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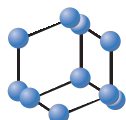
Carboxylate-Functionalized *P, N*-Ligated Cobalt Catalysts for Alkene Hydrosilylation

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Abstract: A series of *N, P*-ligands bearing carboxyl groups have been synthesized. These have been applied in conjunction with cobalt naphthenate in a facile, economic, and efficient method for the catalytic hydrosilylation of alkenes. In the presence of KO*t*Bu as an additive, the reaction time and activation energy are greatly reduced.

Keywords: Cobalt complex, *N, P*-Ligands, hydrosilylation, alkene, KO*t*Bu, facile.

1. INTRODUCTION

The hydrosilylation of alkenes is the most important C-Si bond-forming reaction besides the Rochow reaction, and it is of paramount importance in silicon chemistry [1-3]. The classical catalysts for the hydrosilylation of alkenes are platinum complexes, such as Speier's catalyst or Karstedt's catalyst [4, 5]. However, the high price of platinum catalysts increases the cost of application of this reaction in industrial processes. There has been great interest in the development of non-noble metal catalysts as alternatives to the applied noble metal catalysts. Literature reports have shown that some non-noble metals, such as iron, cobalt, and nickel and their complexes, can be used in specific hydrosilylations [6-9]; however, the application of these non-noble metal catalysts in industry has not yet been reported.

In 1965, Chalk and Harrod's team first reported that the hydrosilylation of terminal alkenes with silanes could be conducted in the presence of $Co_2(CO)_8$ [10]. In 2018, a series of *N*-heterocyclic carbene cobalt complexes were synthesized and used to catalyze hydrosilylation reactions [11]. Mitsudome [12] reported the synthesis of a new cobalt-ion-doped titanium dioxide (Co/TiO_2) catalyst by a hydrogen treatment method. The obtained Co/TiO_2 served as a highly efficient heterogeneous catalyst for the anti-Markovnikov hydrosilylation of alkenes under solvent-free conditions. Moret [13] demonstrated the catalytic activity of well-characterized Co(II) and Co(I) complexes of the *p*-Tol-dpbp ligand in the hydrosilylation of 1-octene with phenylsilane. In addition, there have been several studies on hydrosilylations catalyzed by cobalt salts [14-23]. Our group also synthesized a series of acylphosphines and investigated the hydrosilylation of alkenes that were catalyzed using RhCl₃-acylphosphine. The results indicated that RhCl₃-(diphenylphosphino) (phenyl)methanone exhibited higher activity as well as higher levels of *β*-adduct selectivity [24].

Nitrogen and phosphine ligands are widely used in organic chemistry, and have proved to be indispensable in catalytic reactions. Nitrogen and phosphorus atoms have a strong ability to provide electrons and so readily coordinate to metal ions [25-31].

In this study, a series of *N, P*-ligands bearing carboxylic acid groups have been synthesized (Scheme **1**). They have been used to ligate cobalt naphthenate, and the resulting complexes have been deployed in a facile, economic, and efficient method for the hydrosilylation of alkenes.
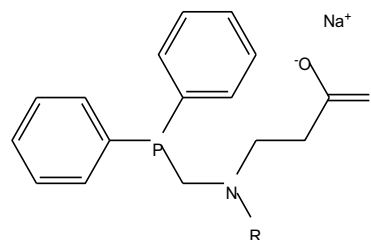
L₁: R = ethyl

L₂: R = propyl

L₃: R = butyl

L₄: R = tert-butyl

L₅: R = benzyl

Scheme 1. Structures of *N, P*-ligands with a carboxyl group.

2. EXPERIMENTAL METHODS

2.1. General Methods

All substances were purchased from Aldrich and were used as received.

Gas chromatography: Trace DSQ GC Column = DB-5 30 m *2.5 mm *0.25 μm, split = 50:1, flow = 1 mL min⁻¹ constant flow, inlet temperature = 260 °C, column temperature = 50 °C (hold 1 min) then 15 °C min⁻¹ up to 260 °C (hold 10 min).

^1H and ^{13}C NMR spectra were measured using a Bruker AV400 MHz spectrometer operating at 400.13 and 100.62 MHz, respectively. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to residual proton of CDCl₃ (^1H: δ 7.26; ^{13}C: δ 77.16) and DMSO-d_6 (^1H: δ 2.50; ^{13}C: δ 39.5).

Elemental analyses were performed on a VARIO EL-3 elemental analyzer.

