

Enhancement on Hemilabile Phosphine-Amide Palladium and Nickel Catalysts for Ethylene (Co)Polymerization with Polar Monomers Using a Cyclizing Strategy

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 Electronic Supplementary Information

Abstract To address the issue of hemilabile catalyst in olefin polymerization catalysis, a cyclizing strategy was used to construct novel *N*-bridged phosphine-carbonyl palladium and nickel catalysts, resulting in improvements on ethylene (co)polymerizations. The *N*-bridged phosphine-carbonyl Pd catalysts (**Pd1–Pd5**) and Ni catalysts (**Ni1–Ni5**) bearing five- to eight-membered-ring structures were designed and synthesized. Catalytic performance for ethylene (co)polymerization became better as the size of *N*-containing bridge increased. The seven-membered-ring bridged catalysts **Pd4** and **Ni4** exhibited the best performance in terms of catalytic activity, polymer molecular weight and incorporation of acrylates and acrylic acid. The better performance of these catalysts bearing larger-size bridges was tentatively attributed to the methylene-induced higher electron density around nitrogen, which strengthens the coordination of carbonyl group to metal center, and also to the steric effect offered by this cyclization. This work provides a new strategy to enhance hemilabile polymerization catalysts.

Keywords Polyolefins; Cyclizing strategy; Phosphine ligands; Polar monomers; Late transition metal catalysts

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INTRODUCTION

Transition-metal-catalyzed olefin polymerization allows a facile control over polymer microstructures and compositions, resulting in tailor-made polymer materials. By using less oxophilic late transition metal catalysts, functional groups can be introduced *via* an insertion copolymerization of commercially available polar vinyl monomers with olefins, greatly broadening the application of polyolefins.^[1–8] In this regard, the selection and modification of ligands that support metal center is paramount, by which the property of catalysts can be rigorously manipulated. Bulky α -diimines first reported by Brookhart *et al.* for nickel and palladium catalysts have since then been extensively studied, and used for copolymerization of olefins with polar monomers.^[9–26] For comparison, ligands containing phosphine donors are more extensively utilized for copolymerization of polar monomers and olefins, and more versatile in terms of applicable polar monomers.^[1–8] For

example, palladium catalysts bearing phosphine-sulfonate ligands are the state-of-the-art catalysts for the copolymerization of olefin with fundamental polar monomers, which are compatible with almost all the challenging functional groups. Phosphine-phenolate nickel complexes remarkably mediate the copolymerization of ethylene with electron-deficient polar monomers such as acrylates, acrylamides and vinyl sulfones.^[27–31] Different from these monoanionic phosphine-containing ligands, Nozaki designed bisphosphine monoxide (BPMO) ligands, which are neutral but resemble phosphine-sulfonates in terms of the distribution of electrons. BPMO palladium systems^[32] are also able to copolymerize ethylene with a broad family of polar vinyl monomers. This completely new generation of copolymerization catalyst creates more opportunities with respect to catalyst design, and naturally brings about further research interests. Nozaki, Carrow, Jordan, and Chen have since then modified these ligands by altering electronic/steric effects and the linkage between the phosphine and phosphine oxide donors.^[33–40] We also designed a series of palladium catalysts containing BPMO ligands bearing hetero-arylene bridges^[41–43] and studied the structure-property relationship for these systems.^[44] The success of BPMO-Pd catalysts have triggered further investigation on other similar

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systems.^[45–48] Very recently, we found that introducing a *N*-bridge enables ethylene polymerization and ethylene/polar monomer copolymerization using phosphine-carbonyl Ni(II) and Pd(II) catalysts.^[49] Prior to that, it was reported that the methylene-bridged phosphine-carbonyl catalysts only oligomerize ethylene due to the weak coordinating capability of carbonyl moiety.^[50–52] Our *N*-bridged phosphine-carbonyl nickel and palladium catalysts behave better but still require improving. We thus would like to enhance the system in this contribution by a new strategy rather than conventional alteration of substituents at P-atom and the backbone.

