

Cobalt bis(2-ethylhexanoate) and terpyridine derivatives as catalysts for the hydrosilylation of olefins

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A simple method for the hydrosilylation of olefins by using air-stable cobalt catalysts is developed. The catalyst system is composed of simple, cheap, and readily available cobalt(II) salts and well-defined terpyridine derivatives as cocatalysts or ligands, and the hydrosilylation processes can be processed smoothly under mild conditions without either Grignard reagents or NaHB_{Et}₃ as activator.

KEYWORDS

catalysis, cobalt, hydrosilylation, olefins

1 | INTRODUCTION

Hydrosilylation processes are very useful for the production of organosilicon compounds that widely used in material science, polymer chemistry and organic synthesis.^[1] Over past decades, a number of transition metal, such as platinum, rhodium, and palladium catalysts, have been successfully developed and used in the hydrosilylation of alkenes and alkynes.^[2] However, non-noble and earth-abundant-based metals, such as iron, nickel, and cobalt, have been proven to be promising alternatives.^[3] In 1965, Chalk and Harrod reported that the hydrosilylation reaction could be conducted in the presence of CO₂(CO)₈.^[4] Recently, the hydrosilylation of alkenes and alkynes catalyzed by cobalt complexes with excellent stereoselectivity and regioselectivity had been reported.^[5] Especially, Holland group's β-diketiminato cobalt complexes,^[6] Lu group's chiral oxazoline iminopyridine (OIP) cobalt complex,^[7] Huang group's phosphine-iminopyridine cobalt complexes,^[8] and Fout group's bis(carbene)cobalt-dinitrogen complex^[9] have been known as the most prominent examples for hydrosilylation of alkenes.

Though these cobalt complexes reported exhibit excellent catalytic properties for hydrosilylation, the main disadvantages including preparation and their high sensitivity toward air and moisture prevent the widely application. Furthermore, the active species must be generated in situ by treating cobalt(II) coordination compounds with reducing agents or additives such as NaEt₃BH, BuLi, NaO^tBu, or EtMgBr as activator. Additionally, the activators used are moisture sensitive and stronger nucleophiles, which could cleave the Si–O bonds in the siloxanes. Therefore, a desirable catalyst for hydrosilylation of alkenes should be air and moisture stable and operated easily under aerobic conditions.^[10] Very recently, the Chirik^[11] and Nagashima^[12] groups have shown the employment of air-stable cobalt salts in the hydrosilylation of alkenes, and then Oña-Burgos group has reported the catalytic hydrosilylation of alkenes under aerobic conditions without solvents and additives by using cobalt(II) carboxylates with terpyridine (tpy) ligand as precursors.^[10] Chen group reported that the synthesis and application of the terpyridines (NNN) cobalt complexes with electron-donating group in the 2-position of the NNN ring on hydrosilylation. These cobalt NNN

complexes showed high activity and selectivity in the hydrosilylation of alkynes and 1,3-diyne with Ph_2SiH_2 .^[13] The hydrosilylation of internal allene with Ph_2SiH_2 conducted with cobalt-dppf complex produced the allylsilanes with high regioselectivity.^[14] The cobalt complex bearing an iminopyridine derivative ligand exhibited high catalytic activity along with olefin selective.^[15]

Herein, we reported the hydrosilylation of olefins catalyzed by commercial cobalt salts without activators under mild reaction conditions. The catalytic system is composed of cobalt(II) salt and terpyridine derivatives. Additionally, the comparison among *N* monodentate, *NN* bidentate, and *NNN* tridentate ligands on the catalytic properties had also been investigated (Scheme 1).

2 | EXPERIMENTAL

The 1-hexene (99%), 1-octene (98%) were purchased from Aladdin Chemical Reagent Co. LTD. Tetradecene (96%) was purchased from Alfa Aesa Chemical Reagent Co. LTD. The silanes were purchased from Merger Chemical Reagent Co. LTD and Aladdin Chemical Reagent Co. LTD. The other reagents were purchased from Sinopharm Chemical Reagent Co. LTD. All reagents were used without further purification.

