPHOSPHINOMETHYL)AMINE LIGANDS: CATALYTIC PROPERTIES IN TRANSFER HYDROGENATION AND HECK COUPLING REACTIONS

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Abstract – Tetradentate *N,N,N,N*-(diphosphinomethyl)amine ligands and their Pd(II) and Ru(II) complexes were synthesized under a nitrogen atmosphere using Schlenk technique. The synthesized ligands and the complexes were characterized with ¹H- and ³¹P-NMR, FT-IR, TG/DTA, and elemental analysis techniques. Pd(II) Complexes were used as catalysts in Heck coupling reactions and Ru(II) complexes were tried in transfer hydrogenation reactions of acetophenone derivatives. According to the results, L4-Pd(II) complex showed the best catalytic activity in the Heck coupling reaction of *p*-methylbromobenzene with *o*-chlorostyrene. It was confirmed that the reduction of bromo and chloroacetophenones in all catalysts the conversions were higher. The results showed that Ru(II) complexes as efficient catalysts and up to 99% conversions was occurred with bromo and chloro acetophenones in K₂CO₃/isopropyl alcohol media at 80 °C.

INTRODUCTION

The synthesis of the functionalized phosphine ligands and their metal complexes are very important area because of their unique catalytic and biological properties. Ditertiary aminomethylphosphines can be synthesized with the reaction of a phosphonium salt derivative and a primary amine R'NH₂.¹⁻⁵ It has been known that phosphine ligands having the ability to forming the chelated structure can promote the

stability of the metal complexes and increase the reactivity in the organic reactions. Besides, these properties can highly increase the formation of the enantioselective products. Phosphine-Pd(II) and Ru(II) complexes can also be used as catalysts in many organic processes such as the reduction of aldehydes and ketones (transfer hydrogenation), hydrogenation, oxidation and coupling reactions.⁶⁻¹⁷ Catalytic activities and selectivities of the phosphine-metal complexes can be increased by changing their sterical environment and electronic properties. Chelated metal complexes of the phosphine ligands can show more specific more active catalytic properties than other many type of the complexes having monodentate ligands.¹⁻¹⁷ Recent years, phosphine-Ru(II) and Pd(II) complexes were used in transfer hydrogenation catalyst system and coupling reactions.¹⁸

It has been synthesized and characterized the *tetradentate*-aminomethylphosphine ligands and their Ru(II) and Pd(II) complexes. The synthesized Pd(II) complexes were used as catalysts in Heck coupling reactions. Pd(II) Complexes catalyzed the Heck coupling reactions in high yields, however, the percentages of the selectivities were low and moderate. On the other hand, high selectivities were obtained using Pd(II) complexes as catalysts in the reactions between aryl halides with acrylates compared to the styrene derivatives. Additionally, all the Ru(II) complexes were also used as catalysts in the transfer hydrogenation reactions of acetophenone derivatives. The GC results showed that the conversions were higher when used having the electron withdrawing groups such as bromine and chlorine substituted acetophenone derivatives than acetophenone derivatives having the electron donor groups (-Me, -OMe).

RESULTS AND DISCUSSION

Syntheses

Tetradentate *N,N,N,N*-(diphosphinomethyl)amine ligands and their Pd(II) and Ru(II) complexes were synthesized under a nitrogen atmosphere with Schlenk technique. *N¹,N¹,N⁴,N⁴*-*Tetrakis*((diphenylphosphino)methyl)benzene-1,4-diamine (L1), *N¹,N¹,N⁵,N⁵*-*tetrakis*((diphenylphosphino)methyl)naphthalene-1,5-diamine (L2), 4,4'-methylenebis(*N,N*-bis((diphenylphosphino)methyl)aniline) (L3) ligands were synthesized with the reaction of 1,4-phenylenediamine, 4,4'-diaminodiphenylmethane, 1,5-naphthalenediamine to [PPh₂(CH₂OH)₂]Cl respectively under a nitrogen atmosphere using Schlenk technique according to the literature.² [PPh₂(CH₂OH)₂]Cl phosphonium salt was obtained according to the literature.^{7,9,13,14} 1,1'-(1,3-Phenylene)bis(*N,N*-bis((diphenylphosphinyl)methyl)methanamine) (L4) was novelly synthesized with reaction of 1,3-bis(aminomethyl)benzene and [PPh₂(CH₂OH)₂]Cl containing NEt₃ using Schlenk technique. Pd(II) and Ru(II) complexes of the *N,N,N,N*-(diphosphinomethyl)amine type ligands have

been obtained from the reactions of the ligands and $[\text{Pd}(\text{COD})\text{Cl}_2]$ and $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ complexes refluxing for 6 h under a nitrogen atmosphere with Schlenk technique (Figure 1).

