Recent Progress on Ni-Based systems for ethylene oligo-/polymerization catalysis

Shaoli Wang,[a] Wen-Hua Sun,[*,a] and Carl Redshaw[*,b]

[a] Key laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.; [b] Department of Chemistry, University of Hull, Hull, HU6 7RX, UK.

*Corresponding author: Tel: +86-10-62557955. Fax: +86-10-62618239. E-mail: whsun@iccas.ac.cn (W.-H. Sun) or Tel: +44 1482 465219; Fax: +44 1482 466410. Email: c.redshaw@hull.ac.uk (C. Redshaw)

Abstract: Recent progress on nickel-based complex pre-catalysts is reviewed herein. The ethylene oligo-/polymerization behaviour is disscussed in terms of the variation of the complex models bearing different kinds of ligand sets. These discussions focus mainly on the influence that the different substituents present have on the observed catalytic activity, the results of which can guide the design of new target structures possessing high ethylene activity.

1 Introduction

Since the discovery of nickel and palladium(II) aryl-substituted α-diimine catalysts for olefin polymerization,[1] late transition metal-based systems have been a topic of significant interest, primarily because they can produce polymers with various types of branches and exhibit good tolerance toward functional groups/polar monomers.[2-10] Moreover, the active sites in α-diimine pre-catalysts have been extensively explored, and the microstructures of the resultant polyethylene can be controlled by modification of the ligand backbone. In the case of nickel-based α-diimine catalysts, it was found that alkyl substituents at the aniline derived moieties were capable of exerting a significant influence on the polymerization activities and polymer microstructures.[11-27] Typically, high molecular weight, branched polyethylene can be obtained by tuning of the sterics/electronics associated with the alkyl substituents.

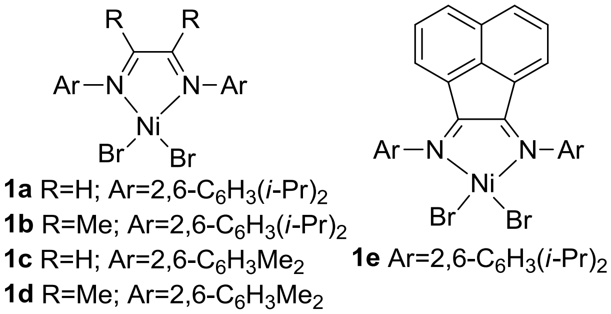
Despite rapid progress in developing the technology associated with Ni-based catalysts, few review articles concerning such developments have appeared in the literature.[28,29] Our group has focused on nickel complex pre-catalysts in ethylene reactivity studies, and besides a pure academic attraction, these catalytic systems and the resultant polyethylene (PE) products have shown promise for industrial application. Herein, recent progress associated with nickel complex pre-catalysts will be discussed, and the review will focus on the types of ancillary ligands deployed at the metal centre, which we hope will illustrate their value, and furthermore will encourage other scientists to become involved in the challenges ahead.

2. Nickel complex pre-catalysts bearing bi-dentate ligands

Studies of nickel complex pre-catalysts initially focussed on bi-dentate systems,[30,31] which when compared with nickel complexes bearing tri-dentate ligands have tended to exhibited relatively higher activities for ethylene oligo-/polymerization, and thus progress in this area has been rapid in recent years. Work on such bi-dentate nickel complexes usually include the use of ligands of the form *N^N*, *N^O*, *N^P*, *P^P* and *P^O*, and these systems tend to yield branched polymer products.

2.1 [N^N] bi-dentate nickel complex pre-catalysts

In 1995, Brookhart *et al* discovered that nickel-based α-diimine olefin polymerization catalysts were unique amongst late metal systems in that they were capable of converting α-olefins to high molecular weight polyethylenes.[1] For example, the nickel dibromide complexes **1a-1e**, in the presence of ethylene and the co-catalyst MAO (Scheme 1, Table 1, entries 1-10), can produce highly linear to moderately (mostly methyl) branched polyethylene. The extent of branching is a function of temperature, ethylene pressure, and catalyst structure. Increased branching occurs on increasing the temperature, which results in lower melting temperatures for the semicrystalline polymers (compare entry 1 with 2, 4 with 5, and 8 with 9, Table 1). At higher ethylene pressure, decreased branching is observed, but polymer yields and molecular weight values were similar (compare entry 4 with 6, Table 1). Reducing the steric bulk of the diimine ligand by replacing the *o*-methyl groups for *o*-isopropyl groups resulted in less branching and decreased molecular weight (compare entry 8 with 3, Table 1). The nickel catalysts exhibited extremely high activities, often comparable to those of metallocene catalysts. For example, **1a**/MAO (entry 2, Table 1) exhibits an apparent tumover frequency of 3.9 x 10^5/h (11000 kg of PE mol^{-1} of Ni h^{-1}).[1]



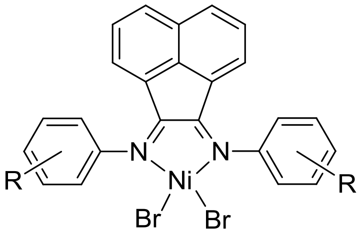
1a R=H; Ar=2,6-C_6H_3(*i*-Pr)$_2$
1b R=Me; Ar=2,6-C_6H_3(*i*-Pr)$_2$
1c R=H; Ar=2,6-$C_6H_3Me_2$
1d R=Me; Ar=2,6-$C_6H_3Me_2$
1e Ar=2,6-C_6H_3(*i*-Pr)$_2$

Scheme 1 *N*,*N*-bi-dentate nickel complexes **1a-1e**[1]

Table 1. Ethylene polymeriation[1] catalyzed by pre-catalysts **1a-1e** [a]

entry	catalyst	moles of catalyst (×10^6)	conditions	yield(g)	M_n [b] (×10^{-4})	M_w (×10^{-4})	M_w/M_n	branches per 1000 carbons
1	**1a**	1.7	0 °C,15 min	2.6	11	28	2.7	7.0
2	**1a**	1.7	25 °C,15 min	4.6	3.1	7.6	2.5	38
3	**1e**	17	0 °C,30 min	7.0	17	39	2.3	74
4	**1e**	0.83	0 °C,30 min	2.2	65	160	2.4	24
5	**1e**	0.83	25 °C,30 min	1.8	19	41	2.2	71
6[c]	**1e**	0.83	0 °C,30 min	2.1	61	140	2.3	5.0
7	**1b**	1.6	0 °C,15 min	1.2	52	81	1.6	48
8	**1c**	17	0 °C,30 min	3.4	4.3	11	2.5	1.2
9	**1c**	17	25 °C,30 min	7.2	1.4	4.0	2.9	29
10	**1d**	17	0 °C,10 min	5.1	17	44	2.6	20

[a] Conditions:100 mL of toluene, 1 atm ethylene, MAO as the co-catalyst unless otherwise indicated. [b] Molecular weight data reported against polystyrene standards. [c] Conditions:200 mL of toluene,4 atm ethylene, MAO as the co-catalyst.



2a R=4-CF_3 **2b** R=4-H
2c R=4-Me **2d** R=4-OMe

Scheme 2 *N*,*N*-Bi-dentate nickel complexes **2a-2d**[12]

The Brookhart group have also investigated use of the *N*,*N*-bidentate (α-diimine)nickel(II) complexes **2a-2d** (Scheme 2) for ethylene oligomerization.[12] Treatment of the Ni(II) dibromide complexes **2** with aluminium alkyl activators such as MAO (methylalumoxane), modified MAO (MMAO), MAO-IP, or Et_2AlCl in toluene generated active cationic catalysts *in-situ* that could oligomerize ethylene with a Schulz-Flory distribution of linear α-olefins. Reaction conditions can be adjusted that lead to selectivities as high as 96 % for linear α-olefins (entry 15, Table 2). The olefins produced were primarily linear α-olefins, with the remainder consisting of linear 2-alkenes. Branched olefins were not observed when reaction times were within one hour or less. Very long reactions (e.g. 3 h or more) with the most active catalysts occasionally yielded very small amounts of branched products (<2 % of total products), which they believed were formed from re-incorporation of oligomerization products that build to high concentrations after long reaction periods.[12]

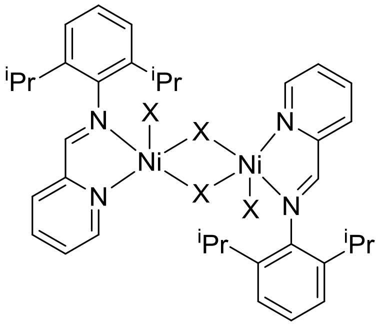
Increasing the ethylene pressure resulted in an increase in the selectivity for α-olefins, as well as an increase in the Schulz-Flory α constant (see entries 1-4, 10-12, Table 2). Turnover frequencies were also ethylene-dependent, reaching a maximum value when the ethylene pressure was near 30 atm. Further increases in ethylene pressure resulted in a decrease in the apparent turnover frequency. Possibilities include a decrease in the solvent polarity at higher ethylene concentrations[32] or inhibition due to formation of an inactive (or less active) five-coordinate intermediate. In addition to ethylene pressure effects, the oligomerization reaction was strongly affected by the temperature. As the temperature increased, both the selectivity for α-olefins and the Schulz-Flory constant α were found to decrease (entries 4-7, Table 2). These results indicated that the rate of chain transfer relative to the rate of chain propagation increases with temperature. Since ethylene solubility in toluene decreases with increasing temperature, the loss of selectivity for α-olefins and concomitant decrease in the Schulz-Flory α constant as the temperature increases could be due in part to lower concentrations of ethylene in solution.[12]

No substantial ligand electronic effects on the selectivity for α-olefins or the Schulz-Flory α constant were observed. There did appear to be a trend of increasing turnover frequencies as the metal center became more electrophilic. For example, as the *para*-substituents on the ligand aryl groups were varied from methyl to trifluoromethyl, the turnover frequencies doubled (entries 4, 8, and 9, Table 2). The electron-poor trifluoromethyl substituent is expected to lead to a more electrophilic metal center relative to that when more electron-rich substituents are present, which leads to an increased rate of ethylene insertion, the turnover-limiting step. However, the methoxy substituent led to turnover frequencies that were higher than expected (entries 10-12, Table 2).[12]

Table 2. Ethylene oligomeriation[12] catalyzed by pre-catalysts **2a-2d** [a]

entry	catalyst	press.(atm)	temp. (°C)	Time (min)	TON[b]×10[-3]	% α-olefins[c]	Schulz-Flory α
1	**2a**/MMAO	1	35	60	22	57	0.50
2	**2a**/MMAO	15	35	60	116	81	0.59
3	**2a**/MMAO	28	35	60	136	87	0.61
4	**2a**/MMAO	56	35	60	113	91	0.68
5	**2a**/MMAO	56	15	60	26	94	0.71
6[c]	**2a**/MMAO	56	55	60	103	88	0.66
7	**2a**/MMAO	56	75	60	74	88	0.63
8	**2a**/MMAO	56	35	60	49	92	0.70
9	**2a**/MMAO	56	35	60	45	91	0.71
10	**2a**/MMAO	15	35	60	102	84	0.64
11	**2a**/MMAO	28	35	60	114	88	0.67
12	**2a**/MMAO	56	35	60	50	95	0.74
13	**2a**/MMAO	28	35	30	65	94	0.68
14	**2a**/MAO	28	35	30	80	94	0.68
15	**2a**/MAO-IP	28	35	30	23	96	0.67
16	**2a**/Et_2AlCl	28	35	30	51	90	0.81

[a] Conditions: 200 mL of toluene, entries 1-12, [Ni]=1.00×10^{-4} M, Al/Ni=240; entries 13-16, [Ni] = 2.50×10^{-5} M, Al/Ni = 200; [b] Turnover number = mol of ethylene consumed/mol of Ni catalyst. [c] Remainder of product is 2-alkenes.



3a: X=Cl; **3b**: X=Br

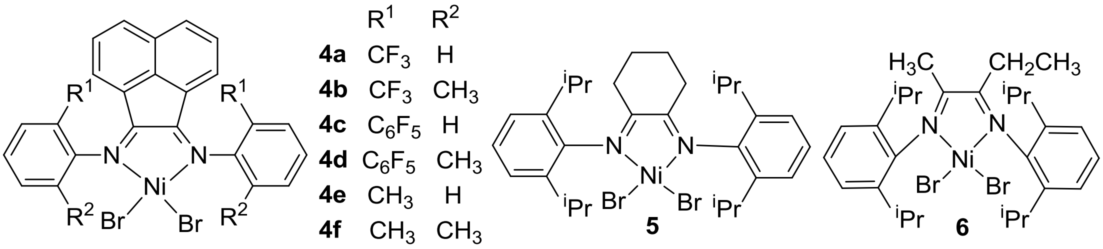
Scheme 3 *N*,*N*-bi-dentate nickel complexes **3a** and **3b** [33]

Laine and co-workers have investigated the ethylene polymerization properties of the diimine nickel complexes **3a** and **3b** in the presence of methylaluminoxane (MAO). No significant difference in polymer properties was observed between the dichloro and dibromo nickel(II) based systems (**1**/MAO and **2**/MAO, respectively), which suggests a similar active species for both catalysts. The two nickel catalysts produced mainly methyl branched polymers with moderate to good activity. In the nickel catalyzed reactions, both the activities and product molecular weights were highly dependent on the polymerization temperature. Polymerizations at 20 and 40 °C (entries 1, 2, 4, and 5, Table 3) provided low-melting or waxy polymers. Lowering the temperature to 0 °C (entries 3 and 6, Table 3) led to a sharp increase in molecular weight, whilst the catalytic activity dropped to one tenth. Besides polymer yield and chain length, the degree of branching and selectivity of unsaturation were also highly dependent on the polymerization conditions. The number of methyl branches varied from 9 to 71/1000 carbon atoms, and the highest values were observed for samples polymerized at 40 °C (entries 1 and 4, Table 3), while polyethylene produced at 0 °C was nearly linear (entries 3 and 6, Table 3).[33]

Table 3. Ethylene polymeriation[33] catalyzed by pre-catalysts **3a** and **3b**/MAO [a]

Entry	Cat.	T_p[b]	$n_{cat.}$/ μmol	p[d]/ bar	Yield/ g	Activity[e]	Mw/ g.mol^{-1}	M_w/M_n	Tm[f] /°C	Methyls per 1000 carbon[g]
1	**3a**	40	2.0	5.5	3.41	6800	2500	1.6	wax	70
2	**3a**	20	2.5	4.3	3.29	5300	6600	1.9	wax	38
3	**3a**	0	5.0	3.0	1.64	660	45000	2.2	125.0	9
4	**3b**	40	2.0	5.5	3.37	6700	2700	1.8	n.a.[h]	71
5	**3b**	20	2.5	4.3	4.21	6700	4800	2.1	n.a.[h]	43
6	**3b**	0	5.0	3.0	1.56	620	40000	1.9	125.7	10

[a] [Al] :[M] = 2000, *tp* = 15 min (except at 0 °C 30 min); [b] Polymerization temperature; [c] Molar amount of the catalyst precursor (in lmol metal); [d] Ethylene pressure; [e] Activity in kg PE (mol catalyst/h)$^{-1}$; [f] Peak melting temperature; [g] Determined by ^{1}H NMR spectroscopy; [h] Only a broad melting range (20-110°C) could be detected.