2.1 | Synthesis

2.1.1 | Synthesis of 4'-phenyl-2,2':6',2''-terpyridine L1

Under magnetic stirring, 2-acetylpyridine (4.84 g, 40 mmol) and then KOH (3.60 g, 40 mmol) were added into ethanol (60 ml) and ammonia water (25–28%, 65 ml) to form the solution. And benzaldehyde (2.12 g, 20 mmol) in the 50-ml ethanol was dropwise added into above solution at 0°C. The solution was stirred at 95°C for 10 h. The mixture was cooled to the room temperature. The off-white solid was obtained by filtration and washed with water and cold ethanol (10 ml). The laurel-green

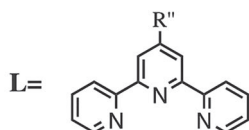
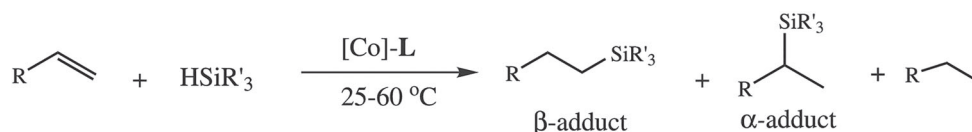
solid was recrystallized from ethanol and then dried at 55°C under vacuum (5.7 g, 82% yield). ¹H NMR (CDCl_3) δ (ppm): 7.32–7.35 (m, 2H, 5-H, 5''-H), 7.42–7.87 (m, 5H, Ph), 7.89–7.91 (d, 2H, 4-H, 4''-H), 8.66–8.68 (d, 2H, 3-H, 3''-H), 8.72–8.73 (d, 2H, 6-H, 6''-H), 8.74 (s, 2H, 3'-H, 5'-H). ¹³C NMR (CDCl_3) δ (ppm): 156.2, 155.8, 150.1, 149.0, 138.4, 136.7, 128.9, 128.8, 127.2, 123.6, 121.2, 118.8. MS: m/z = 310.1.

2.1.2 | Synthesis of 4'-methylphenyl-2,2':6',2''-terpyridine L2

Under magnetic stirring, 2-acetylpyridine (4.84 g, 40 mmol) and 4-methylbenzaldehyde (2.40 g, 20 mmol) were added into ethanol (100 ml), and then, NaOH (1.60 g, 40 mmol) and ammonia water (25–28%, 65 ml) were added into the solution. The solution was stirred at 34°C for 24 h. The mixture was cooled to the room temperature. The off-white solid was obtained by filtration, washed with cold ethanol (10 ml), and then dried at 55°C under vacuum. The white crystalline solid was obtained by recrystallization from ethanol and then dried at 55°C under vacuum (4.0 g, 62% yield). ¹H NMR (CDCl_3) δ (ppm): 2.43 (s, 3H, $-\text{CH}_3$), 7.30 (d, 2H, 5-H, 5''-H), 7.35 (t, 2H, 4-H, 4''-H), 7.83 (d, 2H, 3-H, 3''-H), 7.85–7.90 (m, 2H, 3'-H, 5'-H), 8.67 (d, 2H, 6-H, 6''-H), 8.73 (s, 4H, Ph). ¹³C NMR (CDCl_3) δ (ppm): 156.3, 155.8, 150.1, 149.1, 139.0, 136.8, 135.5, 129.6, 127.1, 123.7, 121.3, 118.6, 21.25. MS: m/z = 324.3.

2.1.3 | Synthesis of 4'-ol-2,2':6',2''-terpyridine L3

In a typical preparation, metallic sodium (0.6 g) and absolute ethanol (100 ml) reaction at room temperature for 30 min. 2-Acetylpyridine (10.0 g, 82 mmol) and dimethyl carbonate (3.7 g, 41 mmol) were added into the previous mixture of sodium and ethanol and then mixing reaction under N_2 at 35°C for 24 h. The reaction mixture is cooled to room temperature and added slowly



$\text{R}'' = \text{Me, Ph, Ph-OH, COOH, OH}$

SCHEME 1 Cobalt catalyzed hydrosilylation of alkenes

ammonium hydroxide (15 ml). After reaction for 2 h, the reaction mixture was heated up to 40°C and reaction for 24 h. After the reaction is finished, the liquid is condensed to half the volume, cooled, and precipitated out of the product. After filtration, the coarse product was recrystallized with anhydrous ethanol to obtain white solid (7.2 g, 52.3% yield). ¹H NMR (CDCl₃) δ (ppm): 6.44 (s, 2H, 5-H, 5''-H), 7.35 (t, 2H, 4-H, 4''-H), 7.81 (m, 2H, 3'-H, 5'-H), 8.10 (d, 2H, 3-H, 3''-H), 8.63 (d, 2H, 6-H, 6''-H), 10.27 (s, 1H, —OH). ¹³C NMR (D₂O) δ (ppm): 125.1, 125.4, 128.8, 142.7, 143.0, 146.0, 148.5, 148.7, 166.7. MS: *m/z* = 250.1.