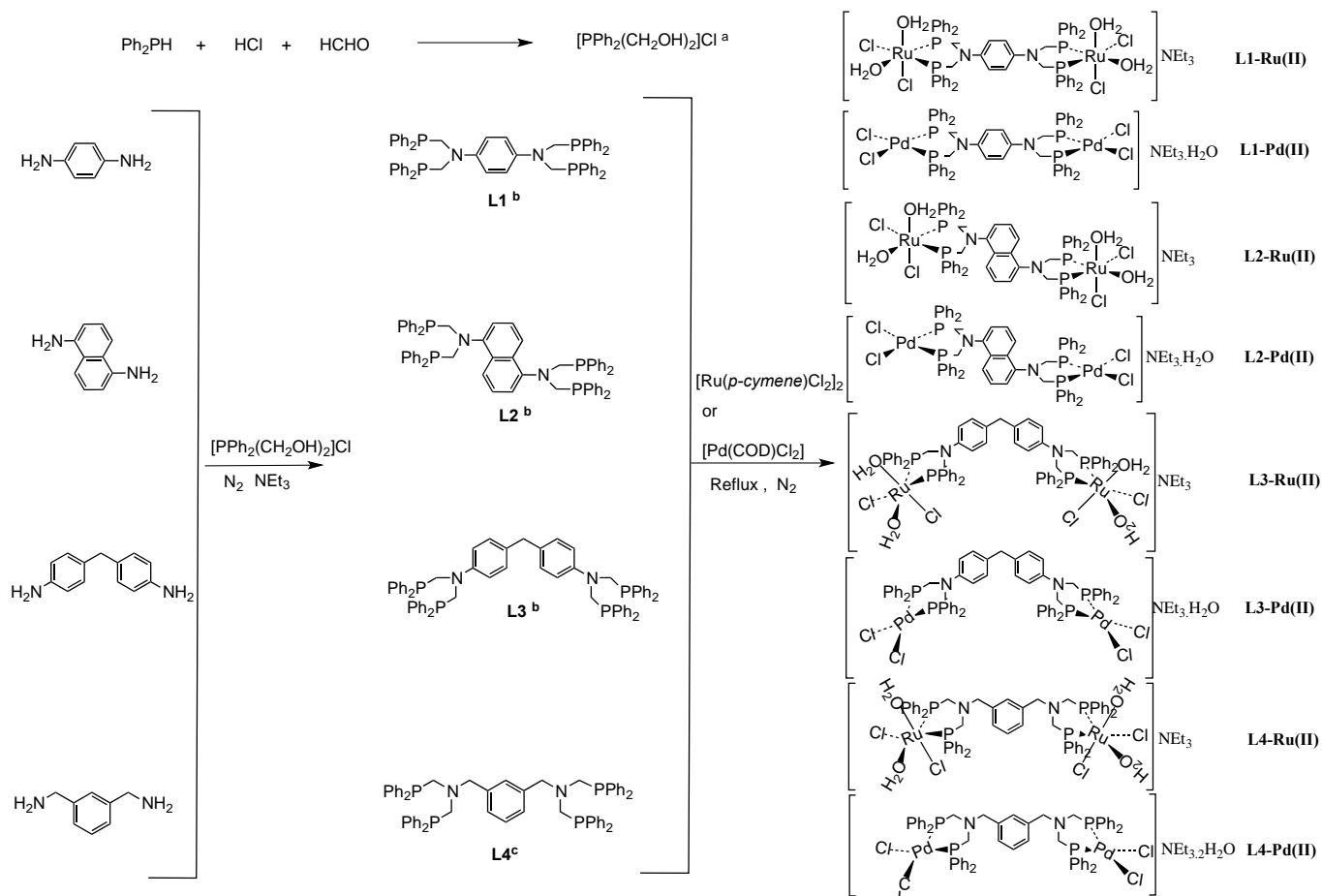


Figure 1. Synthesis of the ligands and metal complexes.

^a Synthesized according to the literature.^{7,9,13,14} ^b Synthesized according to our previous study.² ^c Novel Ligand.

The ligands and their metal complexes were characterized with elemental analysis (C, H, N and metal%), ^{31}P and ^1H -NMR, FT-IR and TG/DTA techniques.

The ligand L4 has two endothermic degradation bands between 100-1000 °C in thermogravimetric analysis (Figure 2). Pd(II) and Ru(II) complexes of L4 have three endothermic peaks in TGA analyses. Triethylamine and water removing were observed between the room temperature to about 210 °C for the complexes. Aminomethylphosphine and the aromatic backbone degradations were recorded up to around 500 °C respectively. Additionally, metal oxide formations were observed in TGA curves of the complexes after 500 °C.

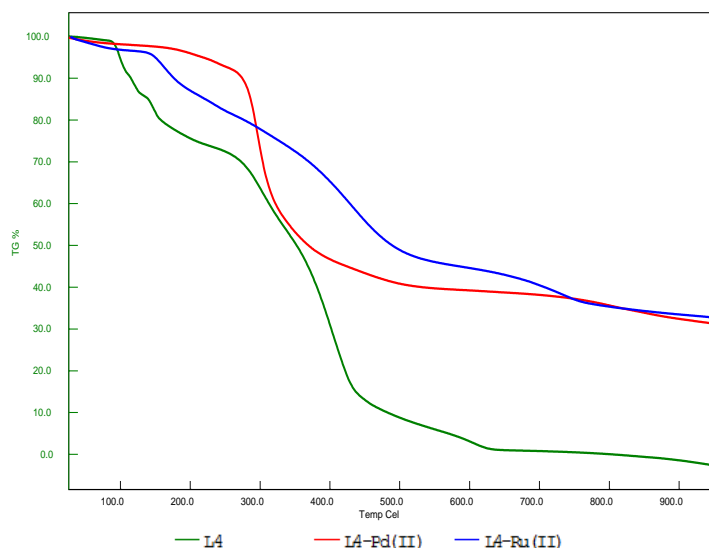
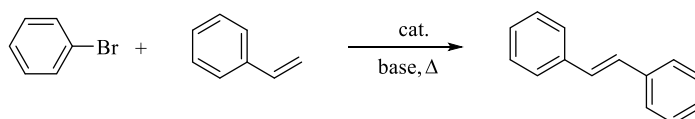