The flexibility of linkage between donors of the chelate ligands is crucial for the performance of olefin polymerization catalysts. For example, catalyst **A** (Chart 1) bearing flexible [P, SO₃[−]] ligand does not promote ethylene polymerization due to easy rotation of the linkage which would result in catalyst deactivation.^[53] In comparison, catalyst **B** with higher linkage rigidity shows improved stability and produces polyethylene.^[54] These two catalysts, however, are both less effective for ethylene (co)polymerization than the more rigid phosphine-benzenesulfonate palladium catalysts **C**.^[55] Similar comparison was also observed for [P,O] nickel catalysts bearing ligands of different linkers. Phosphine-phenolate catalysts (**E**) can promote the insertion copolymerization of acrylates and ethylene, while phosphine-enolate (**D**) catalysts were deactivated in the presence of these polar monomers.^[56]

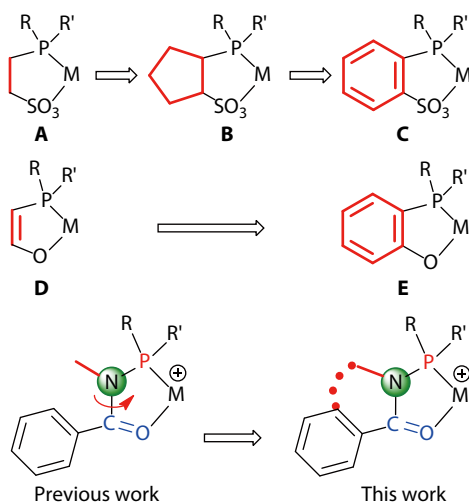


Chart 1 Late transition metal catalysts bearing different linkers between [P,O] coordinating donors.

We thus envision that altering the molecular structure of phosphine-carbonyl nickel and palladium catalysts by controlling the rotational freedom of C—N bond and affecting the electron density around the metal center will modulate the hemilabile nature of the ligand and bring advantageous properties. This leads to the catalyst design strategy used in this work, where the nitrogen atom is jointed to the adjacent aryl group using different linkers. The preferred cyclized catalysts expectedly show superior catalytic performance relative to that using the parent nitrogen-bridged catalysts, evidencing the versatile function of the bridges for further catalyst

design.