2.1.4 | Synthesis of 4'-carboxylic acid-2,2':6',2''-terpyridine L4

2-Acetylpyridine (2.42 g, 20 mmol) and furfural (0.96 g, 10 mmol) were added into ethanol (45 ml), and then KOH (1.68 g, 30 mmol) and ammonia water (25–28%, 30 ml) were added into the solution under magnetic stirring. The solution was stirred at room temperature for 8 h and the solid precipitate out of solution. The white solid was obtained by filtration and washed with cold ethanol (10 ml); the white solid was obtained and then dried at 55°C under vacuum (1.96 g, 58% yield). And then, the attained solid (0.9 g, 6.7 mmol) are combined in H₂O (50 ml) made basic (pH 10) with addition KOH. KMnO₄ (1.9 g, 12 mmol) was added into the solution and heated to reflux for 3 h. The reaction mix is cooled to room temperature and filtered to remove MnO₂. The pH of the filtrate is adjusted to pH 5 with addition of HCl (aq, conc.), forming an initial precipitate. The precipitate was then removed by filtration and washed with water and copious amounts of diethyl ether and dry to obtain a pure white solid (0.67 g, 60% yield). ¹H NMR (DMSO) δ (ppm): 7.49–8.02 (m, 4H, 4-H, 5-H, 4''-H, 5''-H), 8.60–8.61 (m, 2H, 3-H, 3''-H), 8.72–8.73 (m, 2H, 6-H, 6''-H), 8.74 (s, 2H, 3'-H, 5'-H), 13.73 (s, 1H, —COOH). ¹³C NMR (DMSO) δ (ppm): 167.35, 157.21, 155.49, 150.71, 141.86, 138.77, 126.03, 122.10, 120.87. MS: *m/z* = 278.1.

2.1.5 | Synthesis of 4'-phenol-2,2':6',2''-terpyridine L5

2-Acetylpyridine (1.21 g, 10 mmol) and NaOH (2.0 g) were added into 15-ml ethanol. After stirring at room temperature for 20 min, 4-hydroxybenzaldehyde (0.61 g, 5 mmol) was added into the solution and stirred for 10 min, aqueous NH₃ (8 ml, 25%) was added to the solution, and the mixture was stirred at 50°C for 8 h. A large amount of green solid was obtained when the pH of the

solution was changed to 3–4 followed by evaporation of ethanol in the solution. The precipitate was filtrated and washed with water and ethanol (10 ml). At last, being recrystallized with methanol and a white solid was obtained after drying (1.02 g, 55% yield). ¹H NMR (CD₃OD) δ ppm: 9.08 (m, 4H, 6-H, 6''-H, 3-H, 3''-H), 8.91 (s, 2H, 3'-H, 5'-H), 8.72 (td, 2H, 4-H, 4''-H), 8.14 (td, 2H, 5-H, 5''-H), 8.02 (d, 2H, 3-H, 5-H, ph), 7.05 (d, 2H, ph). ¹³C NMR (CD₃OD) δ (ppm): 160.5, 156.3, 155.9, 149.8, 149.1, 136.8, 131.7, 129.4, 123.7, 121.2, 118.4, 116.5. MS: *m/z* = 326.1.

2.1.6 | Synthesis of the cobalt complexes with L1–L5

Co(*iso*-octoate)₂ (1 mmol) and ligands (1 mmol) were added into methanol (30 ml) in the flask, and then, the solution complex was stirred at 65°C for 2 days. Filtering out the solid, the filtrate by rotary evaporation device to remove the methanol and the brown solid was attained. The solid was dissolved in CH₂Cl₂, and then n-hexane was dropped slowly into the solution, solid precipitate from the solution. After filtrating, the solvent was removed from the filtrate by rotary evaporation device and form solid. The solid was dried in the vacuum drying oven. The molecular structures and parameter of L1-Co and L2-Co are shown in Tables S1–S12.