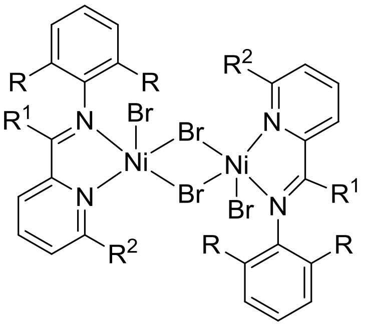


Scheme 4 *N*,*N*-bi-dentate nickel complexes **4-6** [34]

The Brookhart group has studied the polymer properties of the α-diimine nickel(II) complexes **4-6** (Scheme 4) towards ethylene polymerization when activated by modified methylaluminoxane (MMAO).[34] When a methyl substituent was introduced into the remaining *ortho* position of these catalysts, the polymer molecular weight increased dramatically. For example, if **4a** (2-CF_3) is compared with **4b** (2-CF_3, 6-CH_3), the *M*n increases from 4100 to 240 000. Similar trends were noted for **4c** (2-C_6F_5) *vs* **4d** (2-C_6F_5, 6-CH_3) (*M*n) 1020 and 41 400, respectively) and **4e** (2-CH_3) *vs* **4f** (2,6-CH_3) (*M*n) 920 vs 14 300). Polymerizations carried out at 200 psig and 35 °C (Table 2) exhibited similar trends. For example, **4a** yields polyethylene with *M*n 3800, whilst **4b** yields polyethylene with *M*n 400000. Similarly, molecular weights of polyethylenes formed by catalysts **4d** and **4f** under these conditions were significantly higher than polyethylenes prepared with **4c** and **4e**, respectively. Increases in the bulk of the *ortho* substituents resulted in increased TOF's. For example, the TOF of **1e** (2,6-di-*i*Pr) is 2.4×10^{6} h^{-1} compared to the less bulky **4f** (2,6-di-Me) of 1.6×10^{6} h^{-1}. Consistent with this trend, the TOF of the monomethyl substituted catalyst **4e** dropped to 2.3×10^{5} h^{-1}. Similarly, the TOF of **4d** (2-C_6F_5, 6-CH_3) of 1.1×10^{6} h^{-1} was about twice that of the TOF of the less bulky **4c** (2-C_6F_5) of 6.5×10^{5} h^{-1}. The one catalyst pair which exhibited the opposite trend was **4a** (2-CF_3)

with a measured TOF of 1.1×10^6 h^{-1} *vs* **4b** (2-CF_3, 2-CH_3) with a TOF of 5.0×10^5 h^{-1}. A possible explanation here may involve the rapid precipitation of the high molecular weight polymer formed by **4b** and thus, even under these conditions, reduction of the measured TOF due to precipitation. The mono-CF_3 substituted catalyst **4a** was considerably more active than the mono-CH_3 system **4e** (1.8×10^6 h^{-1} *vs* 2.3×10^5 h^{-1} TOF). While part of the explanation may be steric, the fairly similar sizes of -CF_3 *vs* -CH_3 groups suggests also that the electron-withdrawing nature of the -CF_3 group, which results in a more electrophilic nickel center, may increase the TOF. In general, the branching numbers were observed to increase with more steric bulk. For example, in experiments run under 1 atm of ethylene pressure, the branching number determined for polyethylene prepared using catalyst **4f** was 67, whereas 106 branches were observed when bulkier **1e** was employed.[7] In addition, a comparison of the branching numbers for the series of catalysts with single substituents in the 2-position of the aryl rings (i.e., **4a**, **4c**, and **4e**) and catalysts containing substituents in the 2- and 6-positions (i.e., **4b**, **4d**, **4f**, and **1e**), showed that the branching was consistently higher for the latter catalysts. For example, catalyst **4a** (2-CF_3) yields polyethylene with 31 branches per thousand carbons, whereas the bulkier catalyst **4b** (2-CF_3, 6-CH_3) affords polyethylene with 75 branches per thousand carbons. [34]

Different backbones for the α-diimine can have a remarkable effect on polymer microstructure and catalyst activity. This backbone effect has been investigated using complexes **1e** (Scheme 1), **5**, and **6** (Scheme 4), all of which contain the same bulky 2,6-di(isopropyl)phenyl groups. Complex **1e** (Scheme 1) contains a planar acenaphthyl backbone, whereas the other two catalysts, **5** and **6** (Scheme 4), contain saturated alkyl groups as substituents on the backbone carbons. All three catalysts were very active polymerization catalysts with turnover frequencies of the order of 10^5/h at 1 atm and 10^6/h at 14 atm. Catalyst **1e** (Scheme 1) exhibited a slightly higher turnover frequency (2.4×10^6/h at 14 atm) than **5** and **6** (Scheme 4) (1.6×10^6 and 9.0×10^5/h, respectively). Although the turnover frequencies were higher for **1e** (Scheme 1), the molecular weights of the polyethylene produced with catalyst **1e** (Scheme 1) were less than the molecular weights for polyethylene produced with catalysts **5** and **6** (Scheme 4). For example, for polymerization experiments conducted at 200 psig, the molecular weight (*M*n) of the polymer generated from catalyst **1e** (Scheme 1) was 337000, whereas from catalysts **5** and **6** (Scheme 4), the molecular weights were 844000 and 766000, respectively. A significant effect of the alkyl-substituted backbone is that the molecular weight distributions of the polyethylenes formed are less than those produced by the planar acenaphthyl systems. [34]



7a: R=Me; $R^1=R^2=H$;
7b: R=^{i}Pr, R^1=H;R^2=Me;
7c: R=^{i}Pr, R^1=Me;R^2=H;
7d: R=^{i}Pr, R^1=Ph;R^2=H

Scheme 5 *N*,*N*-bi-dentate nickel complexes **7a-7d** [35]

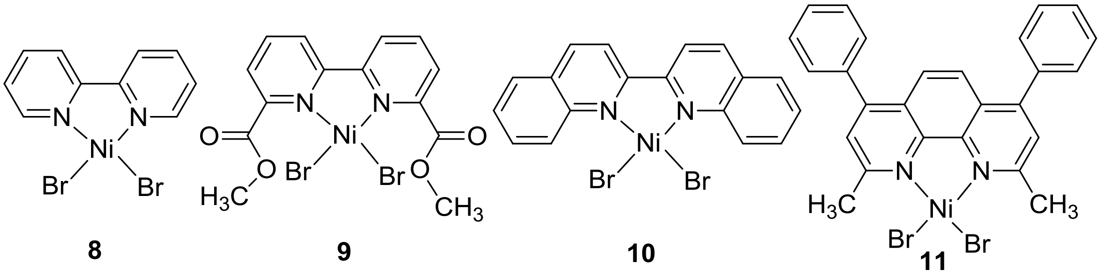
Laine and his coworkers have investigated the four dimeric nickel(II) complexes **7a-7d** (Scheme 5) for the polymerization of ethylene when activated by the methylaluminoxane (MAO). Such systems produced nearly linear or primarily methyl-branched polymers.[35] All the catalysts **7a**-**7d** (Scheme 5) lost activity with decreasing reaction temperature: the highest catalytic activities were obtained at 20 °C (except for catalyst **7d**/MAO), whilst lowering the temperature to 0 °C led to a significant decline in polymer production. Reduced polymer yields at 40 °C (entries 1, 4, 7, and 10, Table 4) can be attributed to catalyst decomposition, which was detected as diminishing ethylene consumption after initially higher activity. Nevertheless, activities for the system **7b**/MAO, which contains a methyl substituent at the 6-position of the ligand pyridine ring, were one order of magnitude lower than for the unsubstituted complex.[33] This indicates severe interference from the protruding methyl group, which obstructs one of the equatorial coordination sites as can be seen in the solid-state structure as well, thus, resulting in diminished activity. Also the phenyl group in the imino bridge of complex **7d** had a slight negative effect on the polymerization activity at higher temperatures (entries 11 and 12, Table 4). Although highly dependant on the polymerization temperature, the molecular weights of produced polymers were in general very similar to the values reported by their analogues **3a** and **3b**.[33] Only a minor increase in chain length was achieved when the 6-methylpyridine-based catalyst **7b**/MAO was employed at 20 and 40 °C (entries 4 and 5, Table 4). Therefore, the dominating factor in controlling the molecular weight, besides the reaction conditions, appears to be the steric bulk of the ligand, which despite all the different modifications made was still rather minimal at the pyridine. As a result, blocking of the axial coordination sites at the nickel center remained limited and products with $M\text{w} < 50000$ g mol^{-1} were isolated.[35] The effect of ligand environment was most clear when the polymer branching was analyzed. Even in this case, the polymerization temperature played an important role, though the extent of branching could be controlled via the ligand structure. Methyl-branched polymers were predominantly obtained, though on decreasing the steric bulk at the aryl ring by replacing two isopropyl groups with methyls at the 2- and 6-positions more linear polymers were afforded. Quite remarkably, the least branching was observed in samples produced with catalyst **7b**/MAO, in which isopropyl groups were present and the pyridine ring was substituted (with a methyl). Introduction of a methyl or phenyl side group to the imino carbon of the ligand, led in turn to increased branching. In summary, the effect of the ligand environment was most evident on the degree of branching, whilst the catalytic activity and molecular weight of the polymer were more dependent on the general catalyst composition as well as reaction conditions for the complexes **7a**-**7d**.[35]

Table 4. Ethylene polymeriation[35] catalyzed by pre-catalysts **7a**-**7d**/MAO [a]

Entry	Cat.	T_p (°C)[b]	$n_{cat.}$ (μmol)[c]	P (bar)[d]	Yield (g)	Acti.[e]	M_w (g.mol^{-1})	M_w/M_n	T_m (°C)[f]	Methyls per 1000 carbon atoms[g]
1	**7a**	40	2.5	5.5	4.44	3600	2800	1.7	Wax	43
2	**7a**	20	2.5	4.3	7.08	5700	5500	2.2	113.3[h]	24
3	**7a**	0	5.0	3.0	3.07	610	26000	1.9	127.0	6
4	**7b**	40	5.0	5.5	1.20	480	5600	2.2	116.7[h]	28
5	**7b**	20	10	4.3	2.93	590	7900	2.7	118.0[h]	23
6	**7b**	0	20	3.0	0.86	43	27000	2.0	127.0	7
7	**7c**	40	2.5	5.5	3.80	3000	3400	1.8	Wax	83
8	**7c**	20	5.0	4.3	12.16	4800	5000	2.6	101.7[h]	50
9	**7c**	0	5.0	3.0	3.02	600	22000	2.4	116.3	17
10	**7d**	40	4.6	5.5	7.12	3100	2300	2.5	Wax	67
11	**7d**	20	4.6	4.3	2.28	990	7000	2.1	101.3[h]	53
12	**7d**	0	4.6	3.0	4.64	1000	30000	2.9	115.7	24

[a] [Al]:[M]=2000, t_p=30min (except at 0°C, 60 min). [b] Polymerization temperature. [c] Molar amount of the catalyst precursor (in mmol Ni). [d] Ethylene pressure. [e] Activity in kg PE (mol catalyst h)$^{-1}$. [f]

Peak melting temperature. [g] Determined by ^{1}H NMR spectroscopy. [h] Broad melting peak.



