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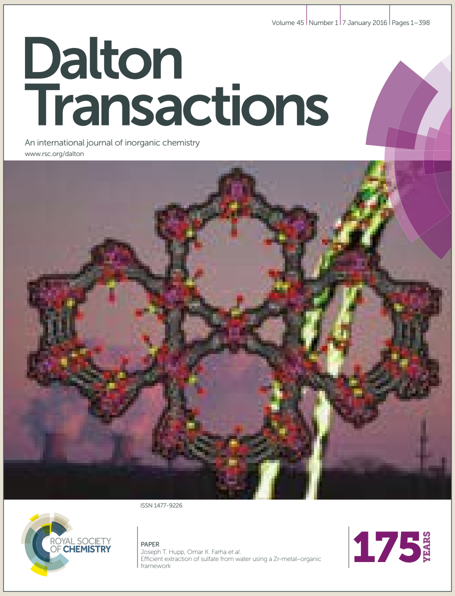

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Dalton Transactions

PAPER

Phosphine Phosphonic Amide Nickel Catalyzed Ethylene Polymerization and Copolymerization with Polar Monomers†

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Changwen Hong, ‡[a] Xuelin Sui, ‡[a] Ziqian Li, [b] Wenmin Pang[a] and Min Chen,*[a]

The phosphine phosphonic amide ligand platform is highly versatile, with three positions that can be independently tuned. In this contribution, we wish to study the nickel complexes based on this ligand system. Interestingly, the nickel dibromide and the nickel allyl complexes are not active in ethylene polymerization. In contrast, the nickel phenyl chloride complexes are highly active in ethylene polymerization in the presence of sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate cocatalyst. In addition, these nickel complexes can initiate ethylene copolymerizations with polar functionalized comonomers including methyl 10-undecenoate, 6-chloro-1-hexene and 5-acetoxy-1-pentene. More interestingly, these nickel complexes can oligomerize 1-hexene and 6-chloro-1-hexene.

Introduction

In olefin polymerization, late transition metal catalysts possess the advantage of low oxophilicity versus their early transition metal counterparts. Therefore, they are potentially applicable to incorporate polar functionalized comonomers during olefin polymerization. For the copolymerization purpose, the metal palladium has been the dominant player. For example, the Brookhart type α-diimine palladium catalyst is a milestone discovery in this field (Chart 1, **I**),[1] which can copolymerize ethylene with acrylates, silyl vinyl ethers and a number of other polar monomers.[2] In contrast, the α-diimine nickel counterpart shows much narrower polar monomer substrate scope, and usually requires a large amount of aluminum cocatalysts.[3] The Drent type phosphine-sulfonate palladium catalyst (Chart 1, **II**) can enable the copolymerizations of ethylene with a variety of polar monomers.[4] However, the nickel counterpart has only recently been demonstrated with the copolymerization capabilities, and with very narrow substrate scope.[5]

The intrinsically higher oxophilicity of the nickel metal makes it highly challenging to design high performance nickel catalyst for the polar monomer problem. In recent years, there have been some great advances in this aspect. For example, salicylaldimine nickel catalysts (Chart 1, **III**),[6] SHOP type (Shell Higher Olefin Process) nickel catalysts (Chart 1, **IV**),[7] N-heterocyclic carbene based nickel catalysts (Chart 1, **V**),[8] and diphosphazane monoxide nickel catalysts (Chart 1, **VI**)[9] can copolymerize ethylene with some polar monomers. We recently showed that some cationic phosphine phosphonic amide palladium complexes (Chart 1, **VII**) are highly active in ethylene polymerization, and are capable of copolymerizing ethylene with polar monomers such as methyl acrylate, vinyl butyl ether and allyl acetate.[10] A great advantage of this catalyst system is that three positions (R^1, R^2 and R^3) can be independently adjusted, making it highly versatile to tune the properties of the metal catalysts. In this contribution, we decide to investigate the synthesis, characterization and polymerization properties of the phosphine phosphonic amide nickel complexes.