2.2 | Catalysis hydrosilylation

General procedure for the catalytic hydrosilylation of olefins was as follows: cobalt salt (0.004 mmol) was charged into a 10-ml pressure glass tube with sealed cover. Then, olefin (4.0 mmol) and diphenylsilane (0.88 g, 4.4 mmol) were charged into the flask, and the resulting mixture was stirred at 25°C to 60°C for desired time under the sealed condition. The product was obtained by decantation separation. The conversion of olefins and selectivity were determined and quantified by GC analysis on an Agilent 7890B. And the structure of the products were determined by GC–MS analysis on an Agilent 7890B-5977B apparatus equipped with a HP-5MS column (30 m × 0.25 mm × 0.25 μm). Gas chromatography: Trace DSQ GC Column, split = 50:1, flow = 1.1 ml min⁻¹ constant flow, inlet temperature = 250°C, column temperature = 55°C (held for 1 min), then 15°C min⁻¹ up to 120°C, then 20°C min⁻¹ up to 200°C, and then 15°C min⁻¹ up to 280°C, (held for 5 min). ¹H NMR (400 MHz) and ¹³C NMR (100.6 MHz) spectra were recorded on a Bruker Advance spectrometer. The data of NMR were listed in the Supporting Information.

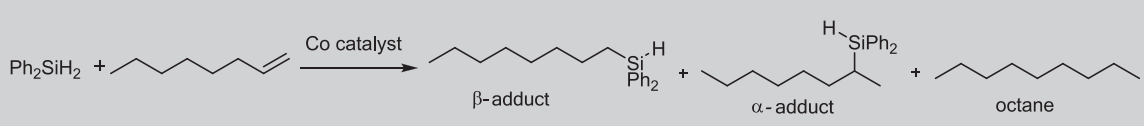
3 | RESULTS AND DISCUSSION

Cobalt(II) bromide, cobalt(II) chloride, cobalt(II) acetate, and cobalt(II) *iso*-octoate were used as precursors in the hydrosilylation of alkenes with silanes. For catalyst screening, the hydrosilylation of 1-octene with Ph_2SiH_2 was chosen as probe reaction under following conditions: 0.1 mol% cobalt precursors and 0.1 mol% of terpyridine derivatives without reducing agent under solvent-free condition. 1-Octene allows assessment of the three reaction pathways, hydrosilylation, dehydrogenative silylation, and alkene isomerization, but only the hydrosilylation products, including anti-Markovnikov (β -adducts) and Markovnikov adducts (α -adducts) were detected, the results were summarized in Table 1. No adducts were detected when CoCl_2 , CoBr_2 , or $\text{Co}(\text{OAc})_2$ was used as catalyst alone (Entries 1–3, Table 1), whereas 79.1% conversion of 1-octene along with 100% selectivity of the β -adduct was attained when $\text{Co}(\text{iso-octoate})_2$ alone was used (Entry 4, Table 1). Following, the cobalt salt was combined with terpyridine derivative **L1**, respectively, and the catalytic activity of the cobalt salt/**L1** was investigated, respectively (Entries 5–8, Table 1). The

conversion is 69.8% with 95.4% selectivity of β -adduct in the hydrosilylation of 1-octene with Ph_2SiH_2 using $\text{Co}(\text{OAc})_2$ and **L1** as catalyst. The yield of β -adduct is 60% in the hydrosilylation of 1-octene and Ph_2SiH_2 catalyzed by cobalt octanoate and terpyridin (tpy).^[3f] Encouragingly, the conversion of 1-octene is 98.2% with 98.3% selectivity of β -adduct when the $\text{Co}(\text{iso-octoate})_2$ was used (Entry 8, Table 1). Thus, the ligand **L1** shows the excellent cocatalyst for hydrosilylation of 1-octene with diphenylsilane, and no dehydrogenative silylation product was detected. This result is similar to the data reported by Oña-Burgos group, cobalt octanoate and terpyridin (tpy) as catalyst, the yield is 99% in hydrosilylation of octene with Ph_2SiH_2 in the THF.^[3f]

