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Catalytic behavior tuning via structural modifications of silylated-diphosphine Ni(II) complexes for ethylene selective dimerization

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The methylene spacers and an uncoordinated diphenylphosphine moiety in the scaffold of the $CH_3Si(CH_2)_n(PPh_2)_3$ and $Si(CH_2PPh_2)_4$-type silylated diphosphine Ni(II) complex systems have a marked impact on their catalytic performance in selective ethylene dimerization. Ni(II)-based precatalyst **1**, bearing two methylene spacers in its framework, exhibited the highest catalytic activity of 1.29×10^8 g $(mol_{Ni})^{-1}$ h^{-1}, while precatalyst **3**, with three methylene spacers, affords the highest product selectivity (88%) toward the C_4 fraction. Crystallographic investigations revealed that the precatalyst **3** adopts the mononuclear bidentate binding mode and the steric constraints of its uncoordinated diphenylphosphine moiety may successfully tailor the catalytic environment of the catalyst. The precatalyst **4** may form a dinuclear complex and exhibits high catalytic activity by changing the ligand/Ni molar ratio. The high C_4 selectivity of precatalyst **3** has been rationalized by density functional theory (DFT) calculations and found to be consistent with the experimental results. The study also revealed that designing new systems of Ni(II)-based complexes and their systematic modifications may further provide potential and industrially viable catalyst systems for selective ethylene oligomerization.

KEYWORDS
1-butene, DFT calculations, ethylene dimerization, nickel, silylated-diphosphine ligands

1 | INTRODUCTION

The interest in ethylene dimerization toward butenes (predominantly 1-butene) is accounted for its main use as a comonomer for the production of linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE). By 2025, the annual demand of 1-butene is speculated to be 3.5 million metric tons and therefore it is considered an important commodity from an industrial perspective.[1–4]

The intractability and multiplicity of active sites observed in heterogeneous catalysts may often complicate activity and selectivity tuning via structural modifications. To govern the catalytic performance of catalysts, researchers therefore mostly rely on homogeneous catalysis.[5] The AlphaButol process, which is used for the industrial-scale production of 1-butene via selective ethylene dimerization, is an excellent example of homogeneous catalysis. In this process the titanium tetrabutoxide catalyst in combination with triethylaluminum cocatalyst offers production of 7 million tons per annum,[6–8] but to further improve the catalytic performance other metal-

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based catalysts (e.g., Ni, Co, and Pd) have also been extensively investigated.[1,9–11]

Since the 1970s, the cationic nickel (Ni) complexes have been reported for the remarkable selectivity of butylene and therefore they are one of the major protagonists for selective ethylene dimerization. In this regard, Ni(II) complexes based on bi- and tridentate ligands are promising candidates for selective ethylene dimerization/polymerization because of their potential to generate oligomers with various levels of branching. Moreover, the systematic modifications in their ligand scaffold can alter electronic and steric properties, which in turn alters the catalytic environment of the catalysts and provides the desired products.[12,13] For instance, the bidentate N^P-based Ni(II) catalysts when activated with diethylaluminum chloride (DEAC) in chlorobenzene catalyzed ethylene dimerization with high catalytic activity and C_4 selectivity.[14] Furthermore, nickel complexes based on phosphine and pyridine ligands when activated with tetrakis(3,5-bis (trifluoromethyl)phenyl)borate (NaBAF) afforded considerable activity for ethylene oligomerization and polymerization.[15] Moreover, the nickel complexes of amidine/phosphine oxide and α-iminoketone ligands exhibited high thermal stability and considerable catalytic activity toward homopolymerization and copolymerization even in the absence of cocatalyst.[16,17] Similarly, tridentate pyrazolyl-based nickel complexes on activation with Methylaluminoxane (MAO) in toluene offered high dimerization activity and excellent C_4 selectivity.[18] Tridentate P^N^N- and P^N^P-based Ni(II) complexes when activated with MAO or $AlEtCl_2$ also show considerable activity for dimerization reaction.[19] Our group recently established that the Ni(II) complexes of silicon-bridged ligands can offer excellent catalytic performance for selective ethylene dimerization (Scheme 1). The Ni(II) complexes based on PCSiP (**A**),[20] silicon-bridged PNP (**B**),[21] and silylated-PNP (**C**)[22] ligands have been shown to be efficient dimerization catalysts that can provide as much as 2.40×10^8 g $(mol_{Ni})^{-1}$ h^{-1} high catalytic activity (in the case of **B**) and more than 97% C_4 selectivity (in the case of **A**).

Considering the unique attributes of silicon-based ligands and their active role in catalytic performance, we report a new class of silylated-diphosphine ligands for selective ethylene dimerization. The Ni(II)-based precatalysts **1–4** of the target **L^1–L^4** ligands were efficiently activated for ethylene dimerization, providing the highest catalytic activity of 1.29×10^8 g $(mol_{Ni})^{-1}$ h^{-1} and 88% C_4 selectivity under experimental conditions. The results were systematically compared with the reported precatalysts **5**[21] and rationalized. Moreover, the high selectivity of complex **3** was elucidated using density functional theory (DFT) calculations and found to be consistent with the experimental results.

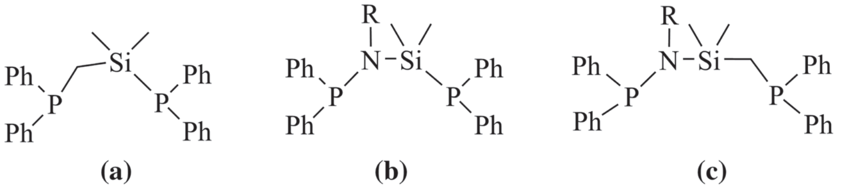
2 | EXPERIMENTAL

2.1 | General comments

All procedures were carried out in oven-dried flasks (Gongyi Shi Yu Hua Instrument, China) under a nitrogen atmosphere using a nitrogen-filled glovebox (Mikrouna, China) or the standard Schlenk technique. DEAC (2.0 mol/L in hexane) was purchased from Albemarle Corporation (USA) and used as received, and all other reagents were purchased from Aldrich (shanghai Aladdin Bio-Chem Technology, China) and used as received. Polymerization-grade ethylene was purchased from Tianjin Summit Specialty Gases (China). Anhydrous solvents were obtained using a multicolumn purification system. NMR spectra were recorded by Bruker AscendIII-400 (Bruker, Switzerland) (400 MHz for ^1H, 162 MHz for ^{31}P, and 101 MHz for ^{13}C in $CDCl_3$) at 300 K. Elemental analyses were performed using an Elemental Vario EL analyzer (Elementar, Germany). Mass spectra were recorded using a MALDI-TOF mass spectrometer (Bruker Daltonics, Germany). X-ray data for the crystal structure determination of complex **3** were collected with a Bruker SMART APEX CCD diffractometer (Bruker, Germany) at 113.15 K using the ω-scan technique (X-ray data for details of the analysis methods see the Supporting Information).