Figure 2. TGA curves of L4 and the complexes

Catalysis

Heck C-C Coupling Reactions

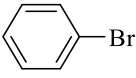
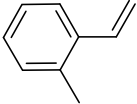
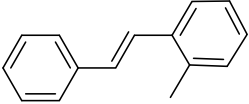
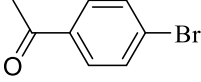
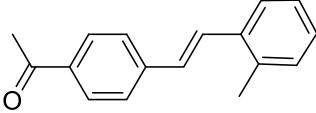
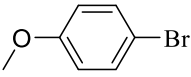
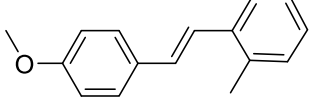
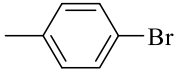
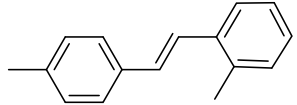
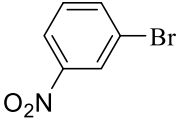
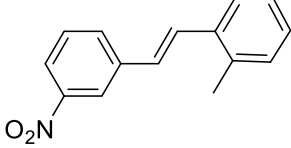
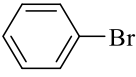
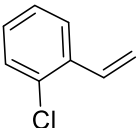
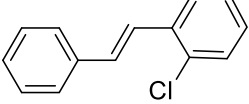
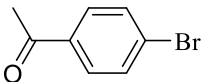
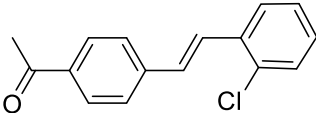
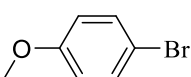
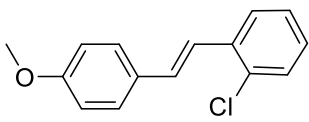
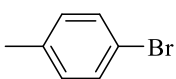
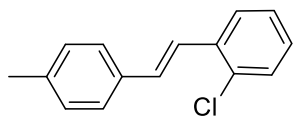
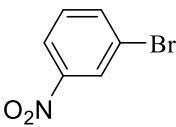
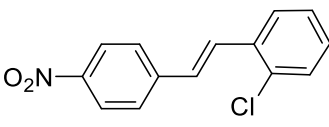


Scheme 1. Heck reaction of bromobenzene with styrene

Initially, styrene and bromobenzene were chosen as the starting materials for Heck coupling to give 1,2-diphenylethene using L1-Pd(II) catalyst in order to determine the optimized reaction conditions. Preliminary, studies were performed in order to investigate the effect of the different reaction conditions to the coupling of the substrates by varying the inorganic and organic base (NEt_3 , Na_2CO_3 , K_2CO_3 and NaOAc), reaction temperature (80, 100, 110 and 140 °C), and the solvent (toluene, 1,4-dioxane, DMF and NMP). Screening for the optimum base showed that the inorganic base K_2CO_3 was optimal compared to the other bases. On specified conditions, 1,2-diphenylethene was the main product; only in the presence of K_2CO_3 was found with 40% of the yield. The best selectivities were obtained using K_2CO_3 , therefore; this base was applied in further experiments (0.01 mol% catalyst) at 140 °C. At the same reaction conditions, 35% selectivity was calculated while applied at 110 °C.

After the specified optimum conditions were determined, the Heck couplings of the derivatives of the styrene with different aryl bromides were examined.¹⁹ In general, the selectivities were achieved at low and moderate percentages. When the formation of products in catalyst presence was examined, a higher selectivity was observed when used the catalyst L4-Pd(II) compared to the other catalysts (L1-L3-Pd(II)) for the reaction of *p*-methylbromobenzene with *o*-chlorostyrene (Table 1, entry 9). However, low selectivities were determined due to occurring of palladium black and its influence on the reaction rate (Table 1, entries 5, 6 and 8).²⁰

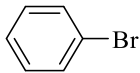
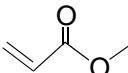
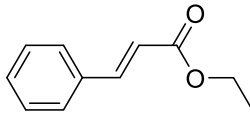
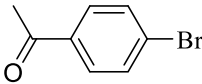
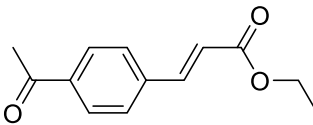
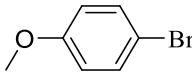
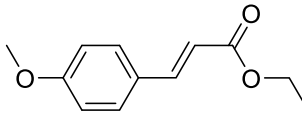

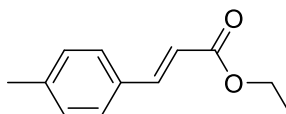
Table 1. The Heck C-C coupling reaction of styrene derivatives with different aryl bromides.