In order to further examine the effect of nitrogen ligands on the cobalt bis(2-ethylhexanoate) catalyzed hydrosilylation of 1-octene, we investigated a series of *N* monodentate, *NN* bidentate, and *NNN* tridentate compounds (Figure 1) as ligands or cocatalyst for the catalytic hydrosilylation of 1-octene with diphenylsilane, and the results were summarized in Table 2. The results listed in Table 2 indicated that the hydrosilylation of 1-octene with diphenylsilane

TABLE 1 Comparison of the various cobalt salts for hydrosilylation



Entry	Catalysts	Temperature (°C)	Conversion of alkene (%) ^d	Selectivity (%) ^d		
				β -Adduct	α -Adduct	Octane
1	CoCl_2	60	/	/	/	/
2	CoBr_2	60	/	/	/	/
3	$\text{Co}(\text{OAc})_2$	60	/	/	/	/
4	$\text{Co}(\text{iso-octoate})_2$	60	79.1	100	/	/
5	$\text{CoBr}_2/\mathbf{L1}$	90	31.3	98.0	2.0	2.2
6	$\text{CoCl}_2/\mathbf{L1}$	90	48.8	98.3	1.7	2.1
7	$\text{Co}(\text{OAc})_2/\mathbf{L1}$	60	69.8	95.4	4.6	1.9
8	$\text{Co}(\text{iso-octoate})_2/\mathbf{L1}$	60	>99	99.0	1.0	0.7
9 ^a	$\text{Co}(\text{iso-octoate})_2/\mathbf{L1}$	60	91.0	98.5	1.5	0.9
10 ^b	$\text{Co}(\text{iso-octoate})_2/\mathbf{L1}$	60	98.3	98.7	1.3	0.7
11 ^c	$\text{Co}(\text{iso-octoate})_2/\mathbf{L1}$	60	95.4	98.6	1.4	1.0

Note: Reaction conditions: cobalt salt 0.1 mol% based on 1-octene, 0.4 mmol 1-octene, 0.44 mmol Ph_2SiH_2 , 3 h. The mole ratio of cobalt(II) salt/**L1** was 1:1.

^aThe mole ratio of cobalt(II) salt/**L1** was 2.0.

^bThe mole ratio of cobalt(II) salt/**L1** was 0.5.

^cThe mole ratio of cobalt(II) salt/**L1** was 1/3.

^dDetermined by GC.

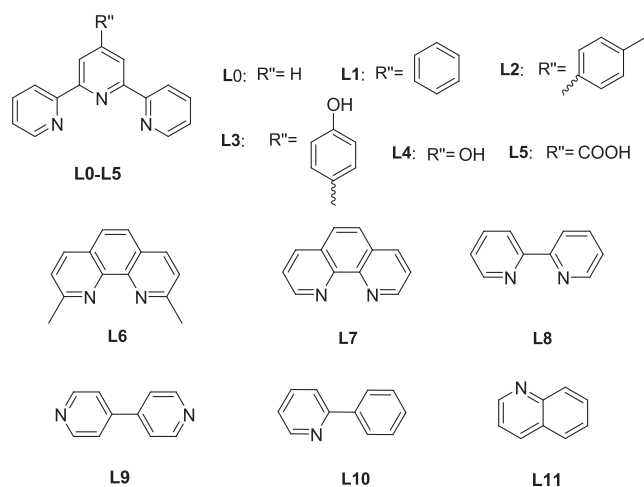


FIGURE 1 Structure of *NNN* tridentate ligands, *NN* bidentate ligands, and *N* monodentate ligands

can be performed smoothly in the presence of $\text{Co}(\text{iso-octoate})_2$ combined with *NN* bidentate or *NNN* tridentate chelating type ligands (**L0–L8**); 42–99% conversion of 1-octene was obtained in the presence of terpyridine **L0** ligand (Entry 1, Table 2). Over 99% conversion of 1-octene along with 98.3% selectivity of β -adduct was obtained when the **L1** was used as ligand (Entry 2, Table 2). When using the *NN* ligands, including 2,9-dimethyl-1,10-phenanthroline, 1,10-phenanthroline and 2,2'-dipyridine, the catalytic activity of $\text{Co}(\text{iso-octoate})_2$ in the hydrosilylation can also be improve (Entries 6, 7 and 8, Table 2). Compared with *NN* bidentate ligands, *NNN* tridentate ligands except **L4** showed better promotion for