Scheme 6 *N,N*-bi-dentate nickel complexes **8-11** [36]

Pakkanen and co-workers have synthesized the four-coordinated bipyridine complexes **8**-**11** (Scheme 6) and screened them for ethylene polymerization using MAO as the co-catalyst.[36] The polymerization activity was observed to increase when bulky dimethoxycarbonyl substituents were used (Fig. 1). In addition to steric effects, the electron withdrawing property of the ester group stabilizes the cation and yields a more active catalyst (Fig. 1). The production of HDPE was also found to be dependent on the polymerization temperature (Fig. 1). A moderate temperature (50 °C) proved to be the most promising, which is close to the reaction temperatures commonly employed when using Brookhart-type catalysts (Fig. 1). Indeed, it was observed that a reaction temperature of 70 °C led to a decrease in the catalytic activity compared to that observed at 50 °C; the optimum activities at 50°C being 2650 for **9**, 2470 for **10**, 954 for **8** and 351 for **11** (Fig. 1). The most active catalyst system at all temperatures was the Ni(II) complex with a 6,6'-disubstituted bipyridine ligand (complex **9**, Scheme 6). The use of ester substituents in the disubstituted bipyridine ligand as in **9** yielded a three times more active catalyst compared to the unsubstituted bipyridine **8** (Fig. 1). Also the use of a 2, 2'-biquinoline ligand increased the activity

(**10**, Scheme 6), yielding comparable activity to **9** at 50 °C. The role of the ligand structure is in agreement with reported results of Brookhart;[1] a successful polymerization requires steric hindrance around the metal center. The activity is still presumed to rise if more bulky substituents are employed close to metal center and above and below the ligand plane. For the sake of comparison, a shorter polymerization experiment with **9** (30 °C, 15 min) showed lower activity (40 % lower) than a longer experiment under similar conditions. This result indicated that complex **9** did not decay to a significant extent under the polymerization conditions used.[36]

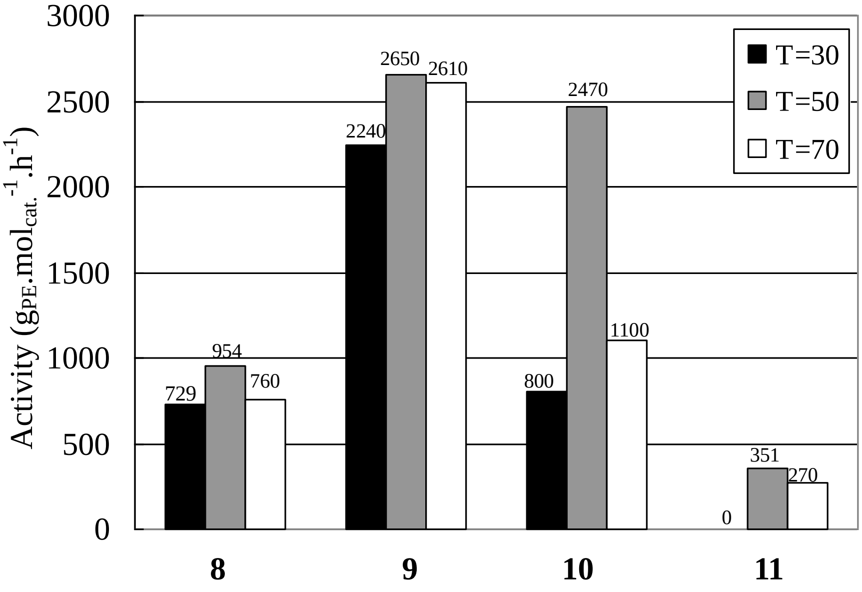
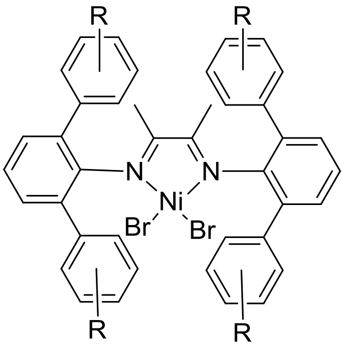


Figure 1. Catalytic activities of Ni(II) bipyridine complexes **8-11**

(3 h, 5 bar ethylene, MAO content Al:Ni 1000:1)[36]



12a: R=H;
12b: R=4-OCH_3;
12c: R=4-tert-butyl

Scheme 7 *N*,*N*-bi-dentate nickel complexes **12a-12c** [37]

Rieger and coworkers have investigated the ethylene polymerization behaviour of the pre-catalysts **12a-12c** (Scheme 7) with MAO as the activator.[37] The activities of **12a-c**/MAO increased substantially at higher monomer concentrations, exceeding those of **1b**/MAO considerably under the same conditions (entries 1-6, Table 5). Surprisingly, the chiral complex **12c**/MAO exhibited the highest activities (Figure 3), which increased up to 2×10^4 g(PE) (mol(Ni) h)$^{-1}$ at 30 bar ethylene pressure (entry 4, table 5). The lower activity of **12b**/MAO (Figure 3) results from a reaction with MAO, probably through coordination via the methoxy units, indicated by the formation of an insoluble precipitate directly after MAO addition. The molecular weight of the polyethylene produced under these conditions exceeded 4.5×10^6 g mol^{-1} by the catalyst **12c/MAO** (entry 3, table 5). In addition, the molecular weight of the polymer products could be effectively controlled by the addition of hydrogen. M_w varied from 2×10^5 to 1×10^6 g mol^{-1} under different H_2 concentrations using **12c**/MAO. Hydrogen does not seem to reduce or inactivate the Ni(II) catalysts. In fact, the activity increased significantly on addition of H_2. A reasonable explanation for this unexpected effect might be the more homogeneous reaction conditions, but also a fast hydrogenation of less reactive intermediates, like those resulting from 2,1-insertions. The melting points attested to the highly crystalline character of the polyethylenes.[37]

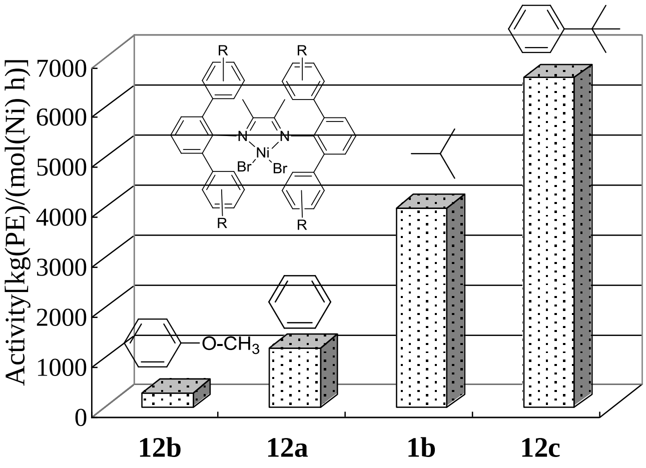
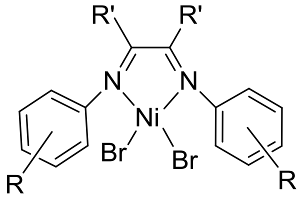


Figure 2. Comparison of the catalyst activities[37]

Table 5. Ethylene polymerizations[37] with nickel catalysts **1b**,**12a-12c**/MAO [a]

Entry	P(bar)	catalyst	amount[b]	time(min)	yield(g)	activity[c]	M_w[d]	M_w/M_n	T_m(°C)
1	10	**12a**	0.04	30	23	1200	n.s.		133
2	30	**12a**	0.04	15	60	6000	n.s.		134
3	10	**12c**	0.02	15	33	6600	4.5	1.3	130
4	30	**12c**	0.02	15	101	20200	n.s.		130
5	10	**12b**	0.04	120	22	300	n.s.		132
6	10	**1b**	0.02	15	20	4000	3.89	2.3	92

[a] Conditions: 2 L steel reactor, 800 mL of toluene, co-catalyst MAO (Al:Ni =500); [b] [mmol]; [c] [g(PE)(mol(Ni) h)$^{-1}$]; [d] [10^6 g mol^{-1}].

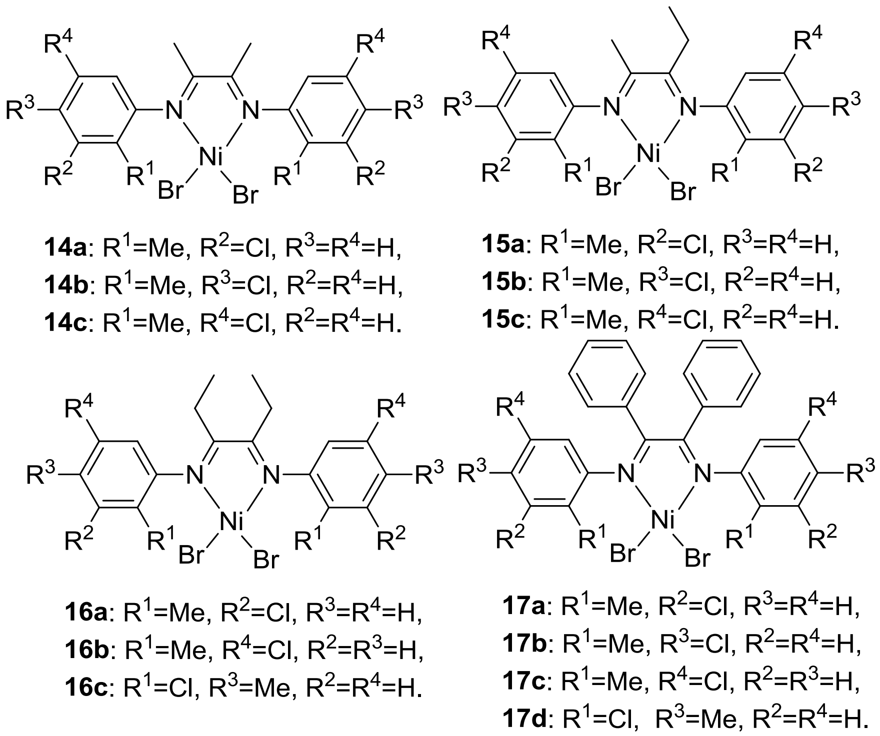


13

R=H,methyl or halogen
R'=methyl, ethyl, phenyl

Scheme 8 *N*,*N*-bi-dentate nickel complexes **13** [13]

The Alt group have investigated the properties of ethylene oligo-/polymerization of the modified α-diimine nickel(II) dihalide complexes **13** (Scheme 8) following activation with methylaluminoxane (MAO).[13] The catalytic properties of these complexes and the character of the obtained polymers depend on the ligand structure of the catalysts employed. Substituents on the arene moiety and/or the backbone of the ligand influenced the active site of the catalyst during the polymerization reaction. Therefore, polymerization products of low molecular weight (oligomers) to high molecular weight (polymers) could be obtained. Activities and molecular weights of the products and the formation of various isomers of the obtained oligomers revealed a clear dependence on the molecular structure of the catalyst precursors. It was found that the pre-catalysts **13**/MAO with bulky iodine substituents showed good activities especially when the iodine substituent was located at the *ortho*-position of the aryl moiety. The influence exerted by the substituents on the ligand backbone has been observed by comparing catalysts with different groups with the same substitution pattern at the aryl moiety. The activity increased if the substituents at the ligand backbone were changed from a methyl and an ethyl group, to two ethyl groups and the activity decreased if there were two bulkier phenyl groups present.[13]



14a: R^1=Me, R^2=Cl, R^3=R^4=H,
14b: R^1=Me, R^3=Cl, R^2=R^4=H,
14c: R^1=Me, R^4=Cl, R^2=R^4=H.

15a: R^1=Me, R^2=Cl, R^3=R^4=H,
15b: R^1=Me, R^3=Cl, R^2=R^4=H,
15c: R^1=Me, R^4=Cl, R^2=R^4=H.

16a: R^1=Me, R^2=Cl, R^3=R^4=H,
16b: R^1=Me, R^4=Cl, R^2=R^3=H,
16c: R^1=Cl, R^3=Me, R^2=R^4=H.

17a: R^1=Me, R^2=Cl, R^3=R^4=H,
17b: R^1=Me, R^3=Cl, R^2=R^4=H,
17c: R^1=Me, R^4=Cl, R^2=R^3=H,
17d: R^1=Cl, R^3=Me, R^2=R^4=H.

Scheme 9 *N*,*N*-bi-dentate nickel complexes **14a-17d** [38]

The Alt group has investigated the ethylene oligo-/polymerization properties of the α-diimine nickel(II) dibromide complexes **14a**-**17d** (Scheme 9) upon activation with methylaluminoxane (MAO). In all cases, a mixture of oligomers and polymers was obtained. A comparison of the observed activities revealed that chloro substituents at the *para*-position (**14b**, **15b**) or the *ortho*-position (**16c**, **17d**) of the aryl groups of the α-diimine ligand led to the highest activities (Fig. 3). There was also a trend that bulkier substituents at the ligand backbone led to a decrease of the activities. Therefore, the activity of **14b** (2230 g (product) $mmol^{-1}$ (Ni) h) with two methyl groups at the ligand backbone was nearly 10 times higher than the activity of **17b** (235 g (product) $mmol^{-1}$ (Ni) h) bearing two phenyl groups.[38] The polymer share determined for the different catalysts also revealed some clear trends (Fig. 4). A comparison of the catalysts with the same substituents at the ligand backbone obtained from **14a-c** showed that **14b** with a chloro substituent in the *para*-position produced the lowest polymer share. Similar effects were also observed for the catalysts derived from **15a-c**, and **17a-c**. It was clear that there is an increase of the polymer share from the catalysts with two methyl groups at the ligand backbone compared to those with two ethyl groups and a further slight decrease of the polymer share for the catalysts with two phenyl groups at the ligand backbone.[38]

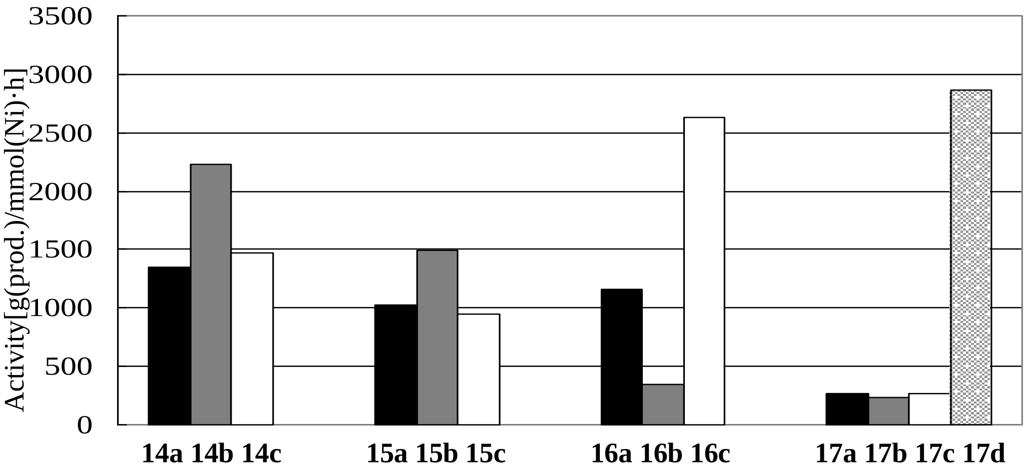


Figure 3. Comparison of the observed activities of the catalyst precursors **14a–17d**.[38]