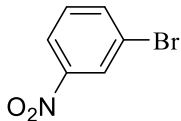
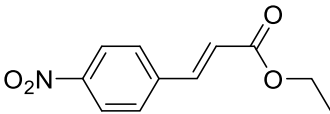
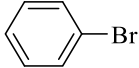
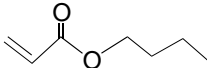
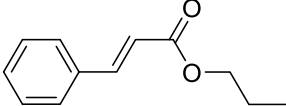
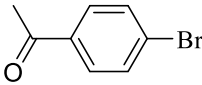
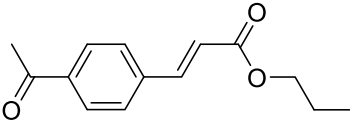
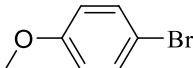
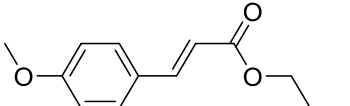
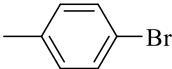
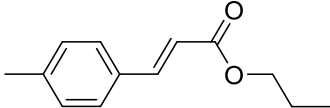
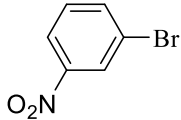
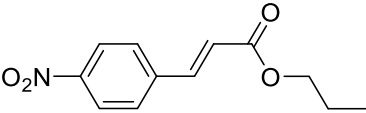
$\text{R}^1\text{-X} + \text{CH}_2=\text{CH-R}^2 \xrightarrow[\text{base}]{\text{cat.}} \text{R}^1\text{-CH}=\text{CH-R}^2 + \text{R}^1\text{-C}(\text{R}^2)=\text{CH}_2$				<div style="display: flex; justify-content: space-around; width: 100%;"> A B </div>			
No	Aryl Halide	Olefin	Product	Selectivity(%) ^{a,b}			
				L1-Pd(II)	L2-Pd(II)	L3-Pd(II)	L4-Pd(II)
1				11	12	8	8
2		"		14	14	5	41
3		"		3	11	11	-
4		"		12	14	6	21
5		"		2	23	4	3
6				29	16	6	nr
7		"		3	11	2	12
8		"		9	8	14	6
9		"		26	10	8	51
10		"		3	20	8	13

Reac. cond.: aryl bromide (0.1 mmol), olefin (0.12 mmol), K₂CO₃ (0.12 mmol), 0.01 mol% catalyst, 1,4-dioxane 2 mL, 6 h, 140 °C.

In the other catalytic experiments, aryl bromides and acrylates (methyl and butyl) have been investigated as different substrates. Higher selectivities were observed in reactions with acrylates compared to the styrene derivatives.²¹ Only, the desired result could not be obtained with L3-Pd(II). Methyl acrylate gave better results than acrylate. The reason is that butyl acrylate cannot approach the aryl halide due to steric hindrance. High selectivities were obtained especially in reactions with butyl acrylates in the presence of catalyst L4-Pd(II) (Table 2, entries 1, 6-9). Low and moderate selectivities were obtained with the catalysts L1-Pd(II) and L2-Pd(II) compared to L4-Pd(II). The selectivities of aliphatic olefins (methyl and butyl acrylates) to the products were higher than styrene because of having less steric hindrance of acrylates compared to styrene derivatives. As a result, methyl acrylate and butyl acrylate has a better approach to the catalyst surface. On the other hand electron donating group 4-methyl was higher selectivities than electron withdrawing 3-NO₂. The reason is that the position of the para is away from the active metal center and although it provides electrons, it does not cause steric hindrance (Table 2 entries 9-10.)

Table 2. The Heck C-C coupling reaction of aryl bromides with methyl and butyl acrylates

$\text{R}^1\text{---X} + \text{CH}_2\text{=CH---R}^2 \xrightarrow[\text{base}]{\text{cat.}} \text{R}^1\text{---CH=CH---R}^2 + \text{R}^1\text{---C(=CH}_2\text{)---R}^2$		A		B			
No	Aryl Bromide	Olefin	Product	Selectivity(%) ^{a,b}			
				L1-Pd(II)	L2-Pd(II)	L3-Pd(II)	L4-Pd(II)
1				15	46	2	88
2		"		2	20	0	0
3		"		7	6	2	5
4		"		7	8	0	0

5		"		6	5	0	0
6				19	23	0	99
7		"		36	28	9	99
8		"		25	23	1	86
9		"		98	80	1	99
10		"		10	13	0	14

Reac. cond.: aryl bromide (0.1 mmol), olefin (0.12 mmol), K_2CO_3 (0.12 mmol), 0.01 mol% catalyst, 1,4-dioxane 2 mL, 6 h, 140 °C.

^aMesitylene used as internal standard and coupled products analyzed by GC-MS.

^bSelectivity (A) (%) = $100 \times \text{Yield (A)}/\text{Yield (A + B)}$.

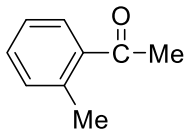
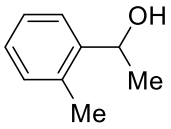
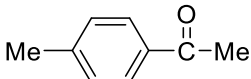
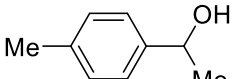
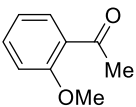
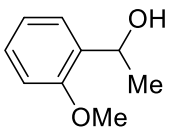
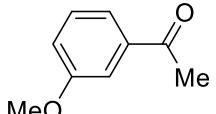
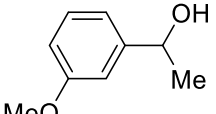
Transfer Hydrogenation

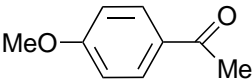
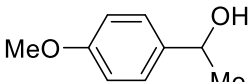
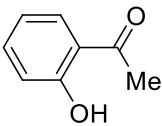
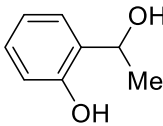
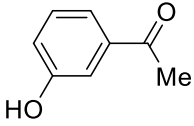
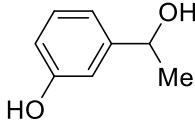
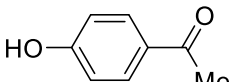
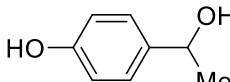
The catalytic activity of the synthesized *N,N,N,N*-(diphosphinomethyl)amine-Ru(II) complexes (L1-4-Ru(II)) was investigated in the transfer hydrogenation reaction of acetophenone and its derivatives. The optimum temperature and time were determined as 82 °C and 12 h for the transfer hydrogenation reactions (Table 3). In all the transfer hydrogenation reactions, acetophenone/catalyst ratio was taken as 1000:1. The any conversion was not observed when the base was not used. Due to the fact that the type of the base is very important; the bases NaOH, K_2CO_3 , KO^tBu, and Et₃N were tried in the transfer hydrogenation reactions. The higher conversions were obtained when used the inorganic bases in transfer hydrogenation reactions compared to organic base Et₃N. The highest conversion took place in the presence of K_2CO_3 .