RESULTS AND DISCUSSION

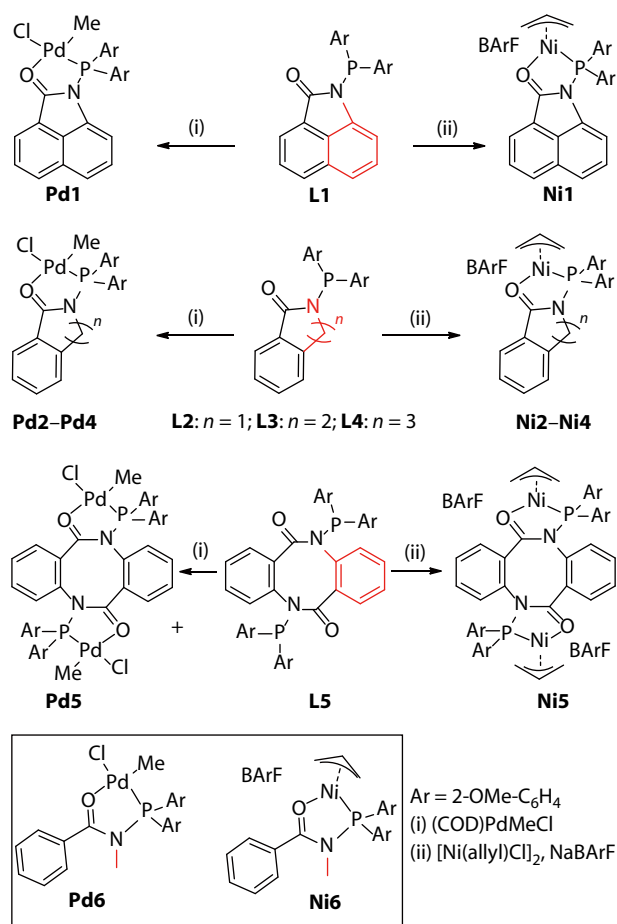
Catalyst Design

Similar to the synthesis of previously reported C- and N-bridged phosphine-carbonyl ligands,^[49] **L1** and **L5** were obtained by the reaction of lithiated acetophenone or benzamide with the phosphorus-containing electrophile bis(2-methoxyphenyl)chlorophosphine (see the electronic supplementary information, ESI). For the synthesis of **L2–L4**, however, LDA or *n*-BuLi is not applicable due to the presence of multiple methylene protons in the ring structure in addition to the NH site in the starting materials. Alternatively, NaN(SiMe₃)₂ was eventually chosen for the selective NH deprotonation. The imides were treated with equal equivalents of NaN(SiMe₃)₂ at room temperature for 1 h, followed by the addition of bis(2-methoxyphenyl)chlorophosphine. The target products were obtained after refluxing for 4 h. Through the reaction of the ligands with one equivalent of (COD)PdMeCl, complexes **Pd1–Pd5** were obtained in high yields (>70%). Similar procedures using [Ni(allyl)Cl]₂ in the presence of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBARf) instead of (COD)PdMeCl afforded **Ni1–Ni5** (Scheme 1) in similar yields.

All these complexes were fully identified by NMR spectroscopy and elemental analysis. The characteristic resonances in NMR spectra derived from Pd-Me and Ni-allyl protons in the complexes can be easily assigned with reference to previous reports.^[49] The solid-state structures of palladium complexes **Pd3** (Fig. 1) and **Pd4** were characterized by single crystal X-ray diffraction analyses. The single crystals of these complexes were obtained by slow diffusion of hexane to dichloromethane solution of these compounds. Unfortunately, high quality single crystals of complex **Pd4** could not be obtained; the X-ray diffraction data of this complex were thus only used for confirming the molecular structure (in ESI).

Ethylene (Co)Polymerizations

Ethylene oligomerization or polymerization using all Pd(II) catalysts was conducted in combination with NaBARf at different temperatures. In **Pd1**, the nitrogen atom is connected with a naphthyl group to form a five-membered ring. This complex produced no solid polymer at both high temperature of 80 °C and low temperature of 30 °C. Similar to methylene-bridged phosphine-carbonyl palladium catalysts, large amounts of oligomers such as C₄, C₆, C₈ were produced. The presence of an aromatic ring directly linked to the nitrogen atom in **Pd1** probably has a negative effect on polymerization. The aromatic group will reduce the electron density around nitrogen atom, which weakens the coordination of carbonyl group to metal center, causing a more hemilabile interaction than in alkyl-*N*-bridged complexes. By comparison, for **Pd2**, a methylene group was used to bridge the nitrogen atom and the phenyl group to form a five membered *N*-containing ring. **Pd2**/NaBARf generated viscous oligomers at high temperature (80 °C, Table 1, entry 3), whereas no polymer was obtained at 30 °C. By enlarging the *N*-containing ring to a six-membered one, **Pd3** showed better performance for ethylene polymerization at 80 °C, in which an increased activity from 0.7×10⁶ g·mol^{−1}·h^{−1} to 1.1×10⁶ g·mol^{−1}·h^{−1} can be observed, yielding polymer with four



times higher molecular weight (Table 1, entry 3 versus entry 5). Importantly, solid polymer was also furnished at 30 °C with the activity of $0.3 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ (Table 1, entry 6).

In view of the above findings, **Pd4** with a seven-membered-ring *N*-containing bridge was further examined, and the influence of bridge size between carbonyl and phosphine donors was studied. **Pd4** showed $\sim 3.3 \times$ higher activity than **Pd3** at high temperature (entry 5 versus entry 8, $1.1 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ versus $3.6 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$) and produced polymer with twice higher molecular weight (Table 1, entry 5 versus entry 8, 800 versus 1700). In a 30 min trial, **Pd4** shows an activity of up to $4.7 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ (Table 1, entry 7), which is a very high value for [P,O] chelated Pd catalysts. The catalytic activity of **Pd4** for ethylene polymerization is $2.1 \times 10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ when the reaction time was extended to 2 h, affording solid polymer with M_w of $2800 \text{ g} \cdot \text{mol}^{-1}$ (Table 1, entry 9). This indicates that the coordination of the carbonyl group to palladium is still tight at high temperature, since the catalyst system still behaves like a chelate [P,O] mode rather than mono-phosphine metal catalyst. With the enlargement of *N*-containing bridges, from five- to seven-membered ring, the electron density on nitrogen atom gradually increases, which causes tightening of the coordination of carbonyl group to Pd center. When comparing with **Pd2** bearing five-membered-ring bridge, more than $\sim 5.1 \times$ higher activity and