2.2 | Ligand synthesis: General procedure

The **L^1–L^6** ligands were prepared via a simple salt metathesis protocol. Treatment of *n*-butyllithium with diphenylphosphane at −80°C provided the lithium-diphenylphosphide salt. Ligands **L^1** and **L^2** were obtained by reacting the corresponding chlorosilyl



SCHEME 1 Silicon-bridged ligands **A**–**C** in Ni(II) complexes reported for ethylene dimerization

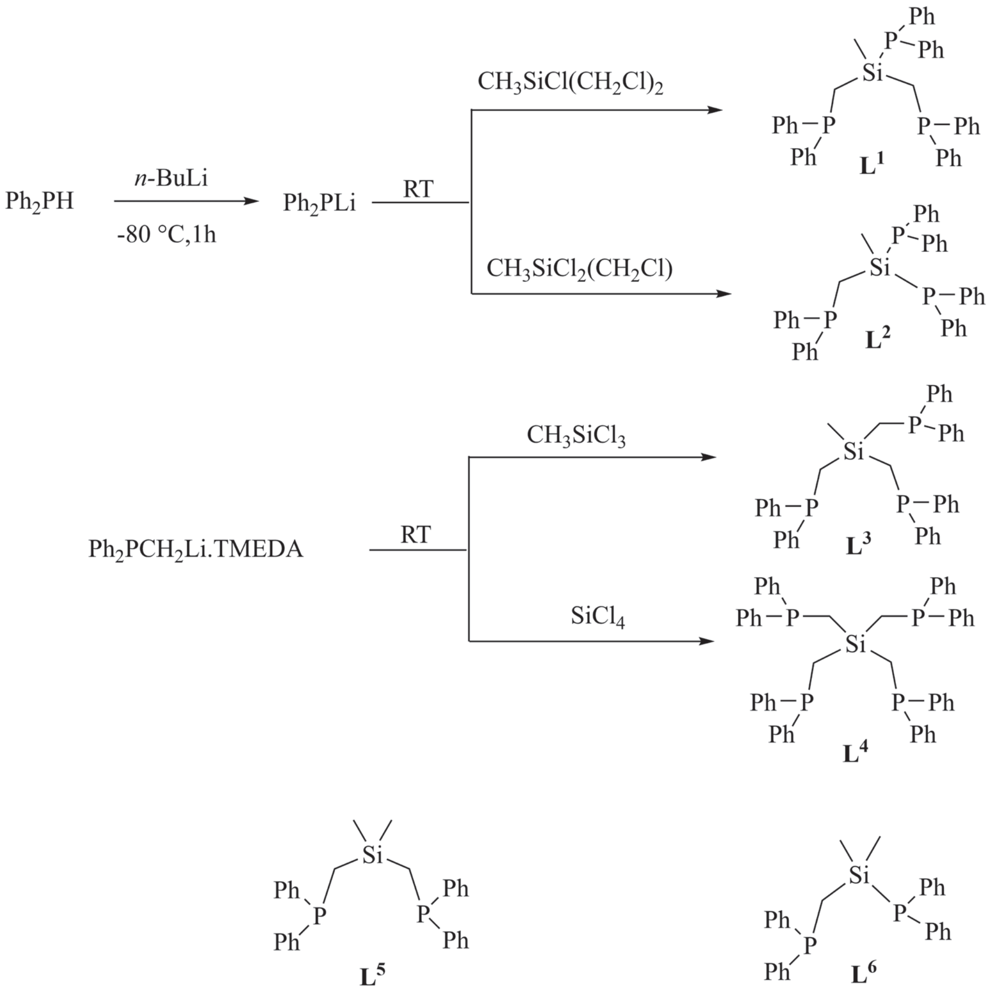
reagents with lithium-diphenylphosphide in *n*-hexane at room temperature. Ligands **L**^{3} and **L**^{4} were prepared by modifying the previously reported methods.[23,24] The relevant chlorosilyl reagents were treated with $Ph_2PCH_2Li{\cdot}(CH_3)_2NCH_2CH_2N(CH_3)_2$[25] complex to provide the **L**^{3} and **L**^{4} ligands. Ligands **L**^{5} and **L**^{6} were prepared according to the method established by our group.[20] The preparation methods for **L**^{1}–**L**^{4} and the structures of **L**^{5} and **L**^{6} are illustrated in Scheme 2 (for detailed synthesis procedures of **L**^{1}–**L**^{6} see the Supporting Information).

2.3 | Complex formation: General procedure

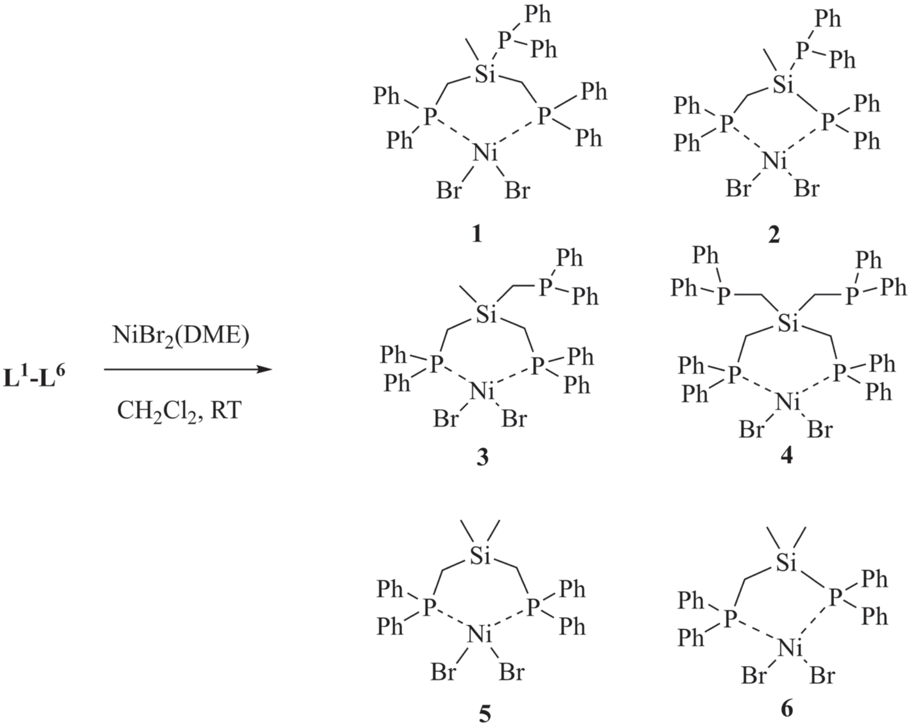
Ligands **L**^{1}–**L**^{6} in CH_2Cl_2, when treated with Dibromonickel,1,2-dimethoxyethane ($NiBr_2$(DME)) at room temperature, afforded the corresponding Ni(II)-based complexes **1–6** in high yield. The synthesis route for complexes **1–6** is illustrated in Scheme 3 (for detailed synthesis procedures of complexes **1–6** see the Supporting Information).