In the industrial applications, it is important to synthesize the prochiral organic compounds in the lower catalyst ratio in transfer hydrogenation reactions. Likewise, the different substrates are used in the synthesis of prochiral organic compounds. Therefore, electron donating groups such as methyl, methoxy

and hydroxyacetophenones and electron withdrawing groups including such as bromo and chloroacetophenones were commonly studied in the literatures.²² When Table 3 was examined, the hydrogenation of *o*-methylacetophenone was lower than *p*-methylacetophenone. Probably, *p*-methylacetophenone can easily coordinate to the active metal center (Table 3, entry 5). Since the methyl or methoxy groups also provide electrons to the phenyl ring, so the electron density of the carbonyl increases and effect the reaction rate.

Table 3. Transfer hydrogenation of acetophenones with catalysts **L1-4-Ru(II)**

Entry	Cat.	Acetophenone	Product	Conversions (%)
1	L1-Ru(II)			5
2	L2-Ru(II)	"	"	7
3	L3-Ru(II)	"	"	3
4	L4-Ru(II)	"	"	-
5	L1-Ru(II)			82
6	L2-Ru(II)	"	"	59
7	L3-Ru(II)	"	"	76
8	L4-Ru(II)	"	"	31
9	L1-Ru(II)			-
10	L2-Ru(II)	"	"	-
11	L3-Ru(II)	"	"	-
12	L4-Ru(II)	"	"	-
13	L1-Ru(II)			93

14	L2-Ru(II)	"	"	82
15	L3-Ru(II)	"	"	66
16	L4-Ru(II)	"	"	78
17	L1-Ru(II)			27
18	L2-Ru(II)	"	"	6
19	L3-Ru(II)	"	"	-
20	L4-Ru(II)	"	"	9
21	L1-Ru(II)			11
22	L2-Ru(II)	"	"	48
23	L3-Ru(II)	"	"	17
24	L4-Ru(II)	"	"	2
25	L1-Ru(II)			15
26	L2-Ru(II)	"	"	-
27	L2-Ru(II)	"	"	-
28	L2-Ru(II)	"	"	19
29	L1-Ru(II)			99≤
30	L2-Ru(II)	"	"	-
31	L2-Ru(II)	"	"	42
32	L2-Ru(II)	"	"	62

Reac. cond.: acetophenones (0.1 mmol), K₂CO₃ (0.12 mmol), cat. (0.1 mmol% [Ru]), IPA 2 mL, 18 h, 82 °C.

High conversions were obtained in the transfer hydrogenation of bromo and chloroacetophenones using catalysts L1-4-Ru(II) (Table 4). The hydrogenation of chloro and bromoacetophenones at 82 °C was determined by GC, the results were showed that the conversion was quite high compared to methyl, methoxy and hydroxyacetophenones. In addition, catalytic reactions were carried out with a substrate:catalyst ratio of 1:1000 although the conversions was high in catalytic ratio such as 1:100 and 1:500. The GC results showed that the conversions were higher when using electron withdrawing group bromine and chlorine groups than the electron donor groups (-Me, -OMe). The reason is that the electron withdrawing group reduces the electron density of the carbonyl and increased the tendency of substrate to the active ruthenium center.²³

Table 4. Transfer hydrogenation of bromo and chloroacetophenones wit catalysts L1-4-Ru(II)

S.No	Cat.	Acetophenones	Product	Conversions (%)
1	L1-Ru(II)			83
2	L2-Ru(II)	"	"	99
3	L3-Ru(II)	"	"	98
4	L4-Ru(II)	"	"	32
5	L1-Ru(II)			96
6	L2-Ru(II)	"	"	96
7	L3-Ru(II)	"	"	94
8	L4-Ru(II)	"	"	98
9	L1-Ru(II)			96
10	L2-Ru(II)	"	"	98
11	L3-Ru(II)	"	"	96
12	L4-Ru(II)	"	"	93
13	L1-Ru(II)			87
14	L2-Ru(II)	"	"	99
15	L3-Ru(II)	"	"	99≤
16	L4-Ru(II)	"	"	96

17	L1-Ru(II)			96
18	L2-Ru(II)	"	"	97
19	L3-Ru(II)	"	"	98
20	L4-Ru(II)	"	"	96
21	L1-Ru(II)			90
22	L2-Ru(II)	"	"	95
23	L3-Ru(II)	"	"	96
24	L4-Ru(II)	"	"	96

Reac. cond.: acetophenones (0.1 mmol), K_2CO_3 (0.12 mmol cat. (0.1 mmol% [Ru]), IPA 2 mL, 18 h, 82 °C.

^aGC yield of the corresponding alcohol .