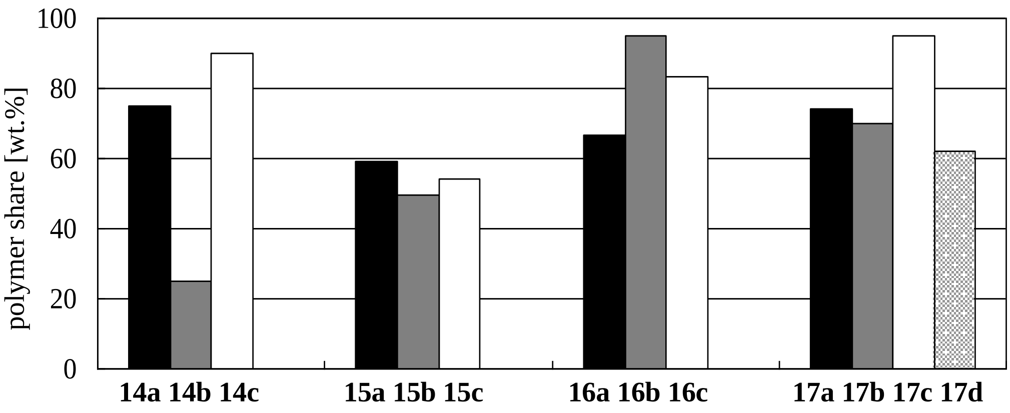
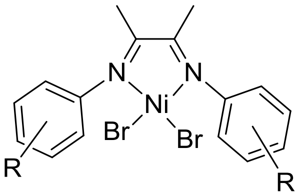


Figure 4. Comparison of the polymer share obtained with the catalyst precursors **14a–17d**.[38]



R	R	R	R	R
18a: H	**19a**: *ortho*-F	**20a**: *ortho*-Cl	**21a**: *ortho*-Br	**22a**: *ortho*-I
18b: *ortho*-Me	**19b**: *meta*-F	**20b**: *meta*-Cl	**21b**: *para*-Br	**22b**: *para*-I
18c: *para*-Me	**19c**: *para*-F	**20c**: *para*-Cl		

Scheme 10 *N*,*N*-bi-dentate nickel dibromide complexes **18a-22b** [39]

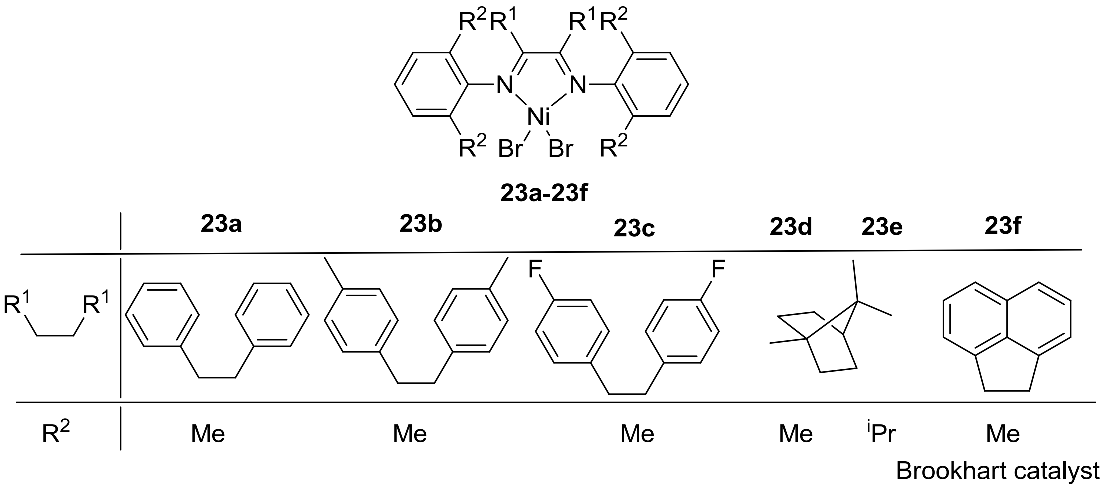
Alt and his coworkers have investigated the influence of halogen substituents at the ligand framework of the (α-diimine)nickel(II) catalyst precursors **18a-22b** (Scheme 10) in relation to their behaviour in ethylene oligo-/polymerization.[39] Upon activation with MAO, the homogeneous nickel catalysts **18a-22b** (Scheme 10) were capable of polymerizing olefins to low molecular oligomers along with some of branched polymers. The variation of the ligand framework of the catalysts with halogen substituents in different positions revealed clear dependencies between these substituents and the properties of the polymerization products.[39] A comparison of the observed activities revealed that complexes bearing the same substituent only in different positions of the aryl moiety showed the highest activities if the substituent was located at the *ortho*-position, except in the case of the catalysts **19a-c** (entries 1-13, table 6). The fluorine containing complexes **19a**, **19b** and **19c** exhibited different behaviour. The catalyst **19c** with a *para*-fluorine substituent provided the highest activity (entries 4-6, table 6). It can be assumed that two effects are responsible for the activity. An *ortho*-substituent interacts with the catalytic center via the axial coordination sites of the metal. Therefore, halogens in that position seem to stabilize the active species. In particular, **22a** with two iodine substituents provided the highest activity of the catalysts studied here (entry 12, table 6).[39] The other effect can be related to the electronic properties of the complex. If the electron density at the metal center is comparatively low, then coordination of the monomer is favored. In **19c** with the strong electronegative fluorine substituent in *para*-position, this electronic effect superimposes the *ortho*-effect of the corresponding *ortho*-substituted complex **19a**. In case of fluorine substituents, the low steric demands of the fluorine atom additionally do not cause an intensive interaction of these substituents with the metal center. Therefore, it can be concluded that the activity of (α-diimine)nickel(II) catalysts of **18a-22b** is a correlation between electronic and steric effects caused by the substituents at the aryl moiety of the ligand.[39]

The formation of oligomers and polymers also can be explained. The obtained oligomer/polymer ratios are shown in table 6.[39] According to the “chain walking mechanism”, the formation of oligomers depends on the number of chain transfers. After a coordinated higher olefin has been formed, it has to be replaced by an ethylene molecule. For this replacement, the axial coordination sites of the metal are decisive. If they are sterically hindered by a substituent, chain transfer is suppressed and polymer is produced. Therefore, the unsubstituted complex **18a** was only able to dimerize ethylene to butene. Higher olefins could only be detected in slight traces. The fluorine substituted complexes **19a**, **19b** and **19c** and complexes with substituents at the *meta*- or *para*-positions (**18c**, **20b**, **20c**, **21b**, **22b**) produced oligomers with an even carbon number of up to 50 carbon atoms (entries 3, 4-6, 8, 9, 11, and 13, table 6). The catalysts bearing a substituent at the *ortho*-position of the aryl moiety produced polymers to a certain extent. The amount of polymer was closely related to the bulk of the substituent. Therefore, **22a** with the most bulky iodine substituents only formed a polymer with an average molecular weight of 36,000 g/mol (entry 12, table 6). The oligomer mixtures obtained with **18b**, **20a** and **21a** were vicous oils or waxes (entries 2, 7, and 10, table 6). Compared to the oligomers produced with the other catalysts, olefins with higher carbon numbers were dominant.[39]

Table 6. Results of ethylene polymerization[39] with nickel catalysts **18a-22b**/MAO [a]

Entry	catlyst	activity[b]	TOF[c]	Polymer share (wt.%)	1-Octene[d]	$M_{w(\text{polymer share})}$ (g/mol)
1	**18a**	822	30825	0	0	-
2	**18b**	869	32588	41	37.6	69000
3	**18c**	464	17400	<1	30.8	n.d.[e]
4	**19a**	939	35213	<1	47.7	n.d.
5	**19b**	499	18713	<1	26.4	n.d.
6	**19c**	1843	69113	<1	7.6	n.d.
7	**20a**	1702	63825	22	n.d.	6700
8	**20b**	1321	49538	1.2	12.8	n.d.
9	**20c**	505	18938	3.1	25.8	n.d.
10	**21a**	733	27488	27	n.d.	18460
11	**21b**	587	22013	1.1	34.5	n.d.
12	**22a**	3991	149663	100	-	35870
13	**22b**	1056	39600	4.2	49.3	n.d.

[a] Polymerization conditions: activation with 30 wt.% methylaluminoxane in toluene (Al:Ni = 1000:1; polymerization in 250 ml pentane,60 °C, 1 L autoclave, 10 bar ethylene pressure, 60 min).
[b] The activities [g (product)/mmol (Ni) h] were calculated from the total consumption of ethylene (1.0 l ethylene = 1.2 g product).
[c] TOF [mol(C_2H_4)/mol(cat.) h]: turn over frequency.
[d] 1-Octene share (mol%) of all octene isomers.
[e] n.d.: not determined.



Scheme 11 *N*,*N*-bi-dentate nickel complexes **23a-23f** [40]

Wu and his coworkers have studied the effects of the substituted backbone structure on the catalytic properties and the branched structure of polyethylene by the α-diimine nickel pre-catalysts **1e** (Scheme 1) and **23a-23f** (Scheme 11) with MAO as co-catalyst.[40] Those possessing a bulky backbone showed significantly higher thermal stability and produced higher molecular weight polyethylene as compared with the acenaphthyl backbone analogues. The catalysts with 2,6-diisopropyl substituent on aniline moieties (**1e**, **23e**) showed higher turnover frequencies (TOF) and yielded higher molecular weight polymer than did their analogues with 2,6-dimethyl substituent (**23d**, **23f**, Scheme 11) under the same polymerization conditions (entries 10-14, 17-19, table 7).[40] The results can be ascribed to the increase in steric hindrance of the *ortho*-substituents, leading to an increase in the rate of chain propagation relative to chain transfer and a stabilization of the insertion transition state relative to the resting state.[34,41] In addition, by using **23e** catalyst containing a camphyl backbone and 2,6-diisopropyl-substituted aniline groups, the catalytic activity, molecular weight and degree of branching of the obtained polyethylene remained essentially constant on increasing the polymerization temperature from 40 to 80 °C (entries 14-16, table 7). Furthermore, the catalyst can remain active for a long period of time even at 80 °C. The contrast in both the catalyst thermal stability and polymer molecular weight between the camphyl backbone complexes and traditional α-diimine complexes suggests that the bulky camphyl backbone environment significantly influences the catalytic properties of the complexes and promotes thermostability of the α-diimine nickel catalyst.

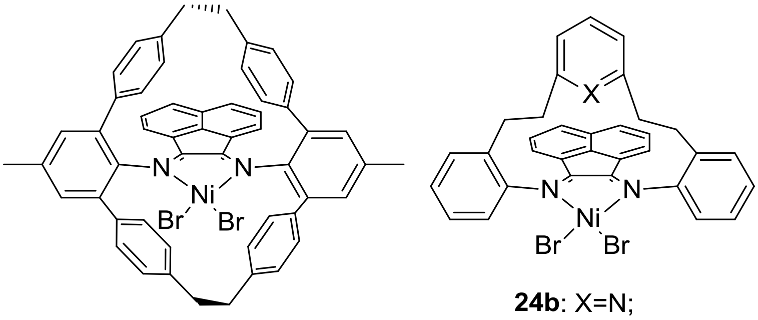
The steric hindrance of the backbone groups can also affect the catalytic properties. Looking at **23a-d** (Scheme 11) and **23f** (Scheme 11) bearing two aryl groups on the backbone, steric effects could impede the rotation of the aniline-derived moieties. In particular, **23d** (Scheme 11) possessing a bicyclic substituted backbone showed a superior steric hindrance on the nickel center. Besides the steric effect, the electronic effect of the backbone framework can also affect the ethylene polymerization by using catalysts **23a-c** (Scheme 11) containing phenyl, 4-methylphenyl, and 4-fluorophenyl substituents, respectively. Catalyst **23c** (Scheme 11) bearing electron-withdrawing 4-fluorophenyl substituents on the backbone showed the highest TOF and yielded the lowest molecular weight polyethylene among these three catalysts (entries 7-9, table 7). Even not all cases true, the nickel complexes bearing more electronic-withdrawing ligands generally showed an overall trend of higher activity but produced polyethylene of lower molecular weight.[42] The backbone structure also influenced the degree of branching of the obtained polyethylene. With catalysts containing the same 2,6-dimethyl-substituent on the aniline moieties (**23a-d**, **23f**), the dependence of branching on the backbone structure followed a similar trend shown for the molecular weight of polyethylene, i.e., polyethylene obtained with **23d** (Scheme 11) had the highest branching degrees (88.5 branches/1000C) and that of polyethylene obtained with **23f** showed the lowest (23.4 branches/1000C) under the same conditions (40 °C) (entries 1-13, table 7). In addition, the branching degrees were also observed to increase with more steric bulk on the aniline-derived moieties. For example, the branching degrees of polyethylene prepared by using catalyst **23d** were 88.5 branches/1000C, whereas 133.3 branches/1000C were found when bulkier **23e** was employed (entries 10 and 14, table 7). These observations suggested that the relative rates of monomer insertion and chain walking (K_{ins}/K_w) were affected equally by the steric bulk of both the aniline-derived moiety and the backbone structure.[40]

Table 7. Results of ethylene polymerization [40] for complexes **1e** and **23a-23f** [a]

Entry	catalyst	temp (°C)	Yield(g)	TOF[c](10^{-4}/h)	M_n(kg/mol)	*PDI*	Branching degrees/1000C
1	**23a**	0	0.83	1.19	150.7	2.2	15.0
2	**23a**	20	1.24	1.77	92.4	2.3	35.2
3	**23a**	40	0.85	1.21	41.0	2.0	69.6
4	**23b**	0	0.80	1.14	177.2	2.0	22.9
5	**23b**	20	1.29	1.84	103.0	2.2	41.8
6	**23b**	40	0.85	1.21	35.1	2.1	81.8
7	**23c**	0	0.94	1.34	119.9	2.5	13.1
8	**23c**	20	1.81	2.59	68.8	2.2	20.7
9	**23c**	40	1.22	1.74	27.6	2.0	62.5
10	**23d**	40	1.02	1.46	61.3	2.3	88.5
11	**23f**	0	0.97	1.39	48.1	2.5	11.8
12	**23f**	20	0.81	1.16	23.8	2.5	15.6
13	**23f**	40	0.54	0.77	12.7	2.7	23.4
14	**23e**	40	1.37	1.96	156.0	2.7	133.3

15	**23e**	60	1.34	1.91	154.9	2.7	135.5
16	**23e**	80	0.88	1.26	122.9	2.0	129.4
17	**1e**	0	2.40	3.43	224.9	2.9	58.1
18	**1e**	20	1.92	2.74	135.6	2.7	102.4
19	**1e**	40	1.54	2.20	109.5	2.5	209.6
20	**1e**	60	1.17	1.67	56.7	2.4	229.2
21	**1e**	80	0.26	0.37	34.2	2.7	219.2

[a] Reaction conditions: Ni = 5 μmol, Al/Ni=600, t_p=0.5h; toluene 20mL; 0.5atm of ethylene.