2.4 | Ethylene oligomerization: General procedure

All the catalytic runs of ethylene oligomerization were performed in a pre-dried (dried at 105°C for 2 hr) 150-ml glass autoclave equipped with a magnetic stirring bar. After repeated evacuation and high purity nitrogen purging, the reactor was charged with a preweighed amount of cocatalyst and methylcyclohexane (20 ml) and stirred for 1 min under an inert atmosphere. Subsequently, the catalyst solution (in 1 ml methylcyclohexane) was added, pressurized with ethylene (1.0 MPa), and the reaction was run for the desired time. All the reaction conditions (ethylene pressure, temperature, and stirring speed) were maintained throughout the run. On completion of the run, the reactor was depressurized and cooled to 0°C (using an ice bath), and the reaction was quenched with acidified methanol (50 ml). In the presence of heptane (an internal standard), the liquid oligomeric fraction was analyzed with an Agilent 7890A GC chromatograph (Agilent Technologies, USA) with a flame ionization detector and an HP-5 GC capillary column.



SCHEME 2 Synthesis of silylated-diphosphine **L**^{1}–**L**^{4} ligands, and **L**^{5} and **L**^{6} structures



SCHEME 3 Synthesis of Ni(II) complexes **1–6** based on ligands **L^1–L^6**

3 | RESULTS AND DISCUSSION

To elucidate the role of ligand structure in controlling the catalytic behavior of silylated-diphosphine-based Ni(II) complexes, precatalysts **1–6** were activated with DEAC in methylcyclohexane solvent and scrutinized for ethylene oligomerization (Table 1). On evaluation, precatalysts **5–6** show similar results in terms of catalytic activity and C_4 selectivity as reported previously (Table 1, entries 5–6).[21] Substitution of one methyl group with a diphenylphosphine moiety at Si in **L^5** and **L^6** respectively afforded **L^1** and **L^2** (Scheme 2), which on reaction with Ni(II) precursors afforded the corresponding complexes **1** and **2** (Scheme 3). This modification may lead to remarkable changes in the catalytic performance of complexes **1** and **2**. In the comparison with complexes **5** and **6**, the catalytic activities of complexes **1** and **2** improved by three and one orders of magnitude, respectively (Table 1, entries 1 and 2). Insertion of a methylene spacer in the structure of complex **1** afforded complex **3**, which exhibited lower activity than complexes **1** and **2**, but higher than complexes **5** and **6** by two and one orders of magnitude, respectively (Table 1, entry 3). Modification of the structure of complex **3** by the addition of a diphenylphosphine moiety afforded complex **4**, which on oligomerization again showed a decrease in catalytic activity by an order of magnitude compared to precatalyst **3** (Table 1, entry 4).

Among the silylated-diphosphine Ni(II) complexes **1–4**, the precatalyst **1** exhibited the highest catalytic activity under identical conditions (Table 1, entry 1). Structural modification of precatalyst **1** by the abstraction (as in **2**) or insertion (as in **3**) of a methylene spacer or addition of

TABLE 1 Ethylene dimerization with silylated-diphosphine based complexes **1–6**[a]

			Product selectivity (%)								
Entry	**Catalyst**	**Activity [10^7g $(mol_{Ni})^{-1}$ h^{-1}]**	**C_4[b]**	**1-$C_4^=$**	***trans*-C_4**	***cis*-C_4**	**C_6[b]**	**1-$C_6^=$**	**C_8[b]**	**1-$C_8^=$**	**C_{10}^{+b}**
1	**1**	12.90	59.73	9.67	28.59	21.47	33.47	1.36	5.63	0.94	1.17
2	**2**	6.00	78.72	36.18	22.89	19.65	19.28	1.81	2.00	0.26	<0.10
3	**3**	2.29	88.32	72.32	8.64	7.36	11.68	2.50	<0.10	<0.10	<0.10
4	**4**	0.31	65.67	54.56	6.54	4.57	29.99	2.78	4.34	0.87	<0.10
5	**5**	0.02	95.08	47.74	33.23	19.03	4.92	21.80	<0.10	<0.10	<0.10
6	**6**	0.14	95.11	22.95	31.01	46.04	4.89	7.56	<0.10	<0.10	<0.10

[a] General conditions: *n* (catalyst), 0.1 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 ml); reaction time, 30 min; *T*, 45°C; *n* (Al)/*n* (Ni), 500 equiv; DEAC used as cocatalyst.
[b] wt% of liquid products (oligomers).

a diphenylphosphine moiety (as in **4**) may tailor the catalytic environment of the catalyst and consequently attenuate the catalytic activity in each case (Table 1, entries 2–4).[26] Under identical conditions, the activities of complexes **1–4** decrease in the order **1** > **2** > **3** > **4** (Table 1, entries 1–4).

In contrast to catalytic activity, the product selectivity of the C_4 fraction exhibited an opposite trend for complexes **1–3**. Structural modification by abstraction/insertion of a methylene spacer in precatalyst **1** increased selectivity from 59% to 88% (Table 1, entries 1–3). The absence of a methylene spacer between the coordinated phosphorus and Si (as in **2**) or its presence between the uncoordinated phosphorus and Si (as in **3**) may play a vital role in ethylene dimerization and enhance C_4 selectivity. Further modification of **3** by addition of a diphenylphosphine moiety (as in **4**) may sterically hinder the catalytic environment and lowered C_4 selectivity from 88% to 65% (Table 1, entry 4).[14] These results suggest that complexes **1–4** are flexible toward modification, and their catalytic activity and product selectivity can be easily tailored by a slight modification in the ligand structure.