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2.1.1. General Procedures for the Synthesis of the N, P-Ligands

Aqueous ethylamine solution (65–70 %, 2.44 g, 38 mmol) was added dropwise over a period of 5 h to methyl acrylate (3.61 g, 42 mmol) in a round-bottomed flask at 35 °C. The excess methyl acrylate was then removed under vacuum at 50 °C. A 30% NaOH solution (1.6 g, 40 mmol) was then added to the residue, and the mixture was heated at 80 °C for 3 h and then cooled to room temperature to afford sodium 2-ethylaminopropanoate. The product was washed with dichloromethane (3×30 mL) and dried over anhydrous Na_2SO_4 to afford a white solid.

Toluene (30 mL) was placed in a 100 mL two-necked flask equipped with a rubber septum, and purged by N_2 bubbling for about 10 min. The above-mentioned sodium 2-ethylaminopro panoate (1.53 g, 11 mmol) and 37% formaldehyde (1.325 mL, 16.5 mmol, 50% excess) were then added. Diphenylphosphine (1.875 mL, 11 mmol) was added by means of a syringe, and the mixture was stirred at 60–63 °C (oil bath) for 2 h. It was then cooled to room temperature, and anhydrous sodium sulfate was added. After filtration and rotary evaporation of the solvent, viscous, light-yellow sodium 3-{[(diphenylphosphino)methyl](ethyl) amino} propanoate was obtained.

3-(((Diphenylphosphino)methyl)(ethyl)amino)propanoate sodium (**L1**)
Yield: 57 %.

L1
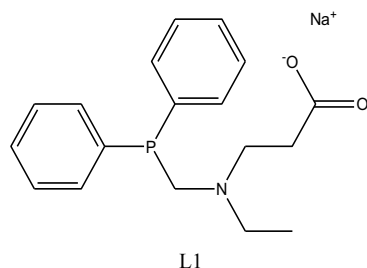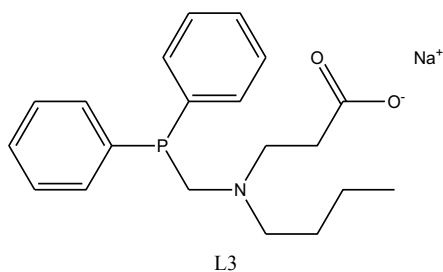
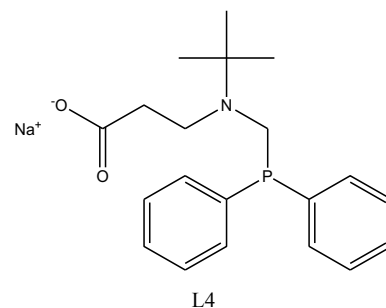The other ligands were prepared by the similar method as **L1**.

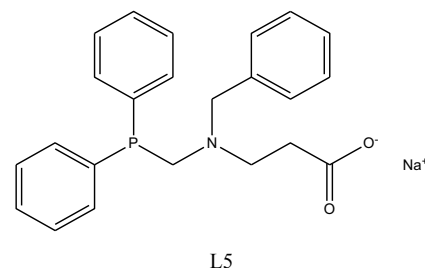3-(((Diphenylphosphino)methyl)(propyl)amino)propanoate sodium (**L2**)
Yield: 60 %.

L2
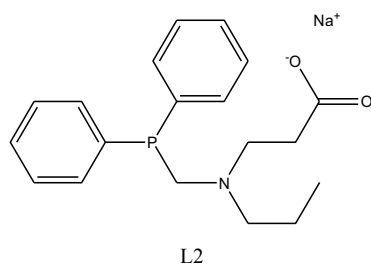
3-(Butyl((diphenylphosphino)methyl)amino)propanoate sodium (**L3**) Yield: 55 %.

L3

3-(Tert-butyl((diphenylphosphino)methyl)amino)propanoate sodium (**L4**)
Yield: 65 %.

L4

3-(Benzyl((diphenylphosphino)methyl)amino)propanoate sodium (**L5**)
Yield: 62 %.

L5

Catalytic hydrosilylation of alkene.

Typical hydrosilylation reaction procedures were as follows: A given amount of metal salt (0.02 mmol) and ligand (0.04 mmol) were added to a 10 mL round-bottomed flask equipped with a magnetic stirrer and the alkene (4 mmol) and silane (4.4 mmol) were then added under nitrogen. No solvent was added. This mixture was heated to the appropriate temperature and the hydrosilylation reaction was allowed to proceed with constant stirring for 5 h. At the end of the reaction, the product phase was separated from the catalyst by decantation and the conversion of alkene and the selectivity were determined by GC-FID (Scheme **2**).