24a

24b: X=N;
24c: X=CH

Scheme 12 *N,N*-bi-dentate nickel complexes **24a-24c**[27,43]

Guan and his coworkers have investigated the ethylene polymerization behaviour of the *N,N*-bi-dentate nickel complexes **24a-24c** (Scheme 12).[27,43] The novel cyclophane ligand changed the catalytic properties significantly for the Ni(II) complexes. The Ni(II) complex **24a** (Scheme 12) exhibited excellent activity for ethylene polymerization with a productivity of 42000 kg of PE mol^{-1} of Ni h^{-1} (the TOF is 1.50×10^6 h^{-1}) when activated with MMAO. The polymerization was run at temperatures of 30-90 ^{o}C to probe the thermal stability. At each temperature, the polymerization was run at three different time periods ranging from 5 to 15 min to evaluate the catalyst lifetime.[43] The catalyst **24a** (Scheme 12) remained highly active at temperatures up to 90 ^{o}C, as evident by the consistent catalyst TOFs.[43]

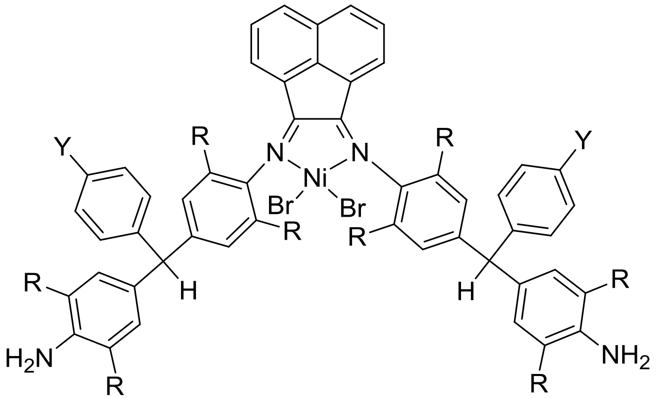
The nickel complex **24b** (Scheme 12) obtained negligible yields with MAO or

$AlMe_3$ for ethylene polymerization, while $AlMe_2Cl$ resulted in a highly active polymerization catalyst (entries 1-6, table 8). Despite lacking steric bulk at the bottom face, catalyst **24b** (Scheme 12) produced PE with high molecular weight and relatively narrow polydispersities (PDI) (entries 3-6, table 8). Similar to other α-diimine-based catalysts, both the activity and molecular weight of PE formed fell as temperature was raised (entries 3-6, table 8). This may be due to the low thermal stability of the active catalytic species or disruption of the pyridine interaction by higher thermal energy. In sharp contrast, nickel catalyst **24c** (Scheme 12), containing a non-donating phenyl group, only afforded low molecular weight oligomers with broad PDI when using MAO, $AlMe_3$, or $AlMe_2Cl$ as activators (entries 8-9, table 8). Under identical polymerization conditions (entries 5 and 9, Table 8), catalyst **24b** (Scheme 12) produced more linear PE with significantly higher melting temperatures (T_m) than did catalyst **24c** (Scheme 12). This suggests that the axial pyridine donor not only inhibits associative chain transfer but also suppresses β-hydride elimination and catalyst chain walking,[44-46] resulting in a highly linear polymer.

Table 8. Results of ethylene polymerization [27] for complexes **24b-24c** [a]

entry	catalyst	activator	temp.(°C)	TOF($\times10^{-3}$/h)	Mn[b]	PDI [c]	Branches [d]	T_m[e](°C)
1	**24b**	MAO	35	< 5	n.d.	n.d.	n.d.	n.d.
2	**24b**	$AlMe_3$	35	< 5	n.d.	n.d.	n.d.	n.d.
3	**24b**	$AlMe_2Cl$	5	187	109224	2.1	1.4	137
4	**24b**	$AlMe_2Cl$	15	535	39337	3.2	3.4	134
5	**24b**	$AlMe_2Cl$	35	588	56464	2.2	3.6	131
6	**24b**	$AlMe_2Cl$	55	428	17687	3.9	11.3	125
7	**24c**	MAO	35	561	5648	7.2	11.3	126
8	**24c**	$AlMe_3$	35	294	6994	6.6	11.6	123
9	**24c**	$AlMe_2Cl$	35	348	6931	5.6	12.9	122

[a] Polymerization conditions: 2μmol catalyst, 6 mmol activator, 100 mL of toluene, 200 psig ethylene, 10 min. [b] Determined by GPC with polystyrene standards. [c] Determined by ^{1}H NMR and is the number of Me's per 1000 carbons. [d] Determined by DSC. [e] Only trace amounts of polyethylene formed.

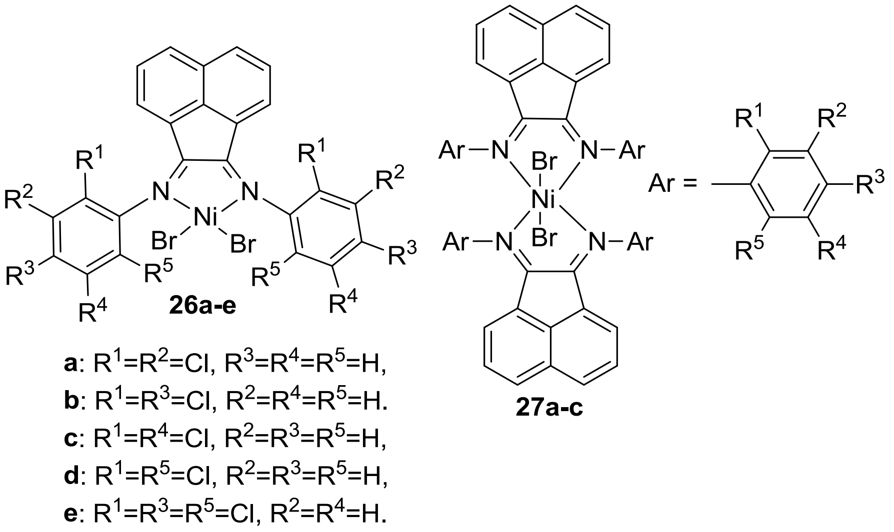


Y	H	H	H	NO_2	NO_2	NO_2	OCH_3	OCH_3	OCH_3
R	Me	Et	^{i}Pr	Me	Et	^{i}Pr	Me	Et	^{i}Pr
	25a	**25b**	**25c**	**25d**	**25e**	**25f**	**25g**	**25h**	**25i**

Scheme 13 *N*,*N*-bi-dentate nickel complexes **25a-25i** [20,24]

Kim and his coworkers have reported a series of highly active ethylene polymerization catalysts **25a-25i** (Scheme 13) based on bi-dentate α-diimine ligands coordinated to nickel.[20,24] Catalytic activity was changed by modifying the *ortho* substituents of *N*-aryl rings from methyl to isopropyl groups. A considerable drop in the activity of complexes bearing isopropyl groups was observed when compared to complexes bearing methyl groups.[24] For example, catalyst **25d** (Scheme 13) bearing *ortho* methyl substituents on the *N*-aryl ring exhibited an activity (as average rate of polymerization for 30 min) of 3.30 × 10^8 $g_{PE}/(mol_{Ni}\cdot h\cdot atm)$ at 30 ^oC when combined with 300 equivalents of MAO. Catalyst **25e** (Scheme 13) bearing ethyl substituents showed an activity of 2.54 × 10^8 $g_{PE}/(mol_{Ni}\cdot h\cdot atm)$, and the isopropyl group substituted complex **25f** revealed an activity of 2.43 × 10^8 $g_{PE}/(mol_{Ni}\cdot h\cdot atm)$ under the same conditions. Similar results were observed with other systems, **25a-i** (Scheme 13). The molecular weight of the polymers increased with *ortho* substituent bulkiness. [24] For example, the methyl substituted catalyst **25a** (Scheme 13) produced polymers with *M*n = 26,100, whereas the isopropyl substituted catalyst **25c** (Scheme 13) gave

Mn = 48,900. Bulky groups in the axial position of the metal center will lead to a decrease in rate of chain transfer relative to the rate of propagation, resulting in high molecular weight polymers. There was an abrupt decrease in the branching for polymers obtained on reducing the steric bulkiness of the diimine ligands. [24] For example, catalyst **25f** (Scheme 13) produced a polymer of 81 branches per 1000 carbon atoms, which was reduced to 3 for the methyl substituted catalyst **25d** (Scheme 13) under the similar conditions. Each catalyst differing only at the remote substituent gave extremely different behaviour on varying the co-catalyst. On comparing the activity of the remote substituted catalysts, the nitro substituted catalyst **3f** gave the highest activity with EAS of the order of 9.84 × 10^8 $g_{PE}/(mol_{Ni}\cdot h\cdot atm)$, whilst the methoxy substituted catalyst **25i** (Scheme 13) gave the lowest activity (7.86 × 10^8 $g_{PE}/(mol_{Ni}\cdot h\cdot atm)$. This can be explained in terms of a late transition metal catalyst bearing strong electron withdrawing groups performing better catalytic activities. From these results, it is clear that EAS cannot form an effective Lewis acid–base complex with methoxy groups as happens with MAO. Note that the same catalyst, **25i** (Scheme 13) was the best candidate with MAO (5.01 × 10^8 $g_{PE}/(mol_{Ni}\cdot h\cdot atm)$, due to the special effect of the methoxy group on the catalyst system as reported by Brookhart and Svejda,[12] even though the activity was lower than with EAS.[24]



a: R^1=R^2=Cl, R^3=R^4=R^5=H,
b: R^1=R^3=Cl, R^2=R^4=R^5=H.
c: R^1=R^4=Cl, R^2=R^3=R^5=H,
d: R^1=R^5=Cl, R^2=R^3=R^5=H,
e: R^1=R^3=R^5=Cl, R^2=R^4=H.

Scheme 14 *N,N*-bi-dentate nickel complexes **26a-e** and **27a-c** [47]

The complex pre-catalysts **26a-e** and **27a-c** containing chloro-substituted ligands (Scheme 14) were investigated for the oligomerization or polymerization of ethylene in the presence of modified methylaluminoxane (MMAO).[47] The catalyst activities and the properties of the products were greatly affected by the number and the location of the chlorine atoms in the ligand. For the presence of chlorine atoms at the *ortho* and *meta* positions of *N*-aryl ring, complex **26a** (R_1=R_2=Cl) displayed the highest catalytic activity at 4.48 × 10^6 g/(mol_{Ni} · h) and produced linear oligomer (M_w = 695, entry 1, table 9). Complex **26b** (R_1=R_3=Cl) bearing electron-withdrawing chlorine atoms at the *ortho* and *para* positions, exhibited a higher catalytic activity of 4.16×10^6 g/(mol_{Ni}·h) and yielded linear oligomer (M_w = 580) (entry 2, table 9). It is well-known that there is a trend that bulkier substituents at the ligand backbone lead to a decrease of the activity for α-diimine nickel catalysts;[36] therefore, complex **26c** (R_1=R_4=Cl) with a bulkier ligand displayed the lowest catalytic activity at 1.22 × 10^6 g/(mol_{Ni}·h) and afforded linear oligomer (M_w = 540) (entry 3, table 9). With two chlorine atoms at the R_1 and R_5 position of the *N*-aryl group, complex **26d** (R_1=R_5=Cl) slightly increased the catalytic activity to 1.68 × 10^6 g/(mol_{Ni}·h) and produced high molecular weight polyethylene (M_w = 2680) (entry 4, table 9). However, if three chlorine atoms were located at R_1, R_3, and R_5, a higher activity of 4.12 × 10^6 g/(mol_{Ni}·h) and high molecular weight polyethylene (M_w = 4800) were obtained (entry 5, table 9). These results indicated that the introduction of the electron-withdrawing group at the same side of *N*-aryl ring, such as **26a** (R_1 and R_2) or **26b** (R_1 and R_3), could considerably increase the catalytic activity, while the introduction of an electron-withdrawing group at the different sides of *N*-aryl ring, such as **26c** (R_1 and R_4) or **26d** (R_1 and R_5), could considerably decrease the catalytic activity, which may be due to the increase of the steric effect of the ligand. Moreover, the catalytic activities ascend with an increase in the number of Cl atoms in the ligand (**26e** > **26d** > **26c**), being probably ascribed to the electron-withdrawing nature of chlorine atom, which results in a more electrophilic nickel center. It is noteworthy that complexes **26a-c** with only one chlorine atom adjacent to the imine nitrogen produced linear oligomers, while complexes **26d** and **26e** with two chlorine atoms adjacent to the imine nitrogen yielded high molecular weights polyethylenes, suggesting that the chlorine atoms adjacent to the imine nitrogen could suppress the β-hydrogen transfer to some extent, which resulted in the formation of high molecular weight polyethylenes.[47]

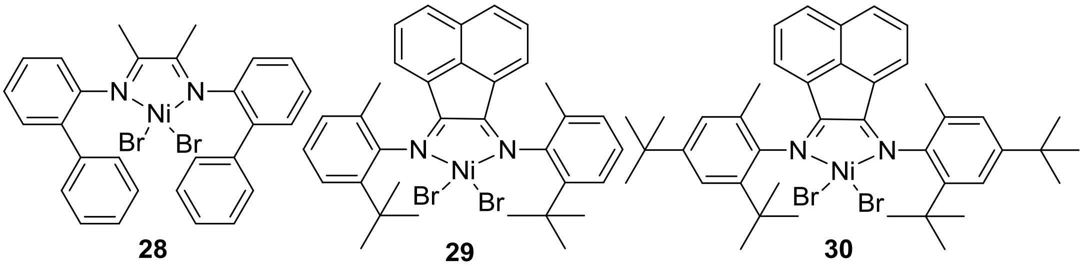
It is very interesting that the complexes **27a-c** also display high activities toward ethylene oligomerization in the presence of MMAO (Entries 6–8, Table 9). The catalytic activities are comparable with the corresponding 16e complexes **26a–c**.