As mentioned earlier, alteration of the ligand scaffold remarkably induced the catalytic activity and product selectivity of complexes **1–4**. To elucidate the role of ligand structure in controlling catalytic performance and to establish the coordination chemistry of silylated-diphosphine Ni(II) complexes, efforts were made to prepare single crystals of these complexes. X-ray quality single crystals of complex **3** were obtained by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **3** at room temperature. The molecular structure of complex **3** [Ni(Br)$_2$(k^2-**P, P-L^3**)] is illustrated in Figure 1.

Complex **3** adopts a mononuclear k^2-P, P bidentate binding mode in which two phosphorus and two bromide atoms coordinated around the central Ni atom in a distorted tetrahedral geometry while the third phosphorus atom (P3) remains uncoordinated. By comparing the structural parameters of complex **3** with the previously reported $Me_2Si(CH_2PPh_2)_2/NiBr_2$ complex **5** with the structure [Ni(Br)$_2$(k^2-**P, P-L^5**)][21] suggested that the uncoordinated diphenylphosphine moiety may successfully tune the catalytic environment of the complex **3** based system. The high activity of catalyst **3**, in comparison to catalyst **5**, is due to the flexible nature of the uncoordinated diphenylphosphine moiety, which may enable complex **3** to exhibit a stable configuration and consequently deliver high catalytic activity. The important differences in the structural parameters between complexes **3** and **5** are illustrated in Table 2.

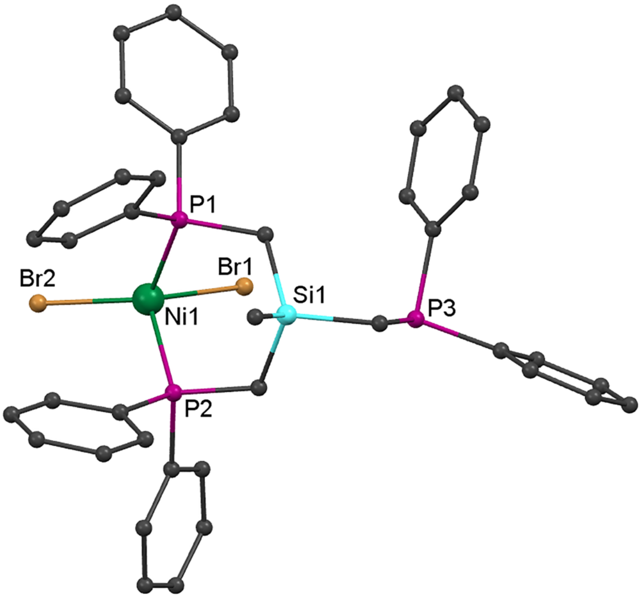


FIGURE 1 Molecular structure of the Ni(II) complex **3**. Partial thermal ellipsoids drawn at 50% probability. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Br1–Ni1 2.3729(16); Br2–Ni1 2.3368(10); Ni1–P1 2.2882(16); Ni1–P2 2.2904(17). Selected bond angles (°): Br2–Ni1–Br1 126.16(4); P1–Ni1–Br1 94.75(5); P1–Ni1–Br2 119.67(5); P1–Ni1–P2 99.39(6); P2–Ni1–Br1 102.14(6); P2–Ni1–Br2 110.40(5)

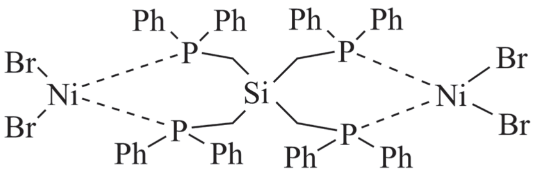
Triphenylphosphine (PPh_3) has been extensively used as an auxiliary ligand to enhance the catalytic performance of ethylene dimerization catalysts. This moiety may be coordinated with the complex and contribute toward the catalyst's stability and consequent catalytic activity and product selectivity.[27,28] For instance, adding 10 equiv PPh_3 at 30 atm ethylene pressure enhances the catalytic activity of N–O-based Ni catalysts by an order of magnitude.[29] To probe the role of the uncoordinated diphenylphosphine moiety in controlling the catalytic performance, we speculated that changing the ligand/Ni molar ratio may increase the ligand–Ni interaction and hence increase the chance of coordination of the uncoordinated diphenylphosphine moiety with the

TABLE 2 Comparison of the bond angles of complexes **3** and 5

Bond angles (°)	Complex 3	Complex 5 [25]
Br1–Ni1–Br2	126.16(4)	127.28(5)
P1–Ni1–Br1	94.75(5)	99.93(7)
P1–Ni1–Br2	119.67(5)	111.58(8)
P2–Ni–Br1	102.14(6)	98.32(7)
P2–Ni–Br2	110.40(5)	115.94(7)
C^{Ph}–P2–Ni1	115.80(average)	113.65(average)

complex. This may stabilize the catalyst and consequently enhance catalytic performance by forming tridentate (in case of **1–3**)[18] or dinuclear (in case of **4**) complexes.[30] For this purpose, the **1–4** complexes were scrutinized at different ligand/Ni ratios for ethylene oligomerization and the results are shown in Table 3. The catalytic activity of complexes **1–3** decreases on changing the ligand/Ni ratio from 1:1 to 1:1.5 (Table 3, entries 1–6), which suggests that these complexes may fail to coordinate in a tridentate fashion. The decrease in activity could be attributed to the excess amount of Ni precursor, which may disturb the catalytic systems of complexes **1–3**. The excess amount of Ni precursor may cause inadequate separation between the Ni cations and counterions in the reaction medium and consequently contribute to low catalytic activity.[31] In contrast to complexes **1–3**, the catalytic activity of complex **4** increased by an order of magnitude when the ligand/Ni ratio was changed from 1:1 to 1:2 (Table 3, entries 7 and 8). Although not definitive, we speculate that this increase in the catalytic activity may be attributed to the formation of a stable complex by the coordination of two molecules of $NiBr_2$ with one molecule of $\mathbf{L^4}$ in a dinuclear fashion, as seen in Scheme 4.