CONCLUSIONS

In summary, we have synthesized *tetradentate* N^1, N^1, N^4, N^4 -(diphosphinomethyl)amine ligands and their Pd(II) and Ru(II) complexes under a nitrogen atmosphere with Schlenk technique. The synthesized ligands and the complexes were characterized using NMR, FT-IR, TG/DTA, and elemental analysis techniques. Pd(II) Complexes were used as catalysts in Heck coupling reactions and Ru(II) complexes were tried in transfer hydrogenation reactions of acetophenone derivatives. In Heck reactions, Pd(II) Complexes catalyzed high conversions and low selectivities. In transfer hydrogenation reactions (TH), Ru(II) complexes catalyzed the acetophenones to corresponding alcohols, in high conversions. The catalytic (Heck, TH) results obtained show that the backbone is effective in the activity of the catalysts and that the functional groups partially affect the activity.

EXPERIMENTAL

General

The 1H -NMR and ^{31}P -NMR spectra were recorded at 25 °C in $CDCl_3$ using an Avance III HD Ascend 600 ULH NMR spectrometer. FT-IR spectra were recorded with a Perkin Elmer Spectrum 400 FT-IR System. Elemental analyses were performed using LECO CHNS 932 instrument. The mass spectra of the ligand were recorded on a Zivak Tandem Gold LC-MSMS spectrometer (ESI). The metal contents of the complexes were analyzed by Perkin Elmer Optima 2100 DV ICP-OES. Before the metal content analysis, the complexes were digested in Berghof MWS 3+ with an appropriate amount of $HNO_3+H_2O_2$ mixture. The calibration standarts of Pd(II) and Ru(II) were prepared from Inorganic Ventures (USA) calibration

stocks (about 1000 mg.L⁻¹). Ultrapure water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA) was used for the calibration standards. The thermal properties of the ligands were investigated on a SII thermal system under nitrogen atmosphere at a heating rate of 10 °C/min in the range 30-1000 °C. All the chemicals and reagents were purchased from Merck, Fluka, Sigma and Aldrich and all the solvents were dried using established procedures and immediately distilled under nitrogen atmosphere prior to use. L1, L2 and L3 have been synthesized according to our previous study.²

Synthesis of 1,1'-(1,3-Phenylene)bis(*N,N*-bis((diphenylphosphinyl)methyl)methanamine) (L4)

[PPh₂(CH₂OH)₂]Cl salt was obtained according to the literature.^{7,9,13,14} The novel *tetradentate N,N,N,N*-(diphosphinomethyl)amine ligand (L4) has been synthesized by the reaction of 1,3-bis(aminomethyl)benzene and [PPh₂(CH₂OH)₂]Cl in CH₂Cl₂ having NEt₃ using Schlenk technique under nitrogen atmosphere.^{2,5-9,13-18} 0.1 g (0.3537 mmol) [Ph₂P(CH₂OH)₂]Cl was dissolved in EtOH:water (1:1) and 1.0 mL triethylamine (99%) and 0.088 mmol 1,3-bis(aminomethyl)benzene were added to this solution respectively. After refluxing this mixture for 1 h, the synthesized ligand was extracted in 10 mL CH₂Cl₂. CH₂Cl₂ phase were washed three times with appropriate amount of water and dried with anhydrous Na₂SO₄. Oily product was obtained when CH₂Cl₂ phase was evaporated. Yield (0.06537 g) 81%. Chemical Formula C₆₀H₅₆N₂P₄: Anal. Calcd for C₆₀H₅₆N₂P₄: C, 77.57, H, 6.08, N, 3.02. Found: C, 77.32, H, 5.82, N, 3.08. FT-IR (KBr, cm⁻¹): ν 3054 (aromatic C-H), 2918 (aliphatic C-H), 1607, 1510 (aromatic C=C), 1432 (P-Ph), 1094 (*tert*-amine C-N). ¹H-NMR (δ, ppm, CDCl₃): 7.44-7.20 (m, 40H, Ar-H), 7.10-6.93 (m, 4H, N-Ar-N), 4.85 (s, 8H, N-CH₂-PPh₂), 3.51 (4H, s, CH₂). ¹³C{¹H}-NMR (δ, ppm, CDCl₃): 128.87, 128.78, 113.88, 106.34, 100.06 (PhC-N and PPh₂ carbons), 86.34 [N-CH₂-P], 85.49 [Ar-N-CH₂]. ³¹P{¹H}-NMR (δ, ppm, CDCl₃): -27.57 (s, -PPh₂). MS-ESI: m/z 990 ([M-H]⁺, 5%), 991 ([M]⁺, 4%).

Synthesis of Metal Complexes

Pd(II) Complexes

Tetradentate N,N,N,N-(diphosphinomethyl)amine ligands (0.088 mmol) was dissolved in CH₂Cl₂ and 0.176 mmol [Pd(COD)Cl₂] (dichloro(1,5-cyclooctadiene)palladium(II)) solution in EtOH was added in Schlenk flask. The mixture was refluxed for 6 h under nitrogen atmosphere. After cooling, the colored solid was precipitated with the addition of hexane which was then filtered off and dried at 60 °C.