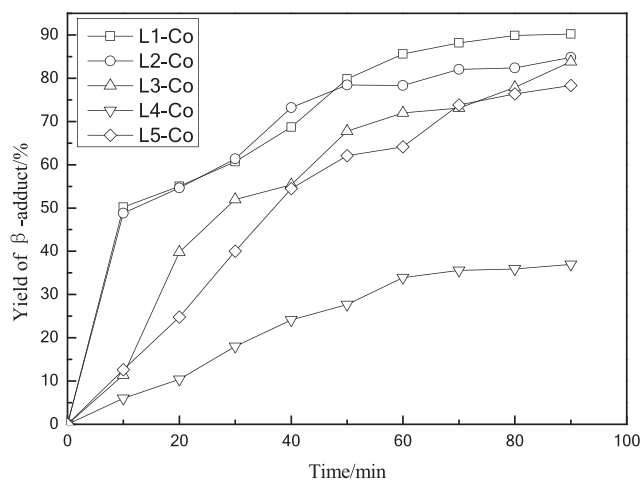


FIGURE 2 Reaction profiles of the hydrosilylation of 1-octene with Ph_2SiH_2

hydrosilylation reaction; the activity was significantly improved using **L1**, **L2**, **L3**, and **L5** as ligands (Entries 2, 3, 4, and 6, Table 2). In contrast, the hydrosilylation reaction was suppressed when the monodentate nitrogen compound such as 2-phenylpyridine **L10** was used as ligand (Entry 10, Table 2).

Additionally, the hydrosilylation of 1-octene with Ph_2SiH_2 was monitored with a catalyst loading of 0.1 mol% $\text{Co}(\text{iso-octoate})_2$ combined with 0.1 mol% ligand at certain intervals over 90 min, and the results were listed in the Figure 2. As depicted in Figure 2, these catalysts have no obvious induction period in the hydrosilylation reaction. The **L1**-cobalt complex showed the highest catalytic activity, and the yield of

TABLE 2 Effect of various ligands on the catalytic properties of cobalt (*iso-octoate*)₂

Entry	Ligands	Conversion of alkene (%) ^a	Selectivity (%) ^a		
			β -Adduct	α -Adduct	Octane
1	L0	91.8	91.7	8.3	/
2	L1	>99	98.3	1.0	0.7
3	L2	91.4	97.1	1.6	1.3
4	L3	94.9	92.5	6.1	1.4
5	L4	42.7	97.3	1.8	0.9
6	L5	92.6	95.3	3.7	1.0
7	L6	74.3	91.4	2.9	5.7
8	L7	90.4	92.7	3.1	4.2
9	L8	90.7	91.8	2.3	5.9
10	L9	71.2	90.2	5.0	4.8
11	L10	16.5	97.4	1.3	1.3
12	L11	37.1	91.1	3.8	5.1

Note: Reaction conditions: $\text{Co}(\text{iso-octoate})_2$ 0.1 mol% based on 1-octene, 0.4 mmol 1-octene, 0.44 mmol Ph_2SiH_2 , 60°C, 3 h.

^aDetermined by GC.

adduct is more than 50% during 10 min. The similar result was attained in the hydrosilylation of 1-octene catalyzed by **L2**-Co(*iso*-octoate)₂ complex. The **L4**-Co(*iso*-octoate)₂ complex shows the lowest catalytic activity, and only 36.9% yield of adduct is obtained after 90 min.

We have also studied on the effect of additives on the catalytic performance of **L1**-cobalt complex for the hydrosilylation of 1-octene with Ph₂SiH₂, and the results were listed in Table 3. As depicted in Table 3, the catalytic activity of catalyst was improved in the presence of NaBHET₃; 99% conversion with 98.1% selectivity of β -adduct is obtained at room temperature for 3 h (Entry 1, Table 3). When the catalysis system has no NaBHET₃, the conversion of 1-octene is only 9.9% at room temperature during 3 h (Entry 2, Table 3). However, the conversion of 1-octene is up to 98.2% when the reaction temperature is raised up to 40°C in the absence of NaBHET₃ (Entry 3, Table 3). The loading of catalyst had also a significant effect on the catalytic performance; 76.2% conversion of 1-octene is obtained when the loading of catalyst is 0.05 mol% (Entry 5 vs. 3, Table 3). However, the conversion can be increased to 89.6% by prolonging the reaction time to 5 h under the same conditions (Entry 8 vs. 5, Table 3).