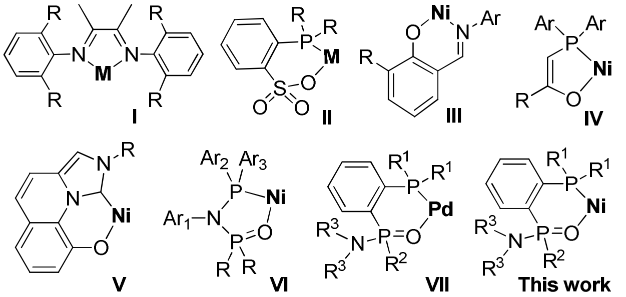

Chart 1 Some recently reported high performance palladium and nickel catalysts.

Results and Discussions

The phosphine phosphonic amide ligands **L1** and **L2** have been reported by us, and the ligand **L3** bearing biaryl substituent was pre-

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[a] Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, 230026, China. E-mail: misschen@ustc.edu.cn

[b] Undergraduate Department, University of Chinese Academy of Sciences, Beijing, 100049, China

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‡ These authors contributed equally to this work.

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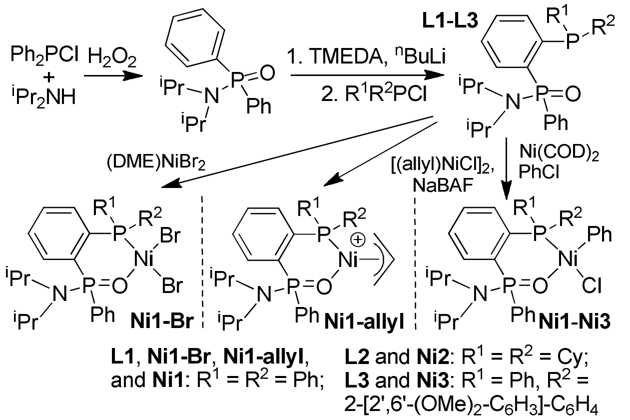

Scheme 1 Synthesis of the phosphine phosphonic amide ligands and the corresponding nickel complexes.

pared using similar procedure (Scheme 1).[10] The biaryl substituent has been shown by Scott and our group to enhance the polymer molecular weight in the phosphine-sulfonate nickel system.[11,5] Since this is a neutral ligand system similar as the α-diimine system, our initial target is nickel dibromide complex. Complex **Ni1-Br** can be obtained from the reaction of ligand **L1** with 1 equiv. of (DME)NiBr$_2$ (DME = ethylene glycol dimethyl ether). However, the addition of methylaluminoxane (MAO) cocatalyst led to the decomposition of this nickel complex, and no activity was observed in ethylene polymerization. Subsequently, the cationic nickel allyl species **Ni1-allyl** was generated from the reaction of the ligand **L1** with [(allyl)NiCl]$_2$ and sodium tetrakis(3,5-bis(trifluoromethyl) phenyl)borate (NaBAF). However, this complex is not active either in ethylene polymerization, which may be due to the strong complexation of the allyl moiety to the nickel center. When coacatalyst MAO or B(C$_6$F$_5$)$_3$ was added, **Ni1-allyl** showed very low activities in ethylene polymerization (Table S1). Eventually, the nickel phenyl species **Ni1-Ni3** were prepared from the reactions of **L1-L3** with bis(1,5-cyclooctadiene)nickel and PhCl. These nickel complexes were characterized with ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and elemental analysis.