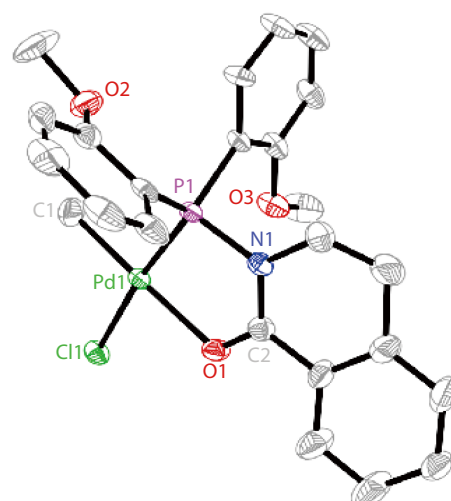


Fig. 1 Molecular structure of **Pd3** drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1–P1=2.195(3), Pd1–C1=2.034(12), Pd1–O1=2.179(7), Pd1–Cl1=2.366(3), C1–Pd1–Cl1=91.3(4), O1–Pd1–P1=83.1(2).

Table 1 Ethylene oligomerization and polymerization by Pd(II) and Ni(II) catalysts.^a

Entry	Cat.	<i>T</i> (°C)	Yield (g)	Act. ^b	<i>M_w</i> ^c	PDI ^c	<i>T_m</i> ^d
1	Pd1	80	trace	–	–	–	–
2	Pd1	30	trace	–	–	–	–
3	Pd2	80	1.3 ^e	0.7	200	–	–
4	Pd2	30	trace	–	–	–	–
5	Pd3	80	2.2	1.1	800	1.49	103.8
6	Pd3	30	0.5	0.3	1800	1.97	117.6
7	Pd4	80	4.7 ^f	4.7	1500	1.91	114.3
8	Pd4	80	7.1	3.6	1700	2.34	113.8
9	Pd4	80	8.3 ^g	2.1	2800	2.12	115.2
10	Pd4	30	0.4	0.2	8900	2.54	129.4
11	Pd5	80	trace	–	–	–	–
12	Pd5	30	trace	–	–	–	–
13	Ni1	80	trace	–	–	–	–
14	Ni1	30	trace	–	–	–	–
15	Ni2	80	4.5 ^e	2.3	200	–	–
16	Ni2	30	10.5 ^e	5.3	300	–	–
17	Ni3	80	4.7	2.4	600	1.47	92.4
18	Ni3	30	11.6	5.8	700	1.63	96.2
19	Ni4	80	8.8	4.4	1400	1.97	116.9
20	Ni4	30	7.1 ^f	7.1	1800	2.13	116.2
21	Ni5	80	0.1	0.05	1000	1.38	110.2
22	Ni5	30	0.6	0.3	1300	1.66	113.4
23 ^[49]	Pd6	80	3.2	1.6	600	1.38	74.6
24 ^[49]	Pd6	30	0.2	0.1	1900	2.52	113.3
25 ^[49]	Ni6	80	6.1	3.2	800	1.57	95.1
26 ^[49]	Ni6	30	16.0	8.0	900	1.79	98.1

^a Polymerization conditions: Pd and Ni catalyst=2 μmol, 1.2 eq. NaBARF for Pd(II), toluene=48 mL, CH₂Cl₂=2 mL, ethylene=8 bar, polymerization time: 1 h, unless noted otherwise; ^b Activity is in unit of $10^6 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$; ^c Determined by GPC in 1,2,4-trichlorobenzene at 150 °C; ^d Determined by DSC; ^e Viscous liquid; ^f Polymerization time: 0.5 h; ^g Polymerization time: 2 h.