To further explore the scope of substrates for the **L1**-Co(*iso*-octoate)₂ catalyst system, hydrosilylation of a

range of alkenes were tested under optimal conditions, and the results were listed in Table 4. Excellent yield with 99:1 linear/branched selectivity of the anti-Markovnikov adduct was obtained for both the hydrosilylation of 1-hexene and 1-octene (Entries 1 and 2, Table 4); 92.3% conversion with 93% anti-Markovnikov adduct is attained when 1-dodecene was used as substrate (Entry 3, Table 4). For longer straight-chain olefin, such as 1-tetradecene, decreased the yield (Entry 5, Table 4), 31.6% with poor selectivity of β -adduct was obtained. Styrene and its derivatives, such as *o*-methyl styrene, 4-methyl styrene, and *m*-chlorostyrene, underwent successful hydrosilylation with excellent yields and selectivities (Entries 6–9, Table 4). Surprisingly, no hydrosilylation adduct was detected for the hydrosilylation of 4-chloromethyl styrene and α -methyl styrene with Ph₂SiH₂.

Under similar conditions, the hydrosilylation of 1-octene with different silanes including (EtO)₂MeSiH, (EtO)₃SiH, (MeO)₃SiH, Ph₂MeSiH, Me₂ClSiH, MeCl₂SiH, Et₃SiH, and tetramethyldisiloxane, respectively, were tested, and the results were listed in Table 5. Over 99% conversion of 1-octene with 98:2 β/α was obtained when (EtO)₂MeSiH was used (Entry 1, Table 5). Meanwhile, (EtO)₃SiH and (MeO)₃SiH gave high conversion of 1-octene, respectively, but decreased selectivity (Entries 2 and 3, Table 5). The corresponding selectivity

TABLE 3 Effect of the reaction condition for hydrosilylation catalyzed by **L1**-Co catalyst

Entry	Catalyst (mol%)	Time (h)	Temperature (°C)	Conversion of octene (%) ^a	Selectivity (%) ^a	
					β -Adduct	α -Adduct
1	0.1/0.1 NaBHET ₃	3	25	>99	98.1	1.9
2	0.1	3	25	9.9	98.5	1.5
3	0.1	3	40	98.2	98.3	1.7
4	0.1	3	60	>99	99.0	1.0
5	0.05	3	40	76.2	97.8	2.2
6	0.1	3	40	98.2	98.3	1.7
7	0.15	3	40	>99	96.4	3.6
8	0.05	5	40	89.6	96.3	3.7
9	0.15	1	40	>99	95.0	5.0
10	0.1	2	60	98.5	97.7	2.3

Note: Reaction condition: 4.0 mmol 1-octene, 4.4 mmol Ph₂SiH₂, **L1**-Co(*iso*-octoate)₂ as catalyst.

^aDetermined by GC.

TABLE 4 Hydrosilylation of alkenes with Ph_2SiH_2

Entry	Olefins	Conversion (%) ^a	β/α	Yield (%) ^a
1		>99	99/1	98.0
2		>99	99/1	98.0
3		92.3	93/7	85.8
4		85.5	81/19	69.3
5		46.5	68/32	31.6
6		98.5	99/1	97.5
7		98.7	96/4	94.6
8		>99	99/1	98.0
9		>99	99/1	98.0
10		/	/	/
11		/	/	/

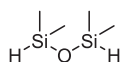
Note: Reaction conditions: 4.0 mmol olefins, 4.4 mmol Ph_2SiH_2 , catalyst 0.1 mol% based on alkenes, 60°C, 3 h.

^aDetermined by GC.

