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Self-immobilized catalysts for ethylene polymerization: neutral, single-component salicylaldiminato phenyl nickel(II) complexes bearing allyl substituents†

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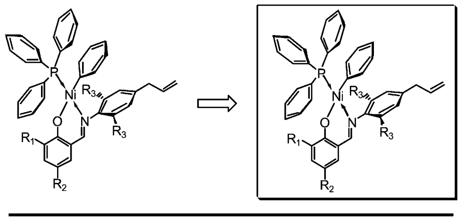
A new family of self-immobilized ethylene polymerization catalysts, derived from neutral, single-component salicylaldiminato phenyl nickel complexes, is described.

Nickel catalysts have provided some of the most significant advances in late transition metal olefin polymerization catalysis and have given some of the most promising results.[1] More recently, Younkin *et al*. reported a new family of neutral, single-component, salicylaldiminato nickel(II) catalysts that were highly active systems for olefin polymerization.[2]

A great deal of interest has been focused on the heterogenization of catalysts for olefin polymerization.[3] Alt *et al*. developed self-immobilized metallocene catalysts, involving the synthesis of metallocene catalysts with an olefin or alkyne function that can be used as a comonomer in the polymerization process.[4] Here we synthesized a series of neutral, single-component salicylaldiminato nickel complexes bearing allyl substituents as self-immobilized catalysts that produce, without any cocatalysts, linear polymers with new microstructure.

The self-immobilized catalysts **1**–**5** (Scheme 1) were synthesized *via* a modified literature procedure. 4-Allyl-2,6-dialkylaniline was obtained from allyl chloride and 2,6-dialkylaniline by rearranging with zinc chloride in refluxing xylene.[5] Treatment of an *o*-substituted phenol derivative with paraformaldehyde in the presence of $SnCl_4$ produced a salicylaldehyde derivative.[6] 3,5-Dinitrosalicylaldehyde was synthesized by nitrating salicylaldehyde twice.[7] This salicylaldehyde derivative reacted with allyl-substituted aniline, *via* Schiff base condensation, to afford a salicyldimine ligand. The corresponding nickel complex was obtained by the reaction of *trans*-$[Ni(Ph)Cl(PPh_3)_2]$ with 1 equiv. of the sodium salt of the ligand.‡ [8]



Complex	1	2	3	4	5
R_1	H	NO_2	^tBu	Ph	Ph
R_2	H	NO_2	Me	H	H
R_3	^iPr	^iPr	^iPr	^iPr	Me

Scheme 1

An X-ray crystallographic structure analysis was carried out for complex **5**.§ As depicted in Fig. 1, complex **5** contains a chelating salicylaldiminato ligand, a triphenylphosphine group and a phenyl group. The Ni atom with four atoms of ligands (P, O, N, C(1)) are arranged almost exactly planar. The plane of the C (1) and C(7) phenyl rings are oriented almost orthogonally (82.6 and 86.1°, respectively) to this plane. However, the dihedral angle defined by C(24) phenyl ring and the nickel coordination plane is only 13.0°. The *cis* angles at nickel are in the range 85.61–93.56°. The Ni–O, Ni–N and Ni–C(1) bond distances are similar to those in known nickel complexes.[8,9] The Ni–P bond of **5** (2.1838(12) Å) is more than 0.01 Å longer than those of other complexes with the N–O bidentate ligand (2.163(2) Å,[9b] 2.172(2) Å[8]).

Table 1 summarizes the catalytic performance of the self-immobilized salicylaldiminato nickel(II) catalysts. In general, high molecular weight and high activity are accomplished by changing the ligand structure (introducing substituents at the R_1, R_2 and R_3 positions) and polymerization conditions (including temperature, pressure of ethylene, and catalyst loading) without any co-catalysts. ^{13}C NMR analyses of the polymers generated by these self-immobilized catalysts reveal that there are only methyl branches in linear polyethylene. The bulk density of PE produced by these catalysts are in the range of 0.148–0.278 g cm^{-3}. In order to improve the morphology of polymer products, catalysts **2**–**5** were co-polymerized with styrene to generate polymerized Ni catalysts and SiO_2-supported core–shell catalysts. Further investigations of these aspects are in progress.