Decreasing the ligand/Ni molar ratio tends to increase the C_4 selectivity for complexes **1–4** (Table 3, entries 1, 3, 5, and 7). These results suggest that an excess amount of free metal precursor may promote C_4 selectivity. To probe the role of excess Ni precursor, a test run for free $NiBr_2$(DME) (without coordination of the silylated-diphosphine ligand) was conducted. This showed that an excess amount of Ni precursor attenuated the activity while enhancing C_4 selectivity (Table 3, entry 9).



SCHEME 4 Proposed Ni(II)-based dinuclear complex $\mathbf{L^4}$

To evaluate the thermal stability of the silylated-diphosphine based Ni(II) catalysts, ethylene oligomerization of complexes **1–4** was performed over a broad range of reaction temperature (Table 4). The catalytic activity of complexes **1–4** increased with increasing reaction temperature, reached a maximum value at 45°C (Table 4, entries 3, 8, 13, and 18). The increase in catalytic activity at 45°C could be attributed to the high rate of oligomerization due to high ethylene solubility in the reaction medium and to the high thermal stability of the catalysts.[18] A further increase in reaction temperature resulted in a marked decrease in catalytic activity for precatalysts **1** and **2** and the lowest activities were obtained at the highest temperature (Table 4, entries 5 and 10). This decrease in activity could be attributed to low ethylene solubility in the reaction medium. Moreover, high temperatures may deactivate the reaction center of precatalysts **1** and **2** and consequently offer low activity.[23] Above 45°C, the catalytic activity of complex **3** remains almost constant while a very small change was observed in the activity of complex **4**, which suggests that the presence of three and four methylene spacers, respectively, in complexes **3** and **4** may offer extra thermal stability to these complexes and therefore provide almost constant activity at high temperature (Table 4, entries 15 and 20).

TABLE 3 Evaluation of the effect of ligand/Ni molar ratios for complexes **1–4** on ethylene dimerization[a]

Entry	Catalyst	L/Ni	Activity [10^7g $(mol_{Ni})^{-1}$ h^{-1}]	Product selectivity (%)								
				C_4[b]	1-$C_4^=$	*trans*-C_4	*cis*-C_4	C_6[b]	1-$C_6^=$	C_8[b]	1-$C_8^=$	C_{10}^{+b}
1	**1**	1:1.5	3.45	88.40	66.39	10.17	11.84	11.60	2.95	<0.10	<0.10	<0.10
2		1:1	12.90	59.73	9.67	28.59	21.47	33.47	1.36	5.63	0.94	1.17
3	**2**	1:1.5	3.37	84.74	49.42	18.30	17.02	15.26	2.94	<0.10	<0.10	<0.10
4		1:1	6.00	78.72	36.18	22.89	19.65	19.28	1.81	2.00	0.26	<0.10
5	**3**	1:1.5	1.93	89.59	73.07	7.12	9.39	10.41	2.85	<0.10	<0.10	<0.10
6		1:1	2.29	88.32	72.32	8.64	7.36	11.68	2.50	<0.10	<0.10	<0.10
7	**4**	1:2	2.48	80.01	49.13	16.12	14.76	19.99	3.38	<0.10	<0.10	<0.10
8		1:1	0.31	65.67	54.56	6.54	4.57	29.99	2.78	4.34	0.87	<0.10
9	$NiBr_2$DME)	-	0.18	82.17	75.53	2.81	3.84	17.83	0.12	<0.10	<0.10	<0.10

[a] General conditions: *n* (catalyst), 0.1 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 ml); reaction time, 30 min; *T*, 45°C; *n* (Al)/*n* (Ni), 500 equiv; DEAC used as cocatalyst.

[b] wt% of liquid products (oligomers).

TABLE 4 Evaluation of the effect of reaction temperature on ethylene dimerization[a]

Entry	Catalyst	*T* (°C)	Activity [10^7g $(\text{mol}_{\text{Ni}})^{-1}$ h^{-1}]	Product selectivity (%)								
				C_4[b]	$1\text{-}C_4^=$	*trans*-C_4	*cis*-C_4	C_6[b]	$1\text{-}C_6^=$	C_8[b]	$1\text{-}C_8^=$	C_{10}^{+}[b]
1	1	15	1.13	74.25	24.58	33.14	16.53	25.75	1.68	<0.10	<0.10	<0.10
2		30	12.10	65.33	16.43	30.54	18.36	29.32	1.52	4.41	0.92	0.94
3		45	12.90	59.73	9.67	28.59	21.47	33.47	1.36	5.63	0.94	1.17
4		60	8.77	57.42	8.12	27.42	21.88	36.23	1.39	5.35	0.73	1.00
5		75	2.63	55.00	6.25	23.39	25.36	36.30	1.31	6.92	0.68	1.78
6	**2**	15	1.93	88.68	57.78	18.22	12.68	10.17	1.30	1.14	0.13	<0.10
7		30	3.78	83.51	47.42	22.14	13.96	14.67	1.68	1.82	0.21	<0.10
8		45	6.00	78.72	36.18	22.89	19.65	19.28	1.81	2.00	0.26	<0.10
9		60	5.35	77.37	28.84	26.72	21.80	19.71	2.11	2.92	0.32	<0.10
10		75	0.20	72.04	25.23	26.60	20.22	20.58	2.42	7.38	0.67	<0.10
11	**3**	15	0.33	91.12	78.34	6.22	6.56	8.88	1.97	<0.10	<0.10	<0.10
12		30	0.82	90.54	75.80	7.66	7.08	9.46	2.21	<0.10	<0.10	<0.10
13		45	2.31	88.32	72.32	8.64	7.36	11.68	2.50	<0.10	<0.10	<0.10
14		60	2.27	86.78	66.66	10.12	10.00	13.22	2.78	<0.10	<0.10	<0.10
15		75	2.31	85.88	63.50	12.24	10.14	13.59	2.91	0.53	0.18	<0.10
16	**4**	15	0.09	71.41	61.52	6.01	3.88	28.59	2.22	<0.10	<0.10	<0.10
17		30	0.23	66.72	56.44	6.22	4.06	29.07	2.54	4.21	0.98	<0.10
18		45	0.31	65.68	54.56	6.54	4.57	29.99	2.78	4.34	0.87	<0.10
19		60	0.22	65.68	53.98	6.67	5.03	30.16	2.65	4.52	0.96	<0.10
20		75	0.11	64.45	52.08	6.85	5.52	30.60	1.41	4.95	0.41	<0.10

[a] General conditions: *n* (catalyst), 0.1 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 ml); reaction time, 30 min; *n* (Al)/*n* (Ni), 500 equiv; DEAC used as cocatalyst.