TABLE 5 Hydrosilylation of 1-octene with various silanes

Entry	Silanes	Conversion of 1-octene (%) ^a	β/α
1	(EtO) ₂ MeSiH	>99	98/2
2	(EtO) ₃ SiH	>99	70/16
3	(MeO) ₃ SiH	>99	79/12
4	Me ₂ PhSiH	52.9	100/0
5	Ph ₂ MeSiH	/	/
6	Et ₃ SiH	/	/
7	/	/	/

8	Me ₂ ClSiH	/	/
9	MeCl ₂ SiH	/	/

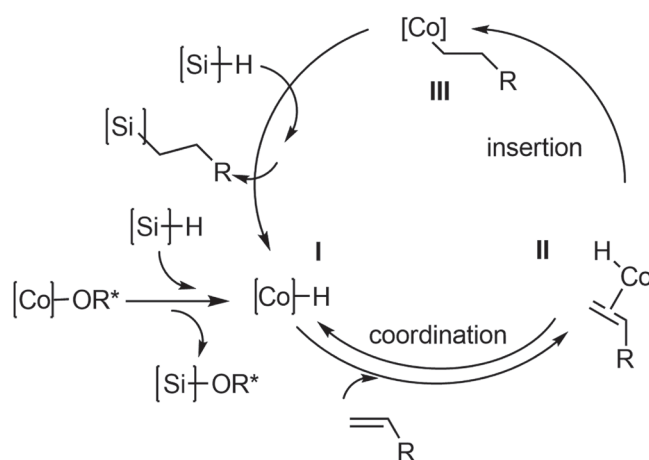


Note: Reaction conditions: 1-octene 4.0 mmol; silanes 4.4 mmol, catalyst 0.1 mol% based on octene, 60°C, 3 h.

^aDetermined by GC.

of β -adduct is 70% and 79%, respectively. If Me₂PhSiH was used, 52.9% conversion with almost 100% selectivity of β -adduct was obtained (Entry 4, Table 5). However, almost no hydrosilylation products could be detected when Ph₂MeSiH, Me₂ClSiH, MeCl₂SiH, Et₃SiH, or tetramethyldisiloxane was used as hydride under the same conditions (Entries 5–9, Table 5). Stranix et al. found that low yield of adducts were obtained when the hydrosilylation of vinyl compound with HSiMeCl₂ or HSiMe₂Cl was conducted in the presence of 2–4 mol% cobalt catalyst.^[14] And the similar results were reported by Chalk group.^[15] Chlorine atom is electron-withdrawing group and reduces the electron cloud density of silicon atom, which results in reducing the reaction activity of hydrosilane.

Based on the experiments and literatures,^[3f] a plausible mechanism has been proposed in Scheme 2. First, the cobalt catalyst precursor was dissociated to provide [Co]⁺. Second, [Co]⁺ species reacts with the silane to produce the Co–H intermediate I. In addition, the species I was in equilibrium with species II. In the third step, the species II reacts with the alkene to form the complex III, which is converted to the hydride complex I upon the reaction with silane, and the cobalt catalyst enters into the next catalytic cycle.

**SCHEME 2** The plausible mechanism for hydrosilylation of alkene with hydrosilane

4 | CONCLUSIONS

In summary, we developed catalytic hydrosilylation of olefins using cobalt bis(2-ethylhexanoate) as catalyst and a series of *NN* bidentate and *NNN* tridentate compounds as cocatalysts in the absence of any activators. The catalytic properties of cobalt bis(2-ethylhexanoate) for the hydrosilylation of olefins were improved by using terpyridine or bipyridine derivatives as cocatalyst. The results demonstrated the crucial role of benzene ring with strongly electron donating at the 4-position of terpyridine derivatives. A variety of linear alkenes and aromatic olefins were suitable for hydrosilylation. Most of the reactions were achieved in short time at low temperature to afford excellent yield of β -adduct without activating reagent and solvents. In contrast, the hydrosilylation reaction was suppressed when the monodentate nitrogen compound was used as ligand. Further mechanistic investigations will be conducted in our laboratory.

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AUTHOR CONTRIBUTIONS

Zinan Dai: Data curation; investigation. **Zehao Yu:** Investigation; methodology. **Ying Bai:** Project administration. **Jiayun Li:** Methodology. **Jiajian Peng:** Funding acquisition; methodology; project administration.

DATA AVAILABILITY STATEMENT

Data are available in article supplementary material: copies of ¹H NMR, ¹³C NMR, and the data of single crystal of products.

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SUPPORTING INFORMATION

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