3. RESULTS AND DISCUSSION

Highly efficient protocols for the synthesis of five *N, P*-ligands (**L1–L5**) are shown in Scheme **1** (Supplementary Material). The five products were characterized by NMR and IR spectroscopies, and the data were fully consistent with the assigned structures.
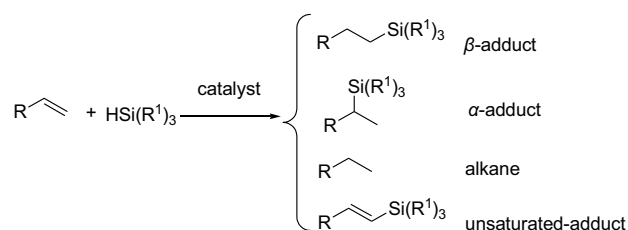
Scheme 2. The hydrosilylation reaction.

3.1. Catalytic Properties of Different Metal Salts for the Hydrosilylation Reaction

Various transition metal salts with ligand **L1** were screened as catalysts for the hydrosilylation of 1-octene with diphenylsilane. The results are summarized in Table **1**. $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$, $CoBr_2$, and $Co(CH_3COO)_2$ showed no catalytic activity at 50 °C. On increasing the temperature to 90 °C, $CoCl_2$, $NiCl_2$, $CoBr_2$, and $Co(CH_3COO)_2$ showed some catalytic activity. Interestingly, both cobalt 2-ethylhexanoate and cobalt naphthenate showed high catalytic activity at 50 °C. Conversions of 1-octene were 95.0% with cobalt 2-ethylhexanoate-**L1** and 98.9% with cobalt naphthenate-**L1**. Notably, no α-adduct, product of dehydrogenative silylation, or octane were detected.

Table 1. Complexes of ligand L1 with different metal-salts catalyzed reaction of 1-octene and diphenylsilane.

Entry	Metal Salt	Temp. (°C)	Conv. (%)	Selectivity (%)			
				β	α	Octene	Dehydrogenative Silylation
1	CoCl$_2$	50	0	0	-	-	-
2	CoCl$_2$	90	42.3	> 99.9	-	-	-
3	NiCl$_2$	90	24.2	>99.9	-	-	-
4	CuCl$_2$	90	-	-	-	-	-
5	ZnCl$_2$	90	-	-	-	-	-
6	CoBr$_2$	50	0	-	-	-	-
7	CoBr$_2$	90	22.5	> 99.9	-	-	-
8	Co(CH$_3$COO)$_2$	50	0	-	-	-	-
9	Co(CH$_3$COO)$_2$	90	93.4	> 99.9	-	-	-
10	Cobalt 2-ethylhexanoate	50	95.0	> 99.9	-	-	-
11	Cobalt naphthenate	50	98.9	> 99.9	-	-	-

Reaction conditions: 1-octene 4 mmol; Ph$_2$SiH$_2$ 4.4 mmol; catalyst 0.5 mol% of olefin; Ligand: **L1**; Metal Salt: **L1**= 1:2, 3 h

Table 2. Cobalt complexes with different nitrogen-phosphine ligands catalyzed reaction of 1-octene and diphenylsilane.

Entry	Ligand	Conv. (%)	Selectivity (%)			
			β	α	Octane	Dehydrogenative Silylation
1	-	34.3	> 99.9	-	-	-
2	L$_1$	> 99.9	> 99.9	-	-	-
3	L$_2$	45.3	> 99.9	-	-	-
4	L$_3$	46.1	> 99.9	-	-	-
5	L$_4$	48.6	> 99.9	-	-	-
6	L$_5$	96.4	> 99.9	-	-	-

Reaction conditions: 1-octene 4 mmol; Ph$_2$SiH$_2$ 4.4 mmol; catalyst: Cobalt naphthenate 0.5 mol % of olefin; Cobalt naphthenate: Ligand= 1:2; 70 °C; 3 h

3.2. Effect of Different Ligands on the Hydrosilylation Reaction

The catalytic properties of cobalt naphthenate-**L** in the hydrosilylation of 1-octene with diphenylsilane were investigated, and the results are listed in Table **2**. Low conversion of 1-octene was obtained when cobalt naphthenate was deployed in the absence of a ligand (Table **2**, entry 1). The results indicated that cobalt naphthenate-**L1** showed the highest catalytic activity (Table **2**, entry 2). When cobalt naphthenate was mixed with L2, L3, L4 separately, they exhibited a lower catalytic activity (Table **2**, entries 3-5). The catalytic activity of cobalt naphthenate-**L5** proved to be similar to that of cobalt naphthenate-**L1**, with a conversion of 1-octene of 96.4% (Table **2**, entry 6). The results clearly indicated that the addition of a ligand could enhance the activity of the catalyst.