[Pd₂(L1)Cl₄]·NEt₃·H₂O (1)

Yield (0.105 g) 69.04%. Molecular formula C₆₄H₆₉Cl₄N₃OP₄Pd₂. Color: brown. Anal. Calcd for

$C_{64}H_{69}Cl_4N_3OP_4Pd_2$: C, 58.99, H, 7.11, N, 5.30, Pd, 15.48%. Found: C, 59.05, H, 7.08, N, 5.27, Pd, 15.59%. FT-IR (KBr, cm^{-1}): ν 3336 (-OH), 3052 (aromatic C-H), 2979 (aliphatic C-H), 1614, 1512 (aromatic C=C), 1435 (P-Ph), 1037 (*tert*-amine C-N). 1H -NMR (δ , ppm, $CDCl_3$): 7.60-6.40 (m, 44H, Ar-H), 4.12 (8H, s, N- \underline{CH}_2 -PPh₂), 3.08 (6H, q, *J*: 7.69 Hz, N- \underline{CH}_2 -CH₃), 1.30 (9H, t, *J*: 7.55 Hz, N- \underline{CH}_2 -CH₃). $^{31}P\{^1H\}$ -NMR (δ , ppm, $CDCl_3$): 29.76 (s, Pd-P(Ph₂)-CH₂).

[Pd₂(L2)Cl₄] \cdot NEt₃ \cdot H₂O (2)

Yield (0.08 g) 63.97%. Molecular formula $C_{68}H_{71}Cl_4N_3OP_4Pd_2$. Color: red. Anal. Calcd for $C_{68}H_{71}Cl_4N_3OP_4Pd_2$: C, 57.32, H, 5.02, N, 2.95, Pd, 14.98%. Found: C, 57.28, H, 4.98, N, 2.98, Pd, 14.89%. FT-IR (KBr, cm^{-1}): ν 3340 (-OH), 3053 (aromatic C-H), 2987 (aliphatic C-H), 1586, 1530 (aromatic C=C), 1434 (P-Ph), 1099 (*tert*-amine C-N). 1H -NMR (δ , ppm, $CDCl_3$): 8.10-7.20 (m, 46H, Ar-H), 4.64 (s, 8H, N- \underline{CH}_2 -PPh₂), 3.17 (q, *J*: 7.44 Hz, 6H, N- \underline{CH}_2 -CH₃), 1.36 (t, *J*: 7.32 Hz, 9H, N- \underline{CH}_2 -CH₃). $^{31}P\{^1H\}$ -NMR (δ , ppm, $CDCl_3$): 28.24 (s, Pd-P(Ph₂)-CH₂).

[Pd₂(L3)Cl₄] \cdot NEt₃ \cdot H₂O (3)

Yield (0.082 g) 67.25%. Molecular formula $C_{75}H_{87}N_3OP_4Pd_2$. Color: orange. Anal. Calcd for $C_{75}H_{87}N_3OP_4Pd_2$: C, 57.55, H, 4.66, N, 2.31, Pd, 15.31%. Found: C, 57.49, H, 4.71, N, 2.28, Pd, 15.25%. FT-IR (KBr, cm^{-1}): ν 3332 (-OH), 3053 (aromatic C-H), 2988 (aliphatic C-H), 1612, 1513 (aromatic C=C), 1435 (P-Ph), 1099 (*tert*-amine C-N). 1H -NMR (δ , ppm, $CDCl_3$): 8.05-6.20 (m, 48H, Ar-H), 4.90 (s, 2H, Ph- \underline{CH}_2 -Ph), 4.07 (s, 8H, N- \underline{CH}_2 -PPh₂), 3.09 (q, *J*: 7.27 Hz, 6H, N- \underline{CH}_2 -CH₃), 1.42 (t, *J*: 7.31 Hz, 9H, N- \underline{CH}_2 -CH₃). $^{31}P\{^1H\}$ -NMR (δ , ppm, $CDCl_3$): 12.50 (s, Pd-P(Ph₂)-CH₂).

[Pd₂(L4)Cl₄] \cdot NEt₃ \cdot 2H₂O (4)

Yield (0.08 g) 64.15%. Molecular formula $C_{70}H_{87}N_3OP_4Pd_2$. Color: tile red. Anal. Calcd for $C_{70}H_{87}N_3OP_4Pd_2$: C, 56.79, H, 5.18, N, 2.96, Pd, 15.02%. Found: C, 56.73, H, 5.14, N, 2.98, Pd, 15.11%. FT-IR (KBr, cm^{-1}): ν 3336 (-OH), 3053 (aromatic C-H), 2987 (aliphatic C-H), 1607, 1518 (aromatic C=C), 1435 (P-Ph), 1098 (*tert*-amine C-N). 1H -NMR (δ , ppm, $CDCl_3$): 8.00-7.05 (m, 44H, Ar-H), 4.05 (8 H, s, N- \underline{CH}_2 -PPh₂), 3.04 (6 H, q, *J*: 7.69 Hz, N- \underline{CH}_2 -CH₃), 1.30 (9 H, t, *J*: 7.55 Hz, N- \underline{CH}_2 -CH₃). $^{31}P\{^1H\}$ -NMR (δ , ppm, $CDCl_3$): 28.21 (s, Pd-P(Ph₂)-CH₂).

Ru(II) Complexes

Tetradentate N,N,N,N-(diphosphinomethyl)amine ligands (0.088 mmol) was dissolved in CH_2Cl_2 and 0.088 mmol $[Ru(p\text{-cymene})Cl_2]_2$ (dichloro(*p*-cymene)ruthenium(II) dimer) was added to the ligand

solution in a Schlenk flask. The mixture was refluxed for 6 h under nitrogen atmosphere. Addition of hexane gave an colored solid which was then filtered off and dried at 60 °C.