The molecular structures of **Ni1-Br**, **Ni1** and **Ni3** were determined by X-ray diffraction analysis (Figure 1). These data show that, **Ni1-Br**, **Ni1** and **Ni3** were intergrated as twinning. The Ni center adopts distorted tetrahedron geometry in **Ni1-Br**, and square planar geometry in **Ni1**/**Ni3**. The R^1 and R^2 substituents reside at the equatorial and axial position of the phosphorus atom. In the structure of **Ni3**, the biaryl substituent forms π-π stacking with the ligand benzo backbone. This could increase the rigidity of the catalyst structure and potentially improve catalyst properties.[12] All of these nickel complexes are highly active in ethylene polymerization when activated using 1.2 equiv. of NaBAF (Table 1). The activities can reach well above 10^6 g·mol^{-1}·h^{-1}, making them among the most active nickel catalysts in ethylene homopolymerization.[13] **Ni1** and **Ni2** can only generate polyethylene with molecular weight of a few thousand (Table 1, entries 1-4). For the case of **Ni3** bearing biaryl substituent, the polyethylene molecular weight can reach 29,000 (Table 1, entry 6). Complex **Ni3** remained active for ethylene polymerization for 4 h at 30^{o}C and 80^{o}C (Figure S1, S2). The melting points of the polyethylene samples are all above 110 ^{o}C, suggesting that they possess relatively linear microstructure. High temperature ^{1}H NMR analysis (Figures S10 and S11) showed that the branching densities of the polyethylene samples generated by **Ni3** are 25 (at 80 ^{o}C) and 4 (at 30 ^{o}C) per 1000 carbon atoms.

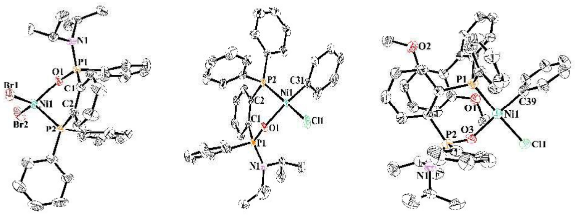

Figure 1 Molecular structures of **Ni1-Br** (a), **Ni1** (b), **Ni3** (c). Hydrogen atoms have been omitted for clarity. (a) Selected bond distances (Å) and angles (deg) for **Ni1-Br**: Ni1-Br1 2.3670(14), Ni1-Br2 2.3381(13), Ni1-O1 1.957(5), Ni1-P2 2.281(2), P1-O1 1.504(5), P1-N1 1.632(6); O1-Ni1-P2 85.99(15), O1-Ni1-Br2 112.78(15), P2-Ni1-Br2 118.42(7), O1-Ni1-Br1 108.47(16), P2-Ni1-Br1 98.62(7), Br2-Ni1-Br1 125.17(6). (b) Selected bond distances (Å) and angles (deg) for **Ni1**: Ni1-C31 1.861(4), Ni1-O1 1.968(3), Ni1-P2 2.1590(12), Ni1-Cl1 2.1966(13), N1-P1 1.635(3), O1-P1 1.499(3); C31-Ni1-O1 168.55(17), C31-Ni1-P2 95.53(13), O1-Ni1-P2 83.72(8), C31-Ni1-Cl1 91.48(13), O1-Ni1-Cl1 91.97(8), P2-Ni1-Cl1 165.10(5). (c) Selected bond distances (Å) and angles (deg) for **Ni3**: Ni1-C39 1.898(7), Ni1-O3 1.946(4), Ni1-P1 2.1450(19), Ni1-Cl1 2.209(2), P2-O3 1.508(4), P2-N1 1.640(5); C39-Ni1-O3 173.9(3), C39-Ni1-P1 90.0(2), O3-Ni1- P1 93.35(14), C39-Ni1-Cl1 87.7(2), O3-Ni1-Cl1 89.66(14), P1-Ni1-Cl1 171.62(9).