[b] wt% of liquid products (oligomers).

Low-temperature ethylene oligomerization provides the highest C_4 selectivity for complexes **1–4**, which suggests that low temperature may increase the rate of dimerization and therefore be favorable for the formation of the C_4 fraction (Table 4, entries 1, 6, 11, and 16).[32] Highest temperature screening provides the lowest C_4 selectivity, it enhances the formation of C_6 products at the expense of the C_4 fraction (Table 4, entries 5, 10, 15, and 20). High temperatures may promote chain propagation instead of the dimerization reaction.

Changing the cocatalyst molar ratio in the oligomerization reaction can tune the catalytic environment and therefore influence the catalytic performance.[20,22] Probing the role of DEAC by changing its molar ratio suggested that the concentration of cocatalyst significantly influences the catalytic activity and C_4 selectivity (Table 5). The precatalysts **1**, **2**, and **4** offer high catalytic activity at 500 equiv DEAC (Table 5, entries 2, 6, 14), while precatalyst **3** exhibited the highest activity at 700 equiv DEAC (Table 5, entry 11). Any increase (Table 5, entries 3, 4, 7, 8, 12, 15, and 16) or decrease (Table 5, entries 1, 5, 9, 10, and 13) in the concentration of DEAC may lead to a decrease in catalytic activity. A low concentration of DEAC may unable to completely activate the catalytic system[20,33] while a higher concentration may cause over-reduction and deactivate the catalytic system.[34] The highest catalytic activity of 1.29×10^8 g $(\text{mol}_{\text{Ni}})^{-1}$ h^{-1} was obtained by precatalyst **1** at 500 equiv DEAC (Table 5, entry 2).

The selectivity of the C_4 product tends to decrease with increasing molar ratio of cocatalyst and the highest C_4 selectivities were obtained at the lowest molar ratio of DEAC (Table 5, entries 1, 5, 9, and 13). Increasing the cocatalyst molar ratio promoted C_6 selectivity at the expense of C_4 product, which suggests that the high molar ratio of DEAC may favor the formation of the C_6 fraction.

The precatalysts **1** and **3** were further selected to probe the role of catalyst loading on ethylene oligomerization. Table 6 shows that on increasing catalyst loading from 0.1 to 0.6 μmol, the catalytic activity significantly

TABLE 5 Evaluation of the effect of Al/Ni molar ratios of complexes **1–4** on ethylene dimerization[a]

				Product selectivity (%)								
Entry	**Catalyst**	$n_{(Al)}$/ $n_{(Ni)}$	Activity [10^7g (mol$_{Ni}$)$^{-1}$ h^{-1}]	C_4^b	1-$C_4^=$	*trans*-C_4	*cis*-C_4	C_6^b	1-$C_6^=$	C_8^b	1-$C_8^=$	C_{10}^{+b}
1	**1**	300	3.22	64.16	15.35	32.17	16.65	30.96	1.32	4.88	1.30	<0.10
2		500	12.90	59.73	9.67	28.59	21.47	33.47	1.36	5.63	0.94	1.17
3		700	11.80	58.26	8.43	27.16	22.67	34.34	1.24	5.17	0.85	2.23
4		1000	10.10	56.50	8.21	23.06	25.23	34.86	1.11	6.22	0.81	2.42
5	**2**	300	0.23	86.60	51.34	16.30	18.96	13.40	1.93	<0.10	<0.10	<0.10
6		500	6.00	78.72	36.18	22.89	19.65	19.28	1.81	2.00	0.26	<0.10
7		700	5.91	76.70	33.27	23.53	19.90	21.89	1.60	1.16	0.21	0.25
8		1000	5.86	72.38	23.20	28.75	20.43	26.16	1.40	0.62	0.12	0.84
9	**3**	300	0.11	89.13	75.57	7.45	6.11	10.87	2.52	<0.10	<0.10	<0.10
10		500	2.29	88.32	72.32	8.64	7.36	11.68	2.50	<0.10	<0.10	<0.10
11		700	3.85	86.94	59.12	14.98	12.84	13.06	2.12	<0.10	<0.10	<0.10
12		1000	2.54	86.25	44.97	20.45	19.19	13.74	1.48	<0.10	<0.10	<0.10
13	**4**	300	0.04	70.44	58.34	7.34	4.76	27.44	4.38	2.12	0.97	<0.10
14		500	0.31	65.67	54.56	6.54	4.57	29.99	2.78	4.34	0.87	<0.10
15		700	0.27	65.75	55.14	6.24	4.37	31.69	2.16	2.56	0.68	<0.10
16		1000	0.20	64.09	53.98	5.92	4.19	33.29	1.82	2.62	0.45	<0.10

[a] General conditions: *n* (catalyst), 0.1 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 ml); reaction time, 30 min; *T*, 45°C; DEAC used as cocatalyst.

[b] wt% of liquid products (oligomers).

TABLE 6 Evaluation of the effect of catalyst loading on ethylene dimerization[a]

				Product selectivity (%)								
Entry	**Catalyst**	***n* (cat) (μmol)**	**Activity [10^7g (mol$_{Ni}$)$^{-1}$ h^{-1}]**	C_4^b	1-$C_4^=$	*trans*-C_4	*cis*-C_4	C_6^b	1-$C_6^=$	C_8^b	1-$C_8^=$	C_{10}^{+b}
1	**1**	0.1	12.9	59.73	9.67	28.59	21.47	33.47	1.36	5.63	0.94	1.17
2		0.2	10.40	58.13	8.58	28.32	21.23	34.07	1.22	6.32	0.86	1.48
3		0.6	4.22	55.21	7.11	27.23	20.87	35.69	0.80	7.36	0.81	1.74
4	**3**	0.1	2.29	88.32	72.32	8.64	7.36	11.68	2.50	<0.10	<0.10	<0.10
5		0.2	1.86	86.32	71.11	8.16	7.05	12.56	3.40	1.12	0.54	<0.10
6		0.6	1.69	83.18	69.08	7.95	6.15	14.42	4.94	2.40	0.89	<0.10

[a] General conditions: pressure, 1.0 MPa; solvent, methylcyclohexane (20 ml); reaction time, 30 min; *T*, 45°C; *n* (Al)/*n* (Ni), 500 equiv; DEAC used as cocatalyst.