$\sim 8.5 \times$ higher molecular weight were achieved by **Pd4** (Table 1, entry 3 versus entry 8). At low temperature (30 °C, Table 1, entry 10), the molecular weight of the polyethylene produced by **Pd4** is $8900 \text{ g} \cdot \text{mol}^{-1}$, much higher than that by **Pd3**

(Table 1, entry 6, 1800 g·mol⁻¹).

Compared to the previously reported methyl N-bridged phosphine-carbonyl complex **Pd6**, the activity of **Pd4** was $\sim 2.3\times$ higher (3.6×10^6 g·mol⁻¹·h⁻¹ versus 1.6×10^6 g·mol⁻¹·h⁻¹), and the molecular weight was $\sim 2.8\times$ higher at 80 °C (Table 1, entry 8 versus entry 23); at 30 °C, the activity was $2\times$ higher (0.2×10^6 g·mol⁻¹·h⁻¹ versus 0.1×10^6 g·mol⁻¹·h⁻¹), and the molecular weight was $\sim 4.7\times$ higher (Table 1 entry 10 versus entry 24). These results further support the fact that the coordination of Pd with the carbonyl group turns more stable by changing the substituent from methyl to N-containing cyclic bridge. Of course, the increased steric bulk of **Pd4** in this process relative to **Pd6** may also contribute to these results.

Moreover, binuclear catalyst **Pd5** was also designed, and it was hoped that the larger size (eight-membered ring) bridge and possible synergistic effect could be beneficial for catalytic (co)polymerization. This catalyst, however, generated only ethylene oligomers. Again, the presence of arylene groups in the eight-membered ring may cause a less stable coordination of the carbonyl group and more obvious hemilabile character, which resembles the case for **Pd1**.

All these Ni(II) catalysts were further studied for ethylene polymerization (Table 1, entries 13–22). Similar to the palladium analogues, **Ni1** bearing the naphthalene-related five-membered N-containing bridge generated oligomers at both 80 and 30 °C, which is consistent with that observed for methylene-bridged phosphine-carbonyl nickel catalyst. The methylene-related five-membered-ring bridged complex **Ni2** gave more viscous oligomers (Table 1, entries 15 and 16). Meanwhile, **Ni3** based on the six-membered-ring bridge produced solid polymers with an increase in molecular weight (Table 1, entries 17 and 18). The seven-membered-ring bridged complex **Ni4** shows the best activity, together with a much higher molecular weight (Table 1, entries 19 and 20). After only 30 min at 30 °C, the polymerization could not proceed because of large amounts of polymer precipitated (Table 1, entry 20). It was noteworthy that **Ni4** still displays very high activity at 80 °C (62% of that at 30 °C), indicating the more stable coordination of the carbonyl group to nickel center than catalysts **Ni2** and **Ni3**, which show much lower activities at 80 °C (Table 1, entries 15 versus 16, 17 versus 18) due to the more obvious hemilabile nature of complexes bearing smaller-sized bridges.

It is thus concluded that the phosphine-carbonyl nickel

complexes behave similarly as their palladium analogues, for which both catalytic activity and polymer molecular weight are significantly improved with the increasing number of N-containing bridge rings. Moreover, **Ni4** bearing the seven-membered-ring bridge showed better (at 80 °C) or similar (at 30 °C) catalytic activity and produced higher molecular weight polymer than our previous N-methyl bridged **Ni6** for ethylene polymerization. Again, the binuclear catalyst **Ni5** did not exhibit good activity either, possibly due to the similar reason as that for its palladium analogue **Pd5**. The fact that palladium catalysts generally perform well at higher temperature while nickel catalysts follow the opposite trend is attributed to the influence of both catalyst stability and chain propagation rate. The electron-deficient nature (relative to palladium) of nickel center facilitates ethylene coordination, leading to high activity at 30 °C, while serious activity loss is expected at higher temperature (80 °C) due to the poor stability of these catalysts.