Furthermore, the properties of the oligomers were also comparable with those of the oligomers obtained with **26a-c**. The possible reason is that the 20e complexes **27a-c** are unstable in dilute solution and decompose into corresponding 16e complexes **26a-c** and the parent ligands.[47]

Table 9. Results of ethylene oligomerization and polymerization[47] for nickel complexes **26a-e** and **27a-c**[a]

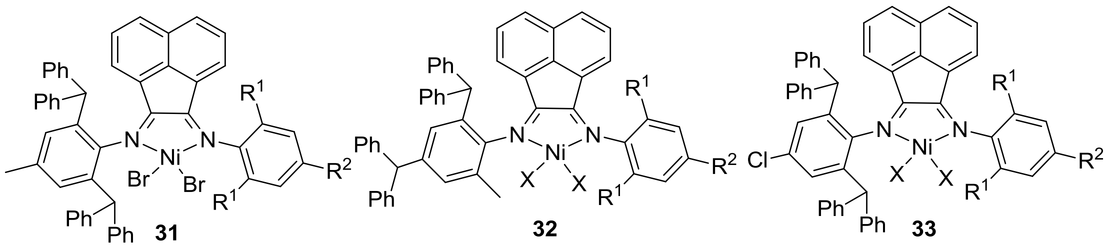
Entry	catalyst	Yield (g)	Activity[b]	Branches (per 1000 carbons)[c]	M_w[d]	M_w/M_n[d]
1	**26a**	2.24	4.48	-	695	1.50
2	**26b**	2.08	4.16	-	580	1.38
3	**26c**	0.61	1.22	-	540	1.47
4	**26d**	0.84	1.68	11	2680	1.87
5	**26e**	2.06	4.12	15	4800	2.63
6	**27a**	2.13	4.26	-	687	1.48
7	**27b**	2.03	4.60	-	592	1.42
8	**27c**	0.71	1.42	-	552	1.46

[a] 1 μmol of cat.; 10 atm of ethylene pressure; the mole ratio of Al/Ni = 1850/1; toluene 60 mL; polymerization reaction at 35 °C for 30 min. [b] 106 g of PE/mol of cat_h. [c] Determined by ^{1}H NMR and ^{13}C NMR. [d] Determined by the GPC.



Scheme 15 *N*,*N*-bi-dentate α-diimine nickel complexes **28-30**[23]

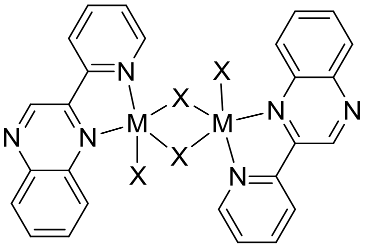
The Wu group isolated polyethylene with a bimodal molecular weight distribution using the α-diimine nickel(II) complexes **28-30** (Scheme 15), which contained unsymmetrically substituted aryl groups, in the presence of methylaluminoxane.[23] The reaction of a diketone and an aniline bearing *ortho* substituents of differing steric bulk can result in *meso*- and *rac*-isomers for the α-diimine ligands. Both isomers can interconvert owing to the rotation of the aromatic ring, the conversion rate of which depends on the steric bulk of the substituents and the temperature. The corresponding unsymmetrical α-diimine nickel(II) complexes can possess both *meso*- and *rac*-isomers, and produce two active species with different steric bulk when combined with MAO. The molecular weight of the polyethylene produced by the *rac*-catalyst was significantly higher than that produced by the *meso*-catalyst under the same polymerization conditions. Using unsymmetrical α-diimine nickel(II) catalysts including *meso*- and *rac*-isomers for ethylene polymerization, bimodal or broad molecular weight distribution polyethylene can be obtained under appropriate polymerization conditions. [23] At low polymerization temperatures, complex **28**/MAO (Scheme 15) afforded polyethylene with bimodal molecular weight distribution, whilst complex **29**/MAO (Scheme 15) yielded polyethylene with single-modal distribution. Moreover, by raising the polymerization temperature or extending the time of catalyst aging, bimodal molecular weight distribution polyethylene was also produced by complex **29**/MAO (Scheme 15). The hypothesis of bimodal molecular weight distribution polyethylene synthesized by unsymmetrical α-diimine nickel(II) complexes was supported that the molecular weight of the polyethylene produced by *rac*-**30**/MAO(Scheme 15), which was significantly higher than that produced by *meso*-**30**/MAO (Scheme 15) under identical polymerization conditions. Thus, a unique methodology to prepare polyethylene with bimodal molecular weight distribution was demonstrated. [23]



Scheme 16 *N*,*N*-bi-dentate unsymmetrical α-diimine nickel complexes **31-33** [48-50]

Our group has investigated the bulky unsymmetrical α-diimine nickel complexes **31-33** (Scheme 16).[48-50] On treatment with the co-catalysts Et_2AlCl, MAO or MMAO, these complexes **31-33** (Scheme 16) afforded outstanding catalytic activity in the range of 10^7 g of PE (mol of Ni)$^{-1}$ h^{-1}, and the polyethylene obtained exhibited a high degree of branching.[48-50] In the presence of Et_2AlCl, the highest activity of complex **31** can reach 9.39×10^6 g mol^{-1}(Ni) h^{-1} under optimal conditions. The melting temperatures of the polyethylenes obtained by this complex were found to be lower than 81 °C. Such unusual properties were caused by polyethylenes with a high degree of branching. The polymerization temperature can affect the branching degree of the polymer, for example, polyethylene with 337 branches/1000 carbons was obtained at 60 °C, while polyethylene with 99 branches/1000 carbons was obtained at 20 °C by complex **31**.[27] Upon treatment with MAO, the activity of complex **33** (bearing bromines) was higher than the complex **31** under the polymerization conditions.[48,50] The activity of the complex **32** was lower than the complex **31** when activated by MMAO. Polyethylene with 166 branches/1000 carbons was obtained at 80 °C by complex **32**, which was much lower than the amount of branching produced by complex **31**.[48,49] Thus, these results suggest that ligands not only affect the activity of the polymerization, but also affect the degree of branching in the polyethylene.

In order to develop new effective catalysts for ethylene catalysis, our group introduced quinoline groups to the skeleton of the catalysts.



32a: M=Ni, X=Cl;
32b: M=Ni, X=Br

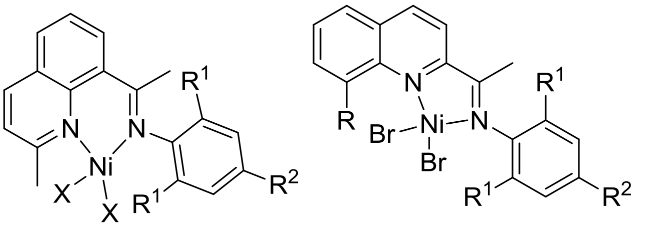
Scheme 17 *N*,*N*-bi-dentate nickel complexes **32a** and **32b**[51]

We investigated ethylene oligomerization using the nickel 2-(2-pyridyl)quinoxaline complexes **32a** and **32b** (Scheme 17) with methylaluminoxane (MAO) as co-catalyst.[51] These nickel systems mainly produced α-olefins with good activity and selectivity for α-olefins. The nickel bromide complex **32b** (Scheme 17) performed with the highest activity at an Al/Ni ratio of 3000:1, reaching 7.1 ×10^5 g C_2H_4/(mol M h atm), whilst the nickel chloride complex **32a** (Scheme 17) at an Al/Ni ratio 1000:1 attained an activity of 4.4 ×10^5 g C_2H_4/(mol M h atm) (entries 1-9, table10). In addition, the reaction temperature affected the catalytic activity (entries 10-13, table10) as well as the lifetime of the catalysts. It was found that a lower temperature can extend the lifetime of the catalyst. For example, at 5 °C, the catalyst can retain good activity over an hour, while at higher temperatures (60 °C) the catalyst lifetime shortens to only 10 min. The distribution of the oligomeric products was observed as three fractions, the major product α-butene, as well as α-hexene and other hexene isomers. Changing the reaction parameters such as temperature and Al/Ni molar ratio merely affects the product distribution over a limited range, which implies that there may be strong β-hydrogen elimination of the reaction intermediate. There were no significant differences for the oligomer distributions between the catalysts **32a** (Scheme 17) and **32b** (Scheme 17) (entries 1-9, table10), which suggested an analogous active species was working for both catalysts.[51]

Table 10. Ethylene oligomerization by **32a** and **32b**[51] /MAO systems [a]

entry	catalyst	temp.(^{o}C)	Al/M	Activity[a]	C_4 [b]	α-C_4 [c]	C_6 [b]	α-C_6 [c]
1	32a	20	500	1.5	85.3	100	14.7	71.4
2	32a	20	1000	4.4	88.7	100	11.3	17.9
3	32a	20	2000	2.7	80.0	100	19.6	-
4	32a	20	3000	2.0	83.9	100	16.1	22.2
5	32b	20	500	1.7	100	100	-	-
6	32b	20	1000	2.0	89.3	100	10.7	-
7	32b	20	1500	2.7	89.2	100	10.8	44.3
8	32b	20	2000	3.5	90.3	100	9.7	-
9	32b	20	3000	7.1	77.5	100	22.5	12
10	32b	5	1000	1.1	85.2	100	14.8	26.8
11	32b	30	1000	3.1	82.1	100	17.9	19.1
12	32b	40	1000	0.69	100	100	-	-
13	32b	60	1000	0.1	100	100	-	-

[a] 10^5 g C_2H_4/(mol M h atm); [b] Weight percentage of olefins; [c] α-olefin percentage in its corresponding C_4 or C_6.



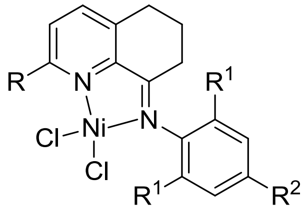
33a: X=Br; **33b**:X=Cl **34a**: R=Me; **34b**: R=Et; **34c**: R=^{i}Pr

Scheme 18 *N*,*N*-bi-dentate nickel complexes **33a-b** and **34a-c**[52,53]

We have also studied the oligomerization behaviour of the complexes **33a-b** and **34a-c** (Scheme 18).[52,53] Upon treatment with diethylaluminium chloride (Et_2AlCl), the nickel pre-catalyst **33a** exhibited high activity for ethylene oligomerization with good thermal stability at 60 ^{o}C under 10 atm of ethylene. For example, the highest activity can reach as high as 1.83 × 10^6 g mol^{-1}(Ni) h^{-1} and the selectivity for C_4 can reach

86.5 under the optimum reaction conditions of molar ratio Et_2AlCl/Ni at 200 : 1, 60 ^oC and 10 atm ethylene.[52] Compared with the bromide analogues **33a**, relatively lower activities were exhibited by the complex **33b** bearing chlorine, presumably because of the better solubility associated with the latter, for example, the highest activity can reach 1.1×10^6 g mol^{-1}(Ni) h^{-1} and the selectivity for C_4 reached 90.7 under the same polymerization conditions. Upon addition of 25 equivalents of PPh_3 to the catalytic system, the catalytic activity of **33a** was greatly increased, with activities observed as high as 1.72×10^7 g mol^{-1}(Ni) h^{-1}, which is almost an order of magnitude higher than those without PPh_3. In addition, the selectivity for α-C4 was dramatically decreased. It is believed that the auxiliary PPh_3 protects the active species during the catalytic reaction, and induces isomerization along with β-hydrogen elimination.[52]

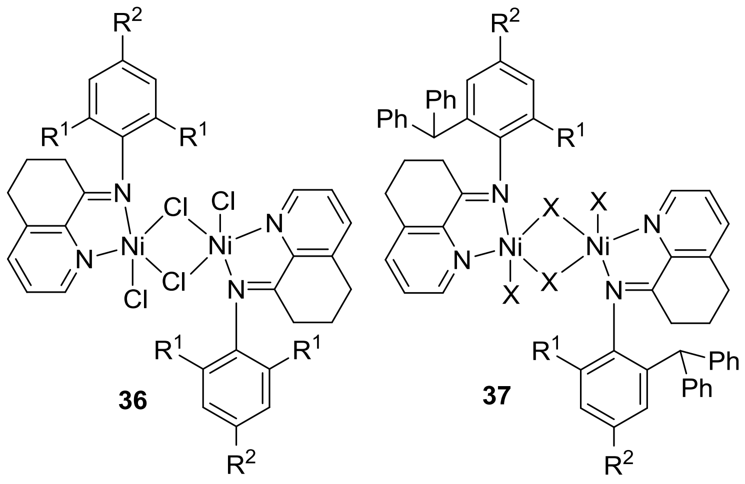
On treatment with diethylaluminium chloride (Et_2AlCl) or ethylaluminium sesquichloride (EASC), the nickel pre-catalysts **34a-c** exhibited high activity for selective ethylene dimerization ($0.89\text{-}3.29 \times 10^6$ g mol^{-1}(Ni) h^{-1}) at 20 ^oC under 10 atm of ethylene.[53] The catalytic activities decreased on elevating the reaction temperature. Further research indicated that the ligand substituents had a remarkable influence on the observed activities. The highest activity was obtained with complexes having R as methyl, R^1 as isopropyl and R^2 as hydrogen, reaching 2.4×10^6 g mol^{-1}(Ni) h^{-1} when treated with Et_2AlCl. This implied that the less bulky R group was favourable for enhanced activity. It could also be observed that electron-withdrawing substituents at the R^2 position led to lower activities. Under optimized conditions, the activity was as high as 3.29×10^6 g mol^{-1} (Ni) h^{-1} with EASC. However, the influence on selectivity for α-olefins was not so obvious.[53]



35a:R=Cl; **35b:**R=Ph;
35c:R=Me; **35d:**R=^{i}Pr

Scheme 19 *N*,*N*-bi-dentate nickel complexes **35a-d** [54,55]