[b] wt% of liquid products (oligomers).

decreased. The decrease in catalytic activity could be explained by the fact that an excess amount of catalyst loading might interfere with the catalytic environment of the active species, resulting in the attenuation of the catalytic activity.[35] Moreover, high catalyst loading may also limit the ethylene concentration and consequently diminish the activity.[36]

In contrast to catalytic activity, high catalyst loading has no remarkable influence on C_4 selectivity. Increasing the catalyst mass loading resulted in only a slight decrease in C_4 selectivity (Table 6, entries 3 and 6).

Furthermore, the effect of reaction time on catalytic performance was investigated by conducting the reactions over a broad range of reaction times from 15 to 75 min (Table 7). The precatalysts **1–4** exhibited high activity during the first 15 min of the reaction, suggesting that these precatalysts completely activated at an early stage of the reaction initiation (Table 7, entries 1, 6, 11, and 16).[35] Increasing the reaction time decreased the

TABLE 7 Evaluation of the effect of reaction time on ethylene dimerization[a]

Entry	Catalyst	Time (min)	Activity [10^7g $(mol_{Ni})^{-1}$ h^{-1}]	Product selectivity (%)								
				C_4[b]	$1\text{-}C_4^=$	*trans*-C_4	*cis*-C_4	C_6[b]	$1\text{-}C_6^=$	C_8[b]	$1\text{-}C_8^=$	C_{10}^+[b]
1	**1**	15	18.50	58.56	8.05	28.72	21.79	34.53	1.51	5.68	0.96	1.23
2		30	12.90	59.73	9.67	28.59	21.47	33.47	1.36	5.63	0.94	1.17
3		45	8.47	60.96	11.09	28.45	21.42	32.60	1.30	5.44	0.88	1.00
4		60	6.67	61.88	13.16	28.23	20.49	31.77	1.23	5.32	0.83	1.03
5		75	5.12	62.13	16.14	27.82	20.17	31.71	1.23	5.21	0.70	0.95
6	**2**	15	6.74	78.06	33.12	24.56	20.38	19.79	1.98	2.15	0.32	<0.10
7		30	6.00	78.72	36.18	22.89	19.65	19.28	1.81	2.00	0.26	<0.10
8		45	4.12	79.21	36.65	23.43	19.13	18.81	1.61	1.98	0.19	<0.10
9		60	2.03	80.11	38.51	23.92	17.68	18.08	1.45	1.81	0.18	<0.10
10		75	1.56	81.51	43.58	22.83	15.10	16.75	1.35	1.74	0.16	<0.10
11	**3**	15	4.77	87.80	71.02	9.05	7.73	12.20	3.02	<0.10	<0.10	<0.10
12		30	2.29	88.32	72.32	8.64	7.36	11.68	2.50	<0.10	<0.10	<0.10
13		45	0.72	89.64	75.36	7.66	6.62	10.36	1.74	<0.10	<0.10	<0.10
14		60	0.29	90.12	76.23	7.34	6.55	9.88	1.64	<0.10	<0.10	<0.10
15		75	0.12	91.45	77.98	6.98	6.49	8.55	1.43	<0.10	<0.10	<0.10
16	**4**	15	0.42	64.38	52.55	6.70	5.13	30.76	3.45	4.86	1.17	<0.10
17		30	0.31	65.67	54.56	6.54	4.57	29.99	2.78	4.34	0.87	<0.10
18		45	0.18	67.22	56.55	6.43	4.24	28.97	2.32	3.81	0.68	<0.10
19		60	0.04	68.37	58.87	5.40	4.10	28.85	2.11	2.78	0.62	<0.10
20		75	0.02	69.29	60.25	5.20	3.24	28.48	1.81	2.23	0.58	<0.10

[a] General conditions: n (catalyst), 0.1 μmol; pressure, 1.0 MPa; solvent, methylcyclohexane (20 ml); T, 45°C; n (Al)/n (Ni), 500 equiv; DEAC used as cocatalyst.

[b] wt% of liquid products (oligomers).

catalytic activity and a long time run may offer low catalytic activity for these catalyst systems (Table 7, entries 5, 10, 15, and 20). This decline in activity is more pronounced for precatalysts **1**, **3**, and **4**, for which the activity dropped by an order of magnitude in each case (Table 7, entries 3–5, 13–15, and 19–20). The decrease in catalytic activity over a long time run could be attributed to the partial deactivation of the catalyst active species during the oligomerization reaction.[35]

In contrast to catalytic activity, the product selectivity of C_4 is slightly affected by reaction time and remains almost stable. The precatalysts **1–4** may have the ability to dimerize ethylene over a long reaction time.[35]

Commercially applied efficient ethylene dimerization catalysts have been known for many years and are considered to be a mature industry. However, its catalytic mechanism has received great interest after the newly developed aryloxy-based Ti catalysts and continuously under investigation.[37–40] Some studies have suggested that high dimerization selectivity could be attributed to a metallacycle mechanism in which oxidative coupling of ethylene with an active metal forms a metallacyclopentane and releases the final product (1-butene) via β-hydride elimination.[33,37,39] Alternatively, the product distribution in these systems, which arises due to the high rate of chain transfer relative to chain propagation, could be rationalized on the basis of the Cossee mechanism.[38,41] Recent experimental and theoretical investigations support the Cossee mechanism for ethylene dimerization while strongly disfavoring the involvement of the metallacycle mechanism.[42,43]

To rationalize the C_4 selectivity of silylated-diphosphine based Ni(II) systems, precatalyst **3** (the best system in terms of selectivity) was selected for DFT calculations.[42–45] Many theoretical investigations have suggested that DFT is a powerful tool for studying the mechanistic aspects of the ethylene dimerization reaction. DFT calculations can be effectively used to find the mechanistic pathway (whether the reaction follows the Cossee or metallacycle mechanism), the role of the ligand in catalytic transformation, and the origin of selectivity in