[Ru₂(L1)(H₂O)₄Cl₄]·NEt₃ (5)

Yield (0.091 g) 72.74%. Molecular formula: C₅₈H₆₀Cl₄N₂O₄P₄Ru₂. Color: military green. Anal. Calcd for C₅₈H₆₀Cl₄N₂O₄P₄Ru₂: C, 54.25, H, 5.38, N, 2.96, Ru, 14.26%. Found: C, 54.25, H, 5.42, N, 3.01 Ru, 14.18%. FT-IR (KBr, cm⁻¹): ν 3324 (-OH), 3052 (aromatic C-H), 2968 (aliphatic C-H), 1606, 1513 (aromatic C=C), 1435 (P-Ph), 1097 ν (C-N). ¹H-NMR (δ, ppm, CDCl₃): 8.00-7.05 (m, 44H, Ar-H), 4.08 (8H, s, N-CH₂-PPh₂), 3.15 (6H, br, N-CH₂-CH₃), 1.40 (9H, t, *J*: 7.01, N-CH₂-CH₃). ³¹P{¹H}-NMR (δ, ppm, CDCl₃): 78.10 (s, Ru-P(Ph₂)-CH₂).

[Ru₂(L2)(H₂O)₄Cl₄]·NEt₃ (6)

Yield (0.099 g) 79.42%. Molecular formula: C₆₂H₆₂Cl₄N₂O₄P₄Ru₂. Color: gray. Anal. Calcd for C₆₂H₆₂Cl₄N₂O₄P₄Ru₂: C, 56.13, H, 5.18, N, 2.34, Ru, 14.22%. Found: C, 56.18, H, 5.21, N, 2.38, Ru, 14.30%. FT-IR (KBr, cm⁻¹): ν 3340 (-OH), 3053 (aromatic C-H), 2970 (aliphatic C-H), 1588,1532 (aromatic C=C), 1435 (P-Ph), 1098 (C-N). ¹H-NMR (δ, ppm, CDCl₃): 8.10-6.10 (m, 46H, Ar-H), 4.40 (8 H, s, N-CH₂-PPh₂), 2.95 (6 H, br, N-CH₂-CH₃), 1.04 (9 H, t, *J*: 7.24, N-CH₂-CH₃). ³¹P{¹H}-NMR (δ, ppm, CDCl₃): 90.31 (s, Ru-P(Ph₂)-CH₂).

[Ru₂(L3)(H₂O)₄Cl₄]·NEt₃ (7)

Yield (0.096 g) 76.85%. molecular formula C₆₀H₆₅Cl₄N₂O₄P₄Ru₂. Color: cream. Anal. Calcd for C₆₀H₆₅Cl₄N₂O₄P₄Ru₂: C, 55.71, H, 4.84, N, 2.16, Ru, 14.17%. Found: C, 55.74, H, 4.88, N, 2.10, Ru, 14.26%. FT-IR (KBr, cm⁻¹): ν 3307 (-OH), 3049 (aromatic C-H), 2964 (aliphatic C-H), 1614, 1514 (aromatic C=C), 1435 (P-Ph), 1098 (C-N). ¹H-NMR (δ, ppm, CDCl₃): 8.05-6.05 (m, 48H, Ar-H), 4.70 (s, 2H, Ph-CH₂-Ph), 3.95 (s, 8H, N-CH₂-PPh₂), 1.90 (q, *J*: 7.17 Hz, 6H, N-CH₂-CH₃), 0.89 (t, *J*: 7.21 Hz, 9H, N-CH₂-CH₃). ³¹P{¹H}-NMR (δ, ppm, CDCl₃): 78.95 (s, Ru-P(Ph₂)-CH₂).

[Ru₂(L4)(H₂O)₄Cl₄]·NEt₃ (8)

Yield (0.089 g) 72.24%. molecular formula C₆₀H₆₄Cl₄N₂O₄P₄Ru₂. Color: oil green. Anal. Calcd for C₆₀H₆₄Cl₄N₂O₄P₄Ru₂: C, 54.28, H, 5.20, N, 2.55, Ru, 14.44%, Found: C, 54.32, H, 5.22, N, 2.55, Ru, 14.39%. FT-IR (KBr, cm⁻¹): ν 3336 (-OH), 3053 (aromatic C-H), 2970 (aliphatic C-H), 1602, 1481 (aromatic C=C), 1435 (P-Ph), 1100 (C-N). ¹H-NMR (δ, ppm, CDCl₃): 8.10-6.90 (m, 44H, Ar-H), 4.05 (8 H, s, N-CH₂-PPh₂), 3.02 (6 H, br, N-CH₂-CH₃), 1.23 (9 H, t, *J*: 7.01, N-CH₂-CH₃). ³¹P{¹H}-NMR (δ,

ppm, CDCl₃): 77.56 (s, Ru-P(Ph₂)-CH₂).

Catalytic Activities

General Procedure for Heck Coupling Reactions

Aryl halide (0.1 mmol), olefin (0.12 mmol), base (0.12 mmol), and the catalyst (0.01 mol%) in 1,4-dioxane (2 mL) were introduced into a 10 mL round bottom flask under argon atmosphere. The obtained reaction mixture was stirred at 80, 100, 110 and 140 °C for 6 h separately. After cooling to room temperature, the solution was filtered and the solvent was removed under reduced pressure and purified by flash chromatography (*n*-hexane–EtOAc, 10:1). The product distribution was determined by GC using mesitylene as an internal.

General Procedure for Transfer Hydrogenation

An acetophenone derivative (1 mmol), 2-propanol (2 mL), catalyst (0.1 mmol%), K₂CO₃ (5 mmol%) were introduced into a Schlenk tube under argon. The resulting solution was heated at 82 °C for 12 h. The solvent was then removed under reduced pressure and purified by flash chromatography (hexane-EtOAc, 10:1). Product distribution was determined by GC yield of the corresponding alcohol.

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