Our group has also investigated the ethylene oligomerization behaviour of the nickel complexes **35a-d** (Scheme 19) when activated by EASC.[54,55] The two sets of data were comparable on the basis of ligands with different R substituents (chloro and Ph) at 20 ^{o}C with the molar ratio of Al/Ni = 400 : 1. The activities decreased in the order 2,6-di(*i*Pr) > 2,6-di(Et) > 2,6-di(Me) > 2,6-di(Et)-4-Me > 2,4,6-tri(Me) with R=Cl; meanwhile, with R=Ph, the activities decreased in the order 2,6-di(*i*Pr) > 2,6-di(Et) > 2,6-di(Me), and 2,6-di(Et)-4-Me > 2,4,6-tri(Me). Such phenomena are consistent with bulky alkyl substituents aiding the solubility of pre-catalysts, which in-turn enhances activity. The activity for **35b** (R=Ph) was much smaller than those for **35a** (R=Cl) due to the steric influence of R around the nickel centre.[54] The same phenomenon has also been observed for **35c** (R=Me) and **35d** (R=*i*Pr), for which the activities observed for **35d** (R=*i*Pr) were lower than those of **35c** (R=Me). In addition, the highest activity of 4.30×10^5 g mol^{-1} (Ni)h^{-1} was observed at 80 ^{o}C by the complexes **35c**, which showed good thermal stability.[55]

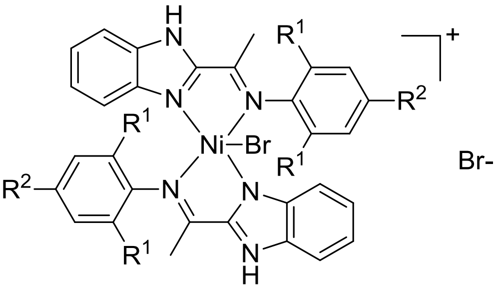


R^1	Me	Me	$-CH(Ph)_2$	$-CH(Ph)_2$
R2	$-CH(Ph)_2$	Me	Me	^iPr
X=Cl	**37a**	**37b**	**37c**	**37d**
X=Br	**37e**	**37f**	**37g**	**37h**

Scheme 20 *N*,*N*-bi-dentate nickel complexes **36** and **37a-h**[56,57]

We have also investigated the ethylene polymerization behaviour by the complexes **36** and **37a-h** (Scheme 20) using diethylaluminium chloride (Et_2AlCl) or methylaluminoxane (MAO) as the co-catalyst.[56,57] Upon treatment with either MAO or Et_2AlCl, the pre-catalysts **36** worked as single-site catalysts for ethylene polymerization, forming polyethylene waxes with an activity of up to 10^7 g(PE) mol(Ni)$^{-1}$ h^{-1}. The molecular weights and distributions of the polyethylene waxes could be controlled by modifying the nature of the different ligands present and the reaction conditions. The resultant polyethylenes were shown to be highly branched polymers.[56]

When a number of bulky substituents were introduced to the *N*-(5,6,7-trihydroquinolinylidene)-2-benzhydrylbenzenamines-Ni(II) pre-catalysts **37a-h** (Scheme 20), catalytic screening revealed that all the nickel complexes **37a-h** exhibited high activity (up to 5.66 ×10^6 g mol(Ni)$^{-1}$·h^{-1}) for ethylene polymerization, producing highly branched wax-like products with narrow molecular weight distribution when activated by MAO or Et_2AlCl.[57] The activity decreased sharply when the *ortho*-position of the phenyl ring was occupied by a bulky dibenzhydryl [-$CH(Ph)_2$] group. Contrastingly, the substituent at the *para*-position played a relatively minor role in influencing the catalytic activity of the ethylene polymerization (**37a**>**37b**>**37c**>**37d**). When the halogen at the nickel was bromide, the activities showed much lower values than did the corresponding nickel chloride complexes; similar trends with the other ligand variations were noted (**37e** > **37f** > **37g** > **37h**). The molecular weight of the resultant polymer can be easily controlled through ligand modification, *i.e.* substituent variation.[57]

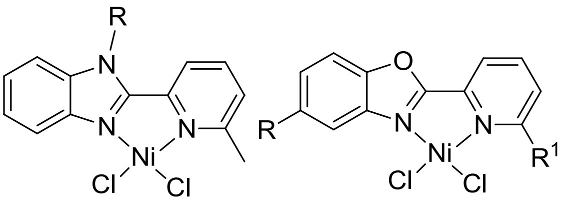


38

38a $R^1=CH_3$, $R^2=H$;
38b $R^1=CH_3$, $R^1=CH_3$,
38c $R^1={}^iPr$, $R^2=H$
38d $R^1=CH_3$, $R^2=Br$
38e $R^1=Et$, $R^2=H$

Scheme 21 *N*,*N*-bi-dentate nickel complexes **38a-e** [58]

The Li group have researched ethylene oligomerization using the nickel complexes **38a-e** (Scheme 21) bearing 2-aryliminobenzimidazole ligands.[58] Upon treatment with methylaluminoxane (MAO), the complexes **38a-e** were active ethylene oligomerization catalysts. The catalytic activity of complex **38b** was sensitive to reaction temperature. Lower temperatures were generally favorable; the best catalytic temperature was 15 °C. The steric and electronic environment around the central metal affects the catalytic activities and the distribution of oligomers. The order of their activities were **38d** > **38a** > **38b** > **38c** > **38e** under the same reaction conditions. Complex **38d** showed the highest activity at 2.35×10^5 g (ethylene) mol^{-1} (Ni) h^{-1}. The oligomers were a mixture of α-olefins and internal olefins in range C_4 to C_{18}.[58]



39a: R=H;
39b: R=Me

40

	40a	40b	40c	40d	40e	40f	40g	40h
R	H	Me	t-Bu	H	H	Me	t-Bu	H
R^1	Me	Me	Me	H	Me	Me	Me	H
X	Cl	Cl	Cl	Cl	Br	Br	Br	Br

Scheme 22 *N*,*N*-bi-dentate nickel complexes **39a-b** and **40a-h** [59,60]

We have studied the ethylene oligomerization behaviour of the nickel complexes **39a-b** (Scheme 22) bearing 2-benzimidazolylpyridines[59] and the nickel complexes **40a-h** (Scheme 22) bearing benzoxazolylpyridines.[60] Comparing the nickel complexes **39b** for which the activity is 0.83×10^4 g (ethylene) mol^{-1} (Ni) h^{-1} atm^{-1}, the complexes **39a** had relatively higher activity at 3.15×10^4 g (ethylene) mol^{-1} (Ni) h^{-1} atm^{-1} under the same polymerization conditions.[59]

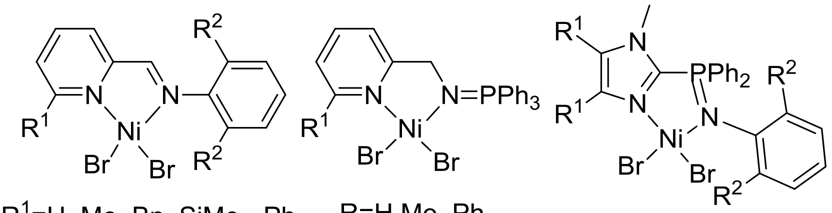
Upon activation with diethylaluminium chloride (Et_2AlCl), the complexes **40a-h** (Scheme 22) exhibited moderate to good catalytic activity for ethylene oligomerization (27–415 g $mmol^{-1}$(Ni) h^{-1} bar^{-1}) with high selectivity for ethylene dimerization to form α-butene.[60] The use of alternative substituents on the ligands strongly affected the catalytic activities of their corresponding nickel complexes. With bulky substituents on the pyridine ring as well as on the benzoxazole ring, the activity of the pre-catalyst was greatly enhanced. Under mild conditions (200 equiv. of

Et_2AlCl, reaction temperature 20 °C), complex **40c**, with a 2-methyl group on the pyridine ring and a 5-*t*-butyl substituent on the benzoxazole ring, exhibited an activity of 404 g $mmol^{-1}$(Ni) h^{-1} bar^{-1}, while nickel complex **40d**, without substituents on the pyridine and benzoxazole rings, exhibited a relatively lower value at 50 g $mmol^{-1}$(Ni) h^{-1} bar^{-1}.[39] More bulky substituents resulted in better catalytic activities and their nickel chlorides showed higher activities than did the bromide analogues. As shown in Table 11, the ethylene oligomerization activity varied in the order **40c** >**40b** >**40a** > **40d** (entries 1-4, table 11) and **40g** > **40f** > **40e** > **40h** (entries 5-8, table 11). This could be explained in terms of the bulky substituents protecting the active sites and enhancing their catalytic activities.[60]

Table 11. Ethylene oligomerization by nickel complexes[60] **40a–h/** Et_2AlCl [a]

entry	catalyst	activity/10^2g $mmol^{-1}$(Ni)$h^{-1}$$bar^{-1}$	oligomer distribution[b] (%)[b]		
			$C_4/\Sigma C$	α-C_4	$C_6/\Sigma C$
1	**40a**	2.10	98.5	72.0	1.5
2	**40b**	2.12	98.9	82.1	1.1
3	**40c**	4.04	99.1	84.9	0.9
4	**40d**	0.50	98.2	93.4	1.8
5	**40e**	1.40	98.6	82.9	1.4
6	**40f**	1.98	98.5	76.3	1.5
7	**40g**	2.76	98.7	75.9	1.3
8	**40h**	0.27	100	100	0

[a] Conditions: 5 μmol Ni, 200 equiv. Et_2AlCl, 20 °C, 10 atm C_2H_4, 30 min, 100 mL of toluene. [b] Determined by GC.



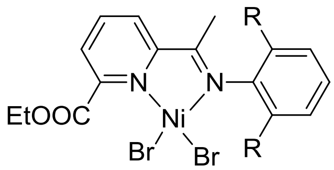
R^1=H, Me, Bn, SiMe$_3$, Ph
41

R=H,Me, Ph
42

R=H, Ph, C_4H_4, t-Bu
43

Scheme 23 *N,N*-bi-dentate nickel complexes **41-43** [61]

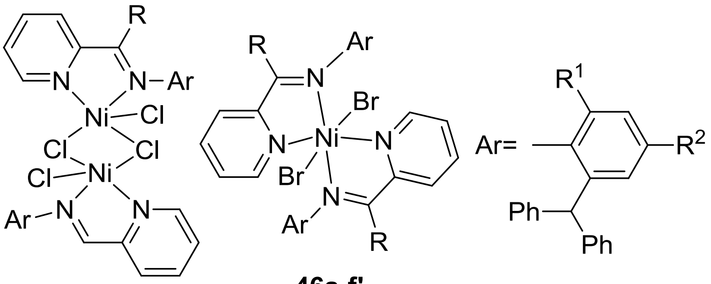
Stephan and coworkers have synthesized a series of complexes **41-43** (Scheme 23) bearing a variety of different substituents, and developed synthetic methods for preparing different classes of dissymmetric phosphinimine chelate ligands.[61] Preliminary screening for activity as catalyst precursors for ethylene polymerization indicated that ethylene oligomerization may be occurring. In the case of complexes **41-43** (Scheme 23), activation with either MAO (toluene as the solvent) or Et_2AlCl (ClC_6H_5 as the solvent) at 35 °C under 20 atm of ethylene effected modest catalytic dimerization of ethylene to mainly C_4 alkenes, for which the activities varied from 2.1 to 48.2 (g of cat.)$^{-1}$ h^{-1} atm^{-1}. [61]



44a: R=^{i}Pr, X=Cl;
44b: R=Cl, X=Br;
44c: R=Br, X=Br.

Scheme 24 *N,N*-bi-dentate nickel complexes **44a-c** [62]

We have synthesized a series of nickel complexes **44a-c** (Scheme 24) bearing 2-carboxylate-6-iminopyridine ligands and studied their properties in terms of ethylene oligomerization.[62] Upon activation with MAO, the complexes **44a-c** showed considerable catalytic activities for ethylene oligomerization with C_4–C_8 olefins as the main products. The ligand environment had a considerable effect on catalytic behavior, such as activity and product distribution. The oligomerization activity (5.47 × 10^4 g mol^{-1} (Ni) h^{-1}) of the complex **44a** with a donating diisopropyl substituted ligand was lower than **44b** (12.10 × 10^4 g mol^{-1} (Ni) h^{-1}) and **44c** (9.04 × 10^4 g mol^{-1} (Ni) h^{-1}) with halogen substituents in the ligand backbone. The complex **44a** produced oligomers with higher order of carbon numbered olefins (C_8 over 40%) and more polyethylene than **44b** (no polymerization) and **44c** with halogen substituents in the ligand backbone. In addtion, the complexes **44c** with dibromo-substitution generated polyethylene in lower activity than **44b** with dichlorine-substituted, while the less bulky substituted **44b** produced only oligomers, which was consistent with the general rule that bulky substituents at the *ortho*-positions provide efficient steric blocking at the axial sites and retard β-hydrogen elimination. Thus, the higher carbon numbered oligomers are favored by pre-catalysts with bulkier substituents.[62]



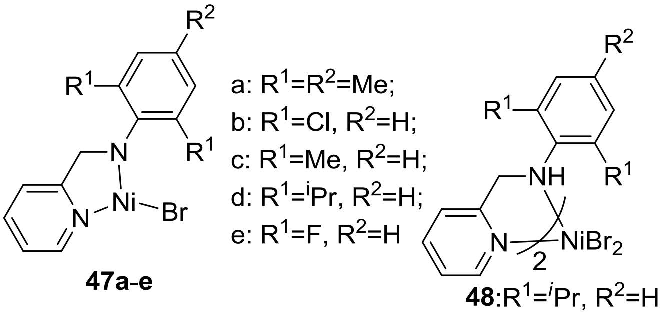
45a-f'

46a-f'

R^1	Me	Et	^{i}Pr	$CH(PH)_2$	$CH(PH)_2$	$CH(PH)_2$	Me
R^2	$CH(PH)_2$	$CH(PH)_2$	$CH(PH)_2$	Me	^{i}Pr	Cl	Me
R=H	**La**	**Lb**	**Lc**	**Ld**	**Le**	**Lf**	**Lg**
R=Me	**La'**	**Lb'**	**Lc'**	**Ld'**	**Le'**	**Lf'**	-