3.3. Effect of Different Reaction Conditions on the Hydrosilylation Reaction

The effects of temperature and time on the reaction efficacy are illustrated in Fig. (**1**). It can be seen that the conversion of 1-octene increased with increasing reaction temperature and time. The conversion of 1-octene was >99.9% in the presence of cobalt naphthenate-**L1** after 3 h at 50 °C. As illustrated in Fig. (**2**), the conversion of 1-octene also increased with the increasing amount of cobalt naphthenate-**L1**. Again, it is noteworthy that no α-adduct, product of dehydrogenative silylation, or octane were detected.
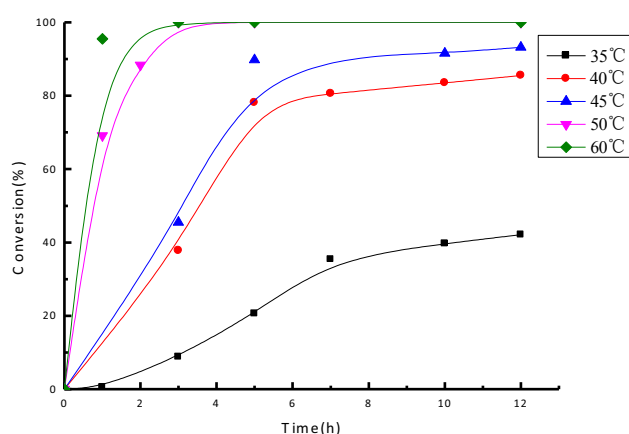

Fig. (1). Effect of reaction temperature and reaction time on the hydrosilylation reaction of Cobalt naphthenate-L1 complex.

Reaction conditions: 1-octene 4 mmol; Ph$_2$SiH$_2$ 4.4 mmol; catalyst: Cobalt naphthenate-L1, Cobalt naphthenate 0.5 mol% of olefin; Cobalt naphthenate: L1= 1:2;

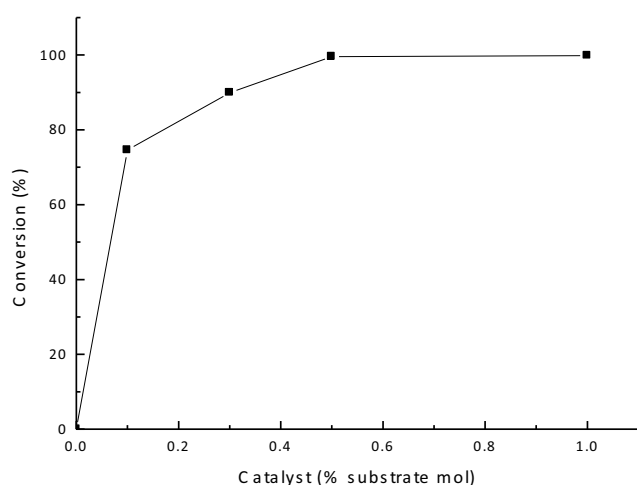**Table 3.** Cobalt naphthenate-L1 catalyzed hydrosilylation reaction of different olefins with silanes.

Entry	Alkene	Silane	Conv. (%)	Selectivity (%)			
				β	α	Alkane	Dehydrogenative Silylation
1	$CH_3(CH_2)_5CH=CH_2$		99.8	> 99.9	-	-	-
2	$CH_3(CH_2)_9CH=CH_2$		99.5	> 99.9	-	-	-
3	$CH_3(CH_2)_{11}CH=CH_2$		99.1	> 99.9	-	-	-
4	$CH_3(CH_2)_{13}CH=CH_2$	Ph_2SiH_2	77.8	> 99.9	-	-	-
5	$CH_3(CH_2)_{15}CH=CH_2$		66.8	> 99.9	-	-	-
6	$PhCH=CH_2$		70.6	> 99.9	-	-	-
7	$CH_3(CH_2)_5CH=CH_2$	$PhMe_2SiH$	99.8	> 99.9	-	-	-
8	$CH_3(CH_2)_5CH=CH_2$	$(EtO)_3SiH$	68.3	> 99.9			

Reaction conditions: 1-octene 4 mmol; Ph_2SiH_2 4.4 mmol; catalyst: Cobalt naphthenate-**L1**, Cobalt naphthenate 0.5 mol% of olefin; Cobalt naphthenate: **L1**= 1:2; 50°C; 3h

Table 4. Cobalt naphthenate-L1 catalyzed hydrosilylation reaction of different additives.