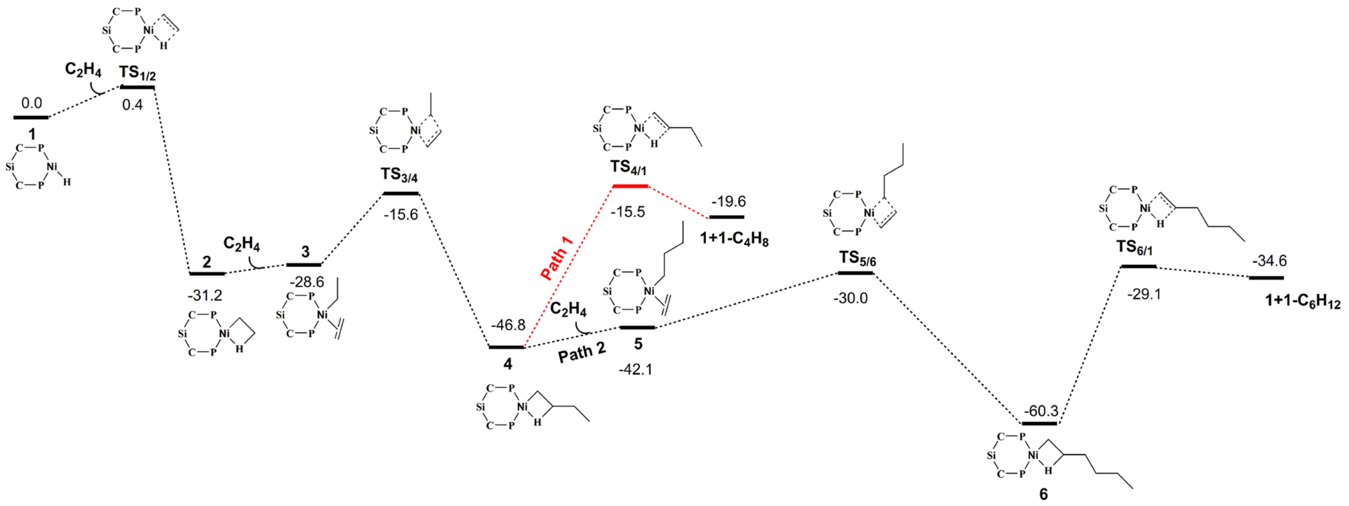


FIGURE 2 Relative Gibbs free energy profile for ethylene dimerization (via the Cossee mechanism) catalyzed by precatalyst **3**

dimerization systems.[44,45] Figure 2 shows the relative Gibbs free energy profile of Cossee-based ethylene dimerization catalyzed by precatalyst **3**. At the beginning, the migratory insertion of the first ethylene molecule into the Ni–hydride bond of complex **1** via $\mathbf{TS_{1/2}}$ needs only 0.4 kcal/mol of energy to form intermediate **2**. The second ethylene coordination (2.6 kcal/mol of energy for the formation of **3**) and subsequent insertion (13.0 kcal/mol of energy to pass through $\mathbf{TS_{3/4}}$) collectively require 15.6 kcal/mol of energy to yield intermediate **4**. Intermediate **4** then opens up two possible pathways: a dimerization pathway (path 1) and a trimerization pathway (path 2). Following path 1, intermediate **4** can pass through $\mathbf{TS_{4/1}}$ with an energy barrier of 31.3 kcal/mol of energy and release 1-butene via β-hydride elimination. Considering path 2, the third ethylene coordination (4.7 kcal/mol of energy to form intermediate **5**) and subsequent insertion (12.1 kcal/mol of energy to pass through $\mathbf{TS_{5/6}}$) collectively require 16.8 kcal/mol of energy to form intermediate **6**. Intermediate **6** can pass through the $\mathbf{TS_{6/1}}$ transition state with an energy barrier of 31.2 kcal/mol of energy and release 1-hexene via β-hydride elimination. The energy barriers for the β-hydride elimination in path 1 (31.3 kcal/mol) and path 2 (31.2 kcal/mol) are almost same, but path 2 needs 16.8 kcal/mol of extra energy (for ethylene coordination and subsequent insertion) compared to path 1 to release 1-hexene. Thus, instead of following path 2, intermediate **4** can readily liberate 1-butene via β-hydride elimination. Moreover, focusing on the mechanism of the β-hydride transfer may provide a reasonable conjecture for 1-butene formation. For electron-deficientmetal-basedcatalysts,[41,44] 1-butene formation requires high energy because of a stepwise β-hydride transfer to ethylene, which is an endergonic and nonspontaneous process. Its rate also depends on the ethylene concertation and proceeds only in the presence of ethylene. On the contrary, for electron-richmetal-based catalysts (Ni in our case),[46–48] a concerted transfer of the β-hydrogen in the alkyl chain to the metal-coordinated ethylene takes place and provides a facile route for the liberation of 1-butene.

4 | CONCLUSIONS

We have reported Ni(II) precatalysts with $CH_3Si(CH_2)_n(PPh_2)_3$ and $Si(CH_2PPh_2)_4$-type silylated diphosphine ligands, which uon activation with DEAC offer active and selective ethylene dimerization systems. We observed that the methylene spacers and a diphenylphosphine moiety in the ligand scaffold strongly influence the catalytic performance of these catalysts. Precatalyst **1**, with two methylene spacers in its structure, exhibited high catalytic activity, while precatalyst **3**, with three methylene spacers, afforded high C_4 (88%) selectivity. Structural modifications in the ligand framework effectively tune the catalytic activity and product selectivity. The highest catalytic activity of 1.29×10^8 g $(mol_{Ni})^{-1}$ h^{-1} was obtained with complex **1** using 0.1 μmol of catalyst loading at 45°C and 1.0 MPa of ethylene, and this high activity was attributed to the catalyst stability and high ethylene solubility under these conditions. The results for complexes **1–4** were systematically compared with the reported precatalysts **5** and **6** and rationalized. Single crystal analysis of precatalyst **3** revealed that the uncoordinated diphenylphosphine moiety in the complex structure effectively tunes the structural parameters, which may tailor the catalytic environment of the catalyst and offer high activity compared to complex **5**. The influence of reaction conditions (ligand/Ni molar ratio, temperature, cocatalyst/catalyst molar ratio, catalyst loading, and reaction time) were investigated and observed to have a marked impact on catalytic activity and C_4 selectivity. The C_4 selectivity of precatalyst **3** was rationalized by DFT calculations and found to be consistent with the experimental results. We suggest that further improvement and modification of these efficient and flexible systems may provide industrially viable catalysts for selective ethylene dimerization and oligomerization.

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SUPPORTING INFORMATION

Synthesis procedures, NMR characterizations, computational details, MALDI-TOF-MS of **1-4** complexes, X-ray crystallographic data for the complex **3** (PDF).

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