The properties of these nickel complexes in ethylene-polar comonomer copolymerizations were also studied. Unfortunately, some fundamental polar monomers such as methyl acrylate or vinyl acetate completely shut down the ethylene polymerization. When some spacers were put between the double bond and the polar groups, these nickel complexes can incorporate the polar comonomers during ethylene polymerization. For example, methyl

Table 1 Ethylene homopolymerization with **Ni1-Ni3**[a]

Ent.	Cat.	cat (μmol)	T (^{o}C)	t (h)	Yield (g)	Act.[b]	T_m[c] (^{o}C)	M_n[d] (10^4)	PDI[d]
1	**Ni1**	1	80	1	3.6	36	112	0.15	2.3
2	**Ni1**	1	30	2	2.2	11	115	0.21	2.6
3	**Ni2**	1	80	1	2.8	28	112	0.16	2.0
4	**Ni2**	1	30	2	2.0	10	126	0.37	2.5
5	**Ni3**	1	80	1	1.2	12	121	0.61	3.3
6	**Ni3**	1	30	2	0.2	1.0	133	2.9	3.0

[a]Polymerization conditions: 18 mL toluene, 2 mL dichloromethane, 9 atm ethylene pressure, 1.2 eq. NaBAF. [b]Activity is in unit of 10^5 g·mol^{-1}·h^{-1}. [c]Determined by differential scanning calorimetry, third heating. [d]Determined by GPC using universal calibration.

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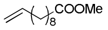
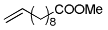
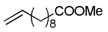
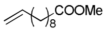
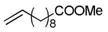
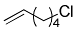
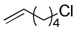
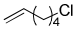
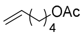
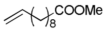
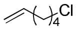
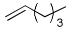
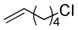
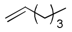
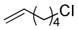
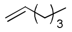
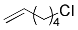
Table 2 Ethylene/polar monomer copolymerizations with **Ni1-Ni3.**[a]

Ent.	Cat.	Comonomer	[M] mol/L	Yield (g)	Act.[b]	Incorp[c] (%)	T_m[d] (°C)	M_n[e] (10^3)	PDI[e]	Aver Como of per Chain[f]
1	**Ni1**		1	0.4	0.10	0.2	99	1.3	1.8	0.09
2	**Ni2**		1	0.5	0.13	0.3	109	1.6	1.9	0.17
3	**Ni3**		1	3.4	0.85	0.6	118	5.1	3.5	1.05
4	**Ni3**		2	0.5	0.13	2.6	102	1.4	1.9	1.12
5	**Ni3**		3	0.1	0.03	3.3	-	1.2	1.6	1.18
6	**Ni3**		1	6.0	1.50	0.8	116	2.2	2.4	0.61
7	**Ni3**		2	2.0	0.50	1.3	114	1.6	2.5	0.71
8	**Ni3**		3	0.3	0.08	2.9	107	1.5	2.0	1.42
9	**Ni3**		1	0.1	0.03	1.2	-	2.0	2.7	0.82
10[g]	**Ni3**		1	0.8	0.20	0.3	129	27	3.8	2.84
11[g]	**Ni3**		1	2.4	0.60	0.4	125	25	3.4	3.53

[a]Polymerization conditions: 18 mL toluene, 2 mL dichloromethane, 9 atm ethylene pressure, 1.2 eq. NaBAF, 20 μmol catalyst, 2 h, 80 °C. [b]Activity is in unit of 10^5 g·mol^{-1}·h^{-1}. [c] Determined by ^{1}H NMR spectroscopy. [d]Determined by differential scanning calorimetry, third heating. [e]Determined by GPC using universal calibration. [f]Aver Como of per Chain = Average number of cmonomer units of per chain. [g]Copolymerization at 30 °C.