Changing the bulky substituents at the R_1 or R_3 position influenced polymerization activity because they could shield the axial faces and retard chain termination. For example, complex **4** (R_1 = Ph) displayed an activity of 1.8×10^5 g PE (mol Ni)$^{-1}$ h^{-1}, while complex **1** (R_1 = H) and complex **3** (R_1 = ^tBu) exhibited no activity for ethylene polymerization.

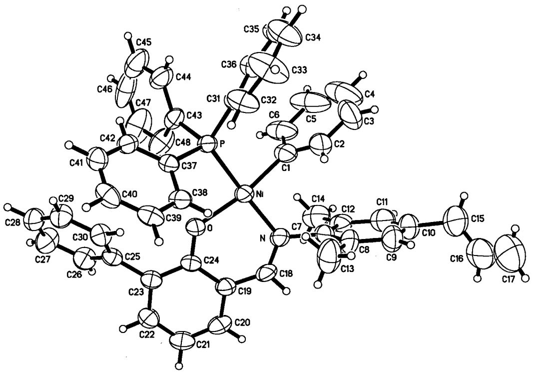


Fig. 1 The molecular structure of **5**. Selected bond lengths (Å) and angles (°): Ni–O 1.903(2), Ni–P 2.1838(12),Ni–N 1.932(3), C(24)–O 1.302(3), C(18)–N 1.293(4), C(7)–N 1.451(4), C(24)–C1(9) 1.438(4), C(18)–C(19) 1.411(4); C(1)–Ni–N 93.56(13), C(1)–Ni–P 85.61(11), N–Ni–O 93.08(11), C(1)–Ni–O 165.7(2), N–Ni–P 171.01(10), O–Ni–P 89.75.

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† Electronic supplementary information (ESI) available. Synthesis and spectroscopic data for **5**, spectroscopic data for **1**–**4**. See http://www.rsc.org/suppdata/cc/b1/b110258n/

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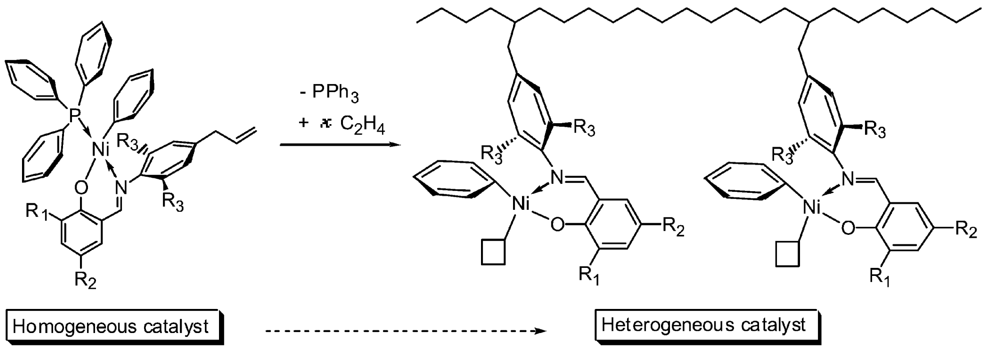

Fig. 2 Proposed mechanism for the 'self-immobilization' of a homogeneous neutral nickel(II) complex.