Entry	Additive	Conv. (%)	Selectivity (%)			
			β	α	Alkane	Dehydrogenative Silylation
1	-	-	-	-	-	-
2	$NaBHEt_3$	70.5	> 99.9	-	-	-
3	$NaBH_4$	10.1	> 99.9	-	-	-
4	NaOEt	95.5	> 99.9	-	-	-
5	NaOMe	97.2	> 99.9	-	-	-
6	NaO^{t}Bu	93.6	> 99.9	-	-	-
7	KO^{t}Bu	98.2	> 99.9	-	-	-

Reaction conditions: 1-octene 4 mmol; Ph_2SiH_2 4.4 mmol; catalyst: Cobalt naphthenate-**L1**, Cobalt naphthenate 0.5 mol% of olefin; Cobalt naphthenate: **L1**= 1:2; rt. 1h; catalyst: additive=1:2.

Fig. (2). Effect of the addition of complex Cobalt naphthenate-**L1** on the hydrosilylation reaction.

Reaction conditions: 1-octene 4 mmol; Ph_2SiH_2 4.4 mmol; 50°C; 3h catalyst: Cobalt naphthenate-**L1**, Cobalt naphthenate: L1= 1:2;

3.4. Scope of the Hydrosilylation Reaction

With the optimized reaction conditions in hand, we next carried out hydrosilylations of a variety of olefins with diphenylsilane. When other alkenes, such as 1-hexene, 1-octene, 1-dodecene, 1-tetradecene, 1-hexadecene, and styrene were used as substrates, excellent conversions were obtained with the cobalt naphthenate-**L1** catalyst system. Good conversions were also obtained when dimethylphenylsilane or triethoxysilane were used in place of diphenylsilane Table **3**.

3.5. Effect of Additives on the Hydrosilylation Reaction

In order to improve the catalytic activity of the cobalt naphthenate-**L1** system, some additives, such as $NaBHEt_3$, $NaBH_4$, NaOEt, NaOMe, NaO^{t}Bu, and KO^{t}Bu, were tested. With the exception of $NaBH_4$, these additives improved the catalytic activity of cobalt naphthenate-**L1**, with KO^{t}Bu being the most effective. The effects of varying the amounts of cobalt naphthenate-**L1** and KO^{t}Bu are illustrated in Table **4**. When the amount of cobalt naphthenate-**L1** was 0.5 mol% and that of KO^{t}Bu was 3 mol% with respect to 1-octene, the conversion reached 91.7% within 0.5 h at room temperature. Thus, the addition of KO^{t}Bu greatly reduced the reaction time and activation energy. The KO^{t}Bu could activate the silane reagent and could weaken the complexation abilities of the central metal cobalt and other ligands, such as naphthenate, *etc.,* that could facilitate the activation of the alkene [17, 18].

CONCLUSION

In summary, a series of *N*, *P*-ligands (**L1-L5**) have been synthesized and used in conjunction with cobalt salts for the hydrosilylation of alkenes using diphenylsilane. These have been applied in conjunction with cobalt naphthenate in a facile, economic, and

Table 5.   Effect of the addition of additive Cobalt naphthenate-L1 on the hydrosilylation reaction.

Entry	Catalyst: additive(mol%)	Conv. (%)	Selectivity (%)			
			β	α	Octene	Dehydrogenative Silylation
1	-	-		-	-	-
2	0.3:0.6	10.5	> 99.9	-	-	-
3	0.3:1.2	13.4	> 99.9	-	-	-
4	0.5:1.0	87.2	> 99.9	-	-	-
5	0.5:2.0	89.2	> 99.9	-	-	-
6	0.5:3.0	91.2	> 99.9	-	-	-
7	0.5:4.0	69.7	> 99.9	-	-	-

Reaction conditions: 1-octene 4 mmol; Ph_2SiH_2 4.4 mmol; rt. 0.5h; catalyst: Cobalt naphthenate-**L1**, Cobalt naphthenate 0.5 mol% of olefin; Cobalt naphthenate: **L1**= 1:2; additive: KO^{t}Bu.

efficient method for the catalytic hydrosilylation of alkenes. Among the studied catalysts, cobalt naphthenate- sodium 2-(diphenylphos-phino)methyl-2-ethylaminopropanoate (**L1**) exhibited the highest activity Table **5**. When the amount of cobalt naphthenate-**L1** was 0.5 mol% and that of KO^{t}Bu was 3 mol% with respect to 1-octene, the conversion reached 91.7% within 0.5 h at room temperature. Evidently, the addition of KO^{t}Bu greatly reduced the reaction time and activation energy.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The data that support the findings of this study are available from the corresponding author upon reasonable request.

FUNDING

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publisher's website along with the published article.

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