10-undecenoate, 6-chloro-1-hexene and 5-acetoxy-1-pentene are all suitable substrates (Table 2). **Ni3** showed much better performance than **Ni1** and **Ni2**, in terms of comonomer incorporation ratios and copolymer molecular weights (Table 2, entries 1-3). At higher comonomer concentration, the activity and copolymer molecular weight were greatly reduced, while the comonomer incorporation ratio can be increase to 3.3% (Table 2, entries 3-5). Similar performances were observed in **Ni3** catalyzed ethylene copolymerizations with 6-chloro-1-hexene and 5-acetoxy-1-pentene (Table 2, entries 6-9). At lower copolymerization temperature (30 °C, Table 2, entries 10 and 11), the copolymer molecular weight can be greatly enhanced (Mn up to 27,000). Through the calculated average number of comonomer units of per chain, we can see that these polymeric products are generally mixtures of copolymer and homopolymer in varying degrees (Table 2, entry 1-9). The reason is that fast chain transfer of metal center at 80°C leads to comparatively low molecular weight polymer. In contrast, high molecular weight polymer obtained at 30°C (Table 2, entry 10-11) are true copolymers.

Table 3 1-hexene and 6-chloro-1-hexene oligomerization with **Ni1-Ni3.**[a]

Ent.	Cat.	α-olefin	Yield (mg)	Act.[b]	M_n[c] (10^3)	PDI[c]
1	**Ni1**		80	0.67	2.3	1.1
2	**Ni1**		20	0.17	0.8	1.2
3	**Ni2**		100	0.83	4.3	1.3
4	**Ni2**		30	0.25	2.6	1.1
5	**Ni3**		trace	-	-	-
6	**Ni3**		trace	-	-	-

[a]Polymerization conditions: 10 μmol Ni catalyst, 4 mL toluene, 0.5 mL dichloromethane, 1 mol/L comonomer, 30 °C, 12 hours, 1.2 eq. NaBAF. [b]Activity is in unit of 10^3 g·mol^{-1}·h^{-1}. [c]Determined by GPC using universal calibration.

Comparing with ethylene, polar comonomers are much worse substrates considering their electronic and steric parameters. Therefore, transition metal catalyzed polar comonomer homopolymerization is even more challenging than their copolymerization with ethylene. In literature, there have been very few successful examples in this regard.[9,14] Base on literature reports[15] and our experiences, the phosphine-sulfonate palladium and phosphine-sulfonate nickel catalysts cannot oligomerize 1-hexene or 6-chloro-1-hexene. Quite interestingly, **Ni1** and **Ni2** can oligomerize 1-hexene and 6-chloro-1-hexene to generate oligomers with molecular weights of a few thousand (Table 3, entries 1-4). **Ni3** is not active at all, which is probably due to steric effect. Currently, the exact reason is not fully understood. This could be due to the cationic and high electrophilicity nature, as well as the sterically open feature of this system. Although, the PDI values (1.1-1.3) are very low, oligomerization of 1-hexene and 6-chloro-1-hexene do not show living behaviors.

Conclusions

In summary, some phosphine phosphonic amide nickel complexes have been prepared and characterized. The choice of metal precursors is critical to obtain high performance polymerization catalyst. Specifically, the nickel phenyl chloride complexes (**Ni1-Ni3**) combined with NaBAF are highly active in ethylene polymerization with activities up to 3.6 × 10^6 g·mol^{-1}·h^{-1}, generating polyethylene with molecular weights of up to 29,000 and melting points of up to 133 °C. In ethylene copolymerizations with methyl 10-undecenoate, 6-chloro-1-hexene and 5-acetoxy-1-pentene, activities of up to 1.5 × 10^5 g·mol^{-1}·h^{-1} could be achieved, along with moderate comonomer incorporations (0.2-3.3%) and moderate copolymer molecular weights (1,200-27,000). Interestingly, this

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nickel system possesses unique capabilities of being able to oligomerize polar monomers such as 6-chloro-1-hexene.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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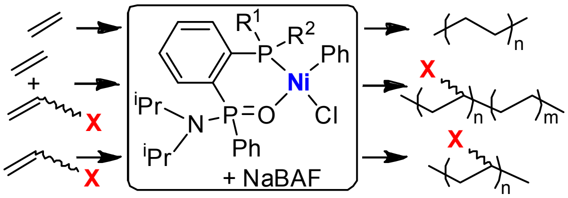

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