Table 1 Ethylene polymerization results of self-immobilized catalysts[a]

Run	Catalyst/ μmol	T/°C	$10^{-5}P$/Pa	Activity[b]	M_w[c]	M_w/M_n[c]
1	**1** (65)	27	4.0	0	—	—
2	**2** (65)	27	4.0	2.9	192.4	32.0
3	**3** (65)	27	4.0	0	—	—
4	**4** (65)	27	4.0	1.8	66.4	12.8
5	**5** (65)	27	4.0	0.9	121.8	4.6
6	**8**[d] (65)	27	4.0	0.1	207.0[d]	2.2[d]
7	**4**[e] (65)	27	4.0	1.3	—	—
8	**4** (65)	27	2.0	0.9	109.5	7.5
9	**4** (33)	27	4.0	3.1	92.7	9.9
10	**4** (15)	27	4.0	2.4	233.3	3.1
11[f]	**4** (33)	27	4.0	3.7	121.6	3.0
12	**4** (33)	37	3.0	1.8	165.9	4.3
13	**4** (33)	57	3.0	2.2	10.6	2.3

Conditions:[a] toluene; 120 ml, polymerization reaction; 1 h. [b] 10^5 g PE (mol Ni)$^{-1}$ h^{-1}. [c] M_w ($\times 10^{-3}$) and M_w/M_n values were determined by GPC measurement. [d] See ref. 2*a*. [e] Polymerization in the presence of 3 ml methacrylate (MA). [f] Reaction time was 36 min.

Attachment of a methyl group, which was sterically smaller than isopropyl group, at the R_3 position, dramatically decreased activity. Moreover, complex **4** showed a slight drop in activity when 3 ml of methylacrylate (MA) was added to the polymerization system, which indicated that the self-immobilized neutral nickel catalysts are also tolerant of polar monomers. The methylacrylate as functional olefin was not incorporated into the polymer chain, which suggested that addition of MA did not destroy the catalytic activity. Results with complex **2** showed electron-withdrawing groups such as nitro groups enhanced catalytic activity.

Most notable is the dramatic increase in polymerization activity and clean behaviour because of the self-immobilizing effect of the neutral nickel catalysts. Catalyst **4** is much more active than the corresponding allyl-free analogues (runs 4, 6). The mechanism of the self-immobilization is still not quite clear. However, the proposed mechanism for the 'self-immobilization' of the neutral nickel catalysts is that as soon as ethylene is applied to the solution of the self-immobilized catalysts, the ethylene is polymerized and simultaneously catalyst molecules are incorporated into the growing polymer due to their allyl functions. As a consequence the homogenous catalyst is transferred to a heterogeneous system without requiring any support. Active centers distributed on the polymer chain are situated to make the best use of their catalytic activities (Fig. 2).

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Notes and references

‡ For example, synthesis of **5**: a solution of 1.0 g (1.44 mmol) chloro(*trans*-di(triphenylphosphine))phenylnickel(II) and 0.545 g (1.5 mmol) of the sodium salt of 3-phenyl-2-hydroxybenzaldehyde (2,6-dimethylanil) in benzene (30 ml) was stirred at room temperature. After 24 h, the reaction mixture was separated by centrifugation and the upper clear solution was concentrated *in vacuo*. Hexane was added to the reaction mixture and a red crystalline solid was obtained on separation by centrifugation and dried *in vacuo*. Yield, 0.95 g (86%). An analogous method was used for preparation of complexes **1**–**4**. **1**: Yield, 0.81 g (78%). **2**: Yield, 1.05 g (90%). **3**: Yield, 0.92 g (81%). **4**: Yield, 0.95 g (83%).

§ *Crystal data* for **5**: $C_{48}H_{42}NNiOP$, M = 738.51, triclinic, space group $P\bar{1}$, a = 9.481(4), b = 9.610(2), c = 22.451(10) Å, α = 101.01(3), β = 100.84(3), γ = 92.93(3)°, V = 1964.0(13) Å^3, Z = 2, D_c = 1.249 g cm^{-3}, μ(Mo-Kα) = 0.71073 Å, T = 293 K, red flat-crystal, 8568 independent measured reflections, F^2 refinement, R_1 = 0.0437, wR_2 = 0.0665, 6927 independent observed reflections ($I > 2\sigma(I)$, $3.78 \leq 2\theta \leq 50.06$), 471 parameters. CCDC reference number 154062. See http://www.rsc.org/suppdata/cc/b1/b110258n/

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