Catalysts **Pd3**, **Pd4**, **Ni3** and **Ni4** that exhibited better performance for ethylene polymerization were chosen for copolymerization of ethylene with commercially available polar monomers methyl acrylate (MA), *tert*-butyl acrylate (TBA) and acrylic acid (AA). **Pd3** with the six-membered-ring bridge could copolymerize ethylene with MA at 80 °C; a low molecular weight copolymer was obtained but a high incorporation of 4.9 mol% was achieved (Table 2, entry 1). **Pd4** containing the seven-membered-ring bridge displayed $\sim 6.0\times$ catalytic activity and $\sim 1.9\times$ higher polymer molecular weight than **Pd3**, with the MA incorporation of 4.1 mol% (Table 2, entry 2). As for the nickel catalysts, **Ni3** containing the six-membered-ring bridge was not productive in the presence of MA at high temperature (80 °C), but showed low activity of 0.4×10^3 g·mol⁻¹·h⁻¹ at 30 °C with an incorporation of 1.4 mol% (Table 2, entry 2). **Ni4** bearing the seven-membered-ring bridge also displayed low activity at high temperature, but afforded solid copolymer ($T_m=95.5$ °C) with M_w of 3500 g·mol⁻¹ and MA incorporation of 4.4 mol% (Table 2, entry 5). As a comparison, under similar conditions, the methyl-N-bridged nickel catalyst **Ni6** gave ethylene/MA copolymer ($T_m=78.9$ °C) with M_w of 600 g·mol⁻¹ and MA incorporation of 3.3 mol%, signifying the positive effect of the cyclic bridge used in this work. More importantly, an order of magnitude improvement in catalytic activity was observed at 30 °C for ethylene/MA copolymerization, giving copolymer ($M_w=$

Table 2 Pd/Ni-catalyzed ethylene/polar monomer copolymerizations.^a

Entry	Cat.	Comono.	<i>T</i> (°C)	Yield (g)	Act. ^b	M_w ^c	PDI ^c	<i>X</i> ^d (%)	Brs ^d	Comonomer units distribution ^d		<i>T_m</i> ^e
										Chain end (%)	In chain (%)	
1	Pd3	MA	80	0.3	2.5	700	1.40	4.9	3	31.4	68.6	70.0
2	Pd4	MA	80	1.8	15.0	1300	1.77	4.1	5	36.3	63.7	104.3
3	Ni3	MA	80	Trace	—	—	—	—	—	—	—	—
4	Ni3	MA	30	0.05	0.4	1400 ^f	—	1.4	3	50.0	50.0	95.5
5	Ni4	MA	80	0.04	0.3	3500 ^f	—	4.4	6	38.9	61.1	95.5
6	Ni4	MA	30	0.4	3.3	1800	1.83	3.1	7	26.2	73.8	104.5
7	Pd4	TBA	80	1.0	8.3	1500	1.72	4.9	2	19.9	80.1	101.5
8	Pd4	AA	80	0.1	0.8	2700 ^f	—	3.9	2	27.0	73.0	104.5

^a Polymerization conditions: Pd(II) and Ni(II) catalyst=20 μmol, 1.2 eq. NaBARf for Pd(II), total volume of solvent 20 mL and $C_{\text{comonomer}}=1.0$ mol/L, ethylene (8 bar), 6 h, 80 °C, unless noted otherwise; ^b Activity is in unit of 10^3 g·mol⁻¹·h⁻¹; ^c Determined by GPC in 1,2,4-trichlorobenzene at 150 °C; ^d Incorporation of comonomer, number of branches per 1000C, and comonomer unit distribution as determined by ¹H-NMR in C₂D₂Cl₄ at 110 °C; ^e Determined by DSC;

^f Molecular weight (M_n) determined by ¹H-NMR spectroscopy in C₂D₂Cl₄ at 110 °C.

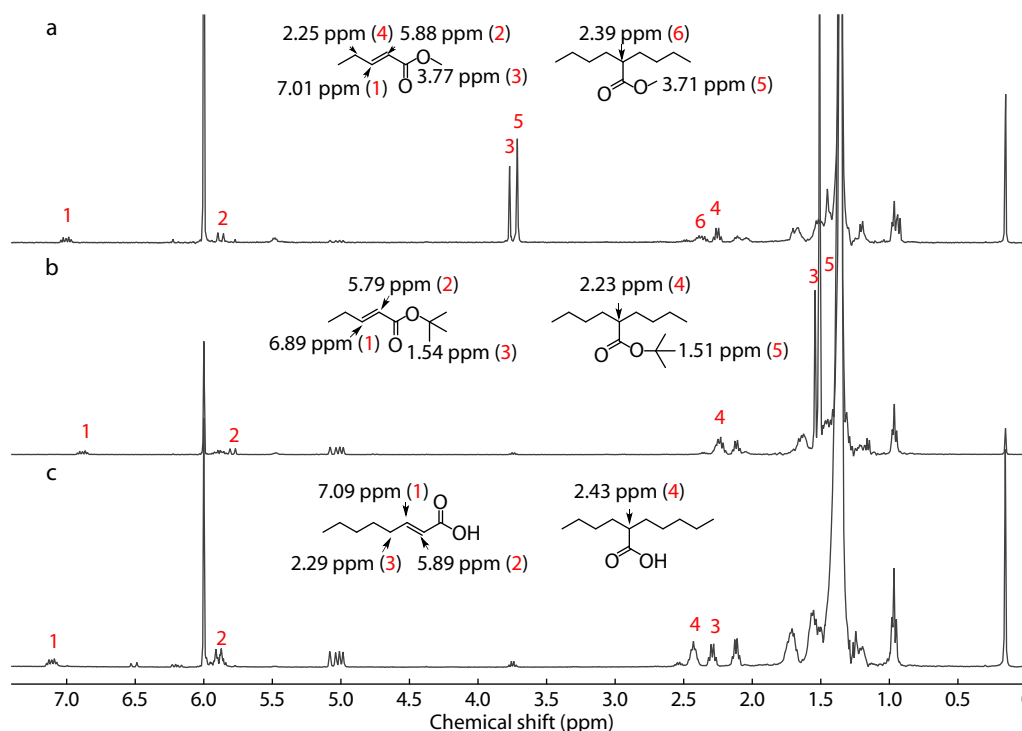


Fig. 2 ^1H -NMR spectra of (a) ethylene-MA copolymer in Table 2, entry 2; (b) ethylene-TBA copolymer in Table 2, entry 7; (c) ethylene-AA copolymer in Table 2, entry 8.

1800 $\text{g}\cdot\text{mol}^{-1}$) with MA incorporation of 3.1 mol% (Table 2, entry 6). By calculation from NMR spectra, it was confirmed that most of the incorporated MA predominantly exists in the form of in-chain units (>60%, Fig. 2a). This result adds a new candidate of cationic nickel catalysts for ethylene copolymerization with acrylates.

The most active catalyst **Pd4** was chosen to promote the copolymerization of ethylene with TBA and AA. For ethylene/TBA copolymerization, the catalytic activity was slightly lower than that for ethylene/MA copolymerization, and similar molecular weight copolymer was obtained. The percentage of in chain comonomer units is higher than that for ethylene/MA copolymer under otherwise identical conditions (Table 2, entry 2 versus entry 7), implying a lower tendency of β -H elimination after TBA insertion than MA insertion (see Figs. 2a versus 2b). In the presence of AA, however, the catalytic activity of one order of magnitude lower can be observed, but the incorporation is up to 3.9 mol% (Table 2, entry 8).

CONCLUSIONS

In summary, by linking the nitrogen atom with the adjacent aryl group using a cyclizing strategy, a series of new *N*-bridged hemilabile phosphine-carbonyl palladium and nickel catalysts were enhanced. With the enlargement of formed cyclic *N*-containing bridges, these phosphine-carbonyl catalysts showed higher activity for both ethylene homopolymerization and copolymerization with fundamental polar monomers, together with higher polymer molecular weight and polar monomer incorporation. Arylene groups in the bridges were found to be detrimental to the catalytic performance, probably due to the electron-withdrawing effect that destabilizes the coordination

of carbonyl group to metal center and enhances the hemilabile nature of the catalyst. The catalysts bearing the preferred seven-membered-ring bridge allowed superior catalytic performance versus that previously reported non-cyclic methyl-*N*-bridged parent catalyst. These results were tentatively ascribed to the improved coordination strength between metal center with the hemilabile carbonyl group and the higher steric hindrance and the electron-donating nature offered by additional methylenes. Although the polymer molecular weights need to be improved for practical use, this work provides a new modification approach for the design of hemilabile catalysts.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-022-2650-3>.

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