Scheme 25 *N*,*N*-bi-dentate nickel complexes **45a-f'** [63]

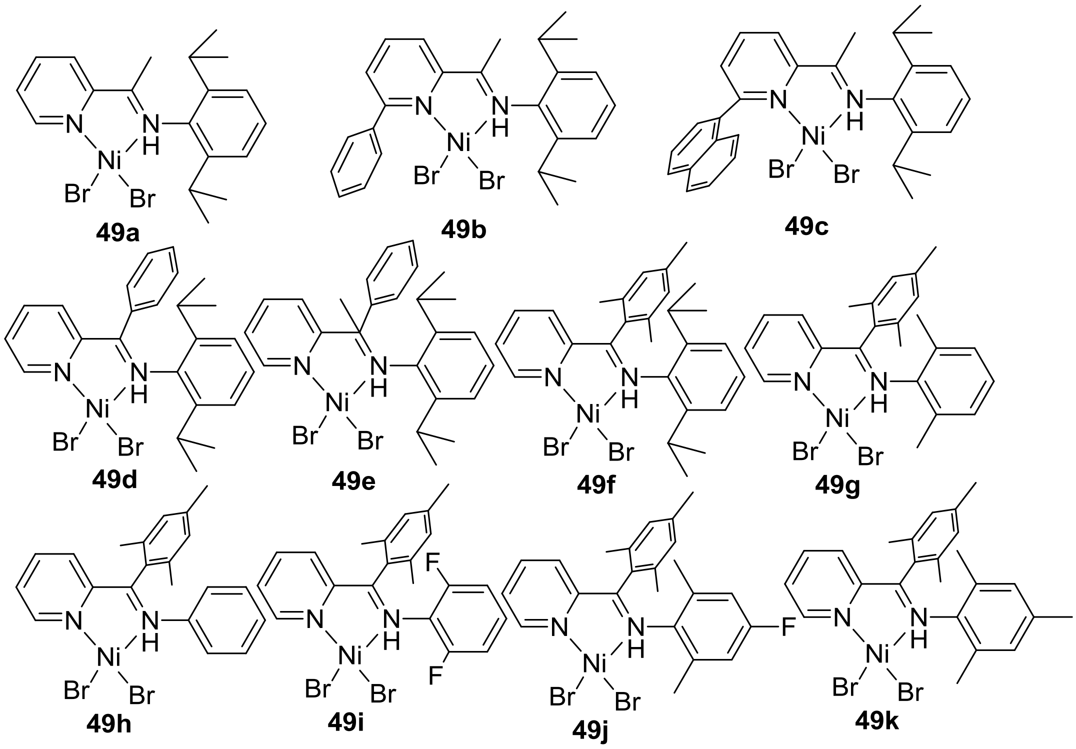
Our group have synthesized a series of 2-(2-benzhydrylbenzenamino)pyridine ligands (**La-Lf'**, Scheme 25) which were used as bi-dentate N^N ligands with nickel halides to afford the corresponding nickel dihalide complexes $L_2Ni_2Cl_4$ **45a-f'** (Scheme 25) and L_2NiBr_2 **46a-f'** (Scheme 25).[42] Upon activation with either methylaluminoxane (MAO) or ethylaluminium sesquichloride ($Et_3Al_2Cl_3$, EASC), these nickel complexes exhibited high activities of up to 1.39×10^7 g mol^{-1} (Ni) h^{-1} in ethylene polymerization under optimum conditions, and produced moderately branched polyethylene of low molecular weight and narrow PDI, indicative of single-site active species. The catalytic activities and the molecular weights decreased on elevating the reaction temperature. Further research efforts indicated that the ligand substituents present had a remarkable influence on the observed activities. The highest activity was obtained with the complex **46f** having R as hydrogen, R^1 as benzhydryl and R^2 as chlorine. Such pre-catalysts could have application in the industrialized production of polyethylene waxes.[63]



Scheme 26 *N*,*N*-bi-dentate nickel complexes **47a-e and 48** [64]

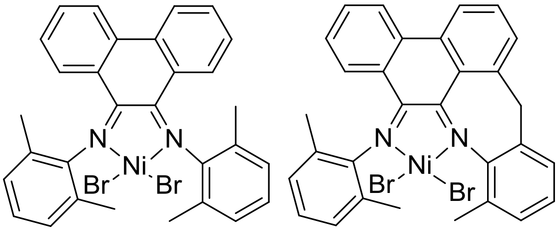
The Wu group have synthesized a series of 2-aminopyridine Ni(II) complexes **47a-e** and **48** (Scheme 26) bearing different substituent groups and investigated the catalysis behaviour for ethylene polymerization in the presence of methylaluminoxane

(MAO).[64] The Ni(II) complexes **47a-e** and **48** (Scheme 26) with *ortho*-alkyl-substitution can catalyze ethylene polymerization effectively in the presence of MAO and produced high molecular weight branched polymers as well as short chain oligomers simultaneously. The catalytic activity, polymer/oligomer ratio, molecular weight, and branching density of the solid polymer depended on the polymerization conditions and the steric and electronic effect of the *ortho*-aryl-substituents of the ligand. Enhancing the steric bulk of the *ortho*-aryl-substituents of the catalyst resulted in a higher ratio of solid polymer to oligomer and a higher molecular weight for the polymer. With *ortho*-dihalosubstitution, the catalysts afforded a product with a low polymer/oligomer ratio (**47b**) and even oligomers only (**47e**); $C_{14}H_{28}$ had the maximum content. Compared with complex **47d** containing an ionic ligand, the complex **48** containing a neutral ligand exhibited lower catalytic activity for ethylene polymerization. These results indicated that the steric bulk of the *ortho*-aryl-substituent favors a high polymer/oligomer ratio and a high molecular weight for the solid polymer, whilst strong electron-withdrawing *ortho*-aryl-substituent favors oligomer production. At high polymerization temperature and low ethylene pressure, a branched polyethylene having high branching density of up to 108 branches/1000C can be obtained using **47a**.[64]



Scheme 27 *N*,*N*-bi-dentate nickel complexes **49a-k** [65,66]

The Wu group have evaluated the substituent effects of catalyst precursors on the reactivity of ethylene polymerization using the pyridine-amine nickel complexes **49a-k** (Scheme 27).[65,66] Substituent effects, including the steric effect of the pyridine moiety, steric effect of the bridge carbon, and steric and electronic effects of the amine moiety, were investigated systematically. The variation of the pyridine-amine framework had a decisive influence on ethylene polymerization. Introduction of bulky aryls onto the pyridine moiety of the amine pyridine nickel led to a significant decrease in the activity and molecular weight of polyethylene, whereas an increase in bulk of substituents on the bridge carbon causes an increase in the polymerization activity and molecular weight of the polyethylene. For the amine moiety, increasing the steric hindrance resulted in decreased activity and afforded a higher molecular weight polyethylene with a narrower polydispersity. Introduction of an electron-donating group on the amine moiety led to formation of a high molecular weight polyethylene with enhanced activity. By optimizing the ligand framework parameters and the reaction conditions, two bulky pyridine-amine nickel complexes were also developed successfully as catalyst precursors for the living polymerization of ethylene. The results showed that two coordinating functionalities (pyridine (sp^2) and amine (sp^3)) can confer distinctive effects and reactivity controls on ethylene polymerization, and that the substituents on the bridge carbon are located at a strategic place for stability, activity, molecular weight of the polymer, and the living polymerization of ethylene. By optimization of the variations in the pyridine-amine frameworks, a living polymerization of ethylene can be achieved using two new pyridineamine nickel catalysts. This type of ethylene living polymerization catalyst will provide more choices for the precise synthesis of monodispersed PE and the corresponding block co-polymers.[65,66]

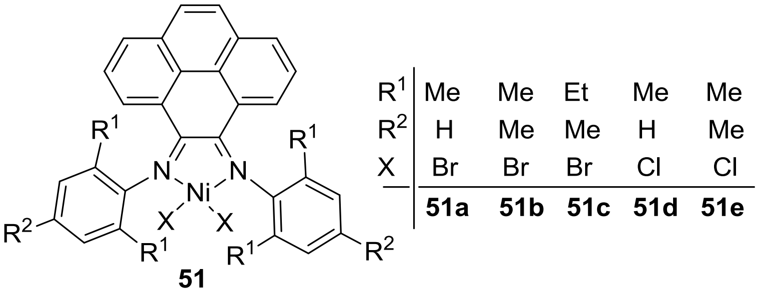


50a

50b

Scheme 28 *N*,*N*-bi-dentate nickel complexes **50a** and **50b** [67]

Li and coworkers have investigated the of ethylene polymerization properties of the nickel dibromide complexes **50a** and **50b** (Scheme 28).[67] Both complexes **50a** and **50b** showed good activities for ethylene polymerisation, in the presence of MAO. The resultant polyethylene obtained by complexes **50a** and **50b** have comparable structures of branching to the Brookhart's α-diimine nickel complexes. Complex **50a** exhibited a higher polymerisation activity than complex **50b**, and yielded polyethylene with higher molecular weight and less extensive branching. Additionally, complex **50a** yielded ultra-high molecular weight polyethylene at low temperature (e.g., 1.26×10^{6} g/mol at -15 ^{o}C), significantly higher than those produced by the corresponding 2,3-butanedione- or acenaphthenequinone-based α-diimine nickel complexes. It was shown that the catalyst structure and reaction conditions, for example reaction temperature and concentration of activator (MAO), have a substantial influence on the polymerisation activities, molecular weights and microstructures of the resulting polymers.[67]



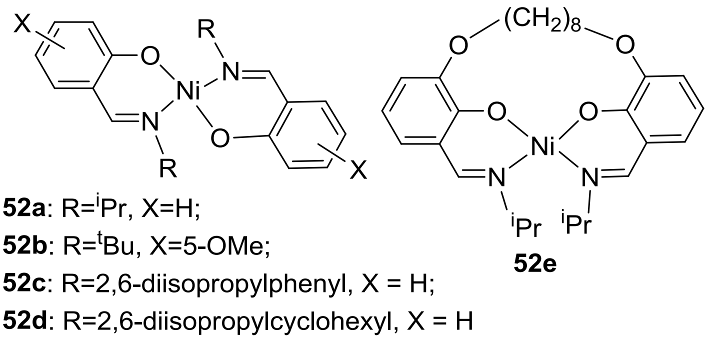
R^1	Me	Me	Et	Me	Me
R^2	H	Me	Me	H	Me
X	Br	Br	Br	Cl	Cl
	51a	**51b**	**51c**	**51d**	**51e**

Scheme 29 *N*,*N*-bi-dentate nickel complexes **51a-e**[68]

Our group have synthesized the nickel halide complexes **51a-e** (Scheme 29) bearing 4,5-bis(arylimino)pyrenylidenes.[68] Upon treatment with the co-catalysts MAO, EASC or MMAO, all the nickel pre-catalysts exhibited high activities (of up to 4.42×10^{6} g(PE) mol(Ni)$^{-1}$ h^{-1}) for ethylene polymerization, and produced polyethylene products with a high degree of branching (up to 130 branched per 1000 carbons) and narrow molecular weight distribution.[68] Whether activated by EASC, MAO or Et_2AlCl, the order of the catalytic activity decreased in the order **51c** >**51b** > **51a** for the bromides, and **51e** > **51d** for the chlorides under the optimum conditions, in line with the decreasing bulk of the aniline-derived aryl groups.[68]

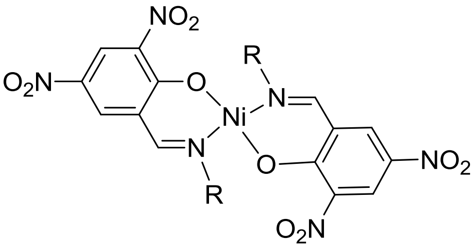
2.2 [N^O] and [N^P]bi-dentate nickel complex pre-catalysts

Extensive work on ethylene polymerization using bi-dentate Ni-based catalysts include ligands of the type *N^O* and *N^P* has been conducted.



Scheme 30 *N*,*O*-bi-dentate nickel complexes **52a-e** [69]

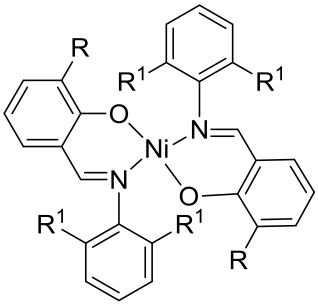
The Carlini group have studied the reactivity of bis(salicylaldiminate)nickel(II) complexes **52a-e** (Scheme 30) with organoaluminium compounds under an ethylene atmosphere, and eventually in the presence of an ancillary phosphine ligand.[69] The catalysts exhibited very high activity with turnover frequencies (TOFs) of up to 10^5 – 10^7 h^{-1}, though this was mainly oligomerization rather than the polymerization of ethylene when activitied by MAO. Changing the nature of the nickel precursor **52** and the reaction parameters, it was possible to strongly modify the chemo- and regio-selectivity of the catalytic process towards the formation of target olefin products, particularly 1-hexene. Depending on the type of **52**, minor amounts of polymeric products were also obtained.[69] The activity of **52c** was high when activated by MAO, for which the TOF reached to 16.5 × 10^5 h^{-1}, and the oligomer distribution was C4 (37.2 %), C6 (41.1 %) and C8 (21.7 %). Compared with **52c,** the catalytic activity (TOF ～ 1 × 10^5 h^{-1}) of complexe **52a** decreased by one order of magnitude. However, in addition to the C_4 and C_6 oligomers, a polymeric product was also obtained (about 20 %). Quite similar results were obtained for complex **52b**, for which the activity was found to correspond to a TOF of 4.5 × 10^5 h^{-1} and about 8 % of a polymeric product was formed. The complex **52d**, a precursor similar to **52c** except for the presence of a cyclohexyl (instead of a phenyl group) on the salicylaldiminate ligand, exhibited an extremely large activity (TOF = 24.0 × 10^5 h^{-1}) and formed mainly of C4 and C6 oligomers. The precursor **52e**, where the two salicylaldiminate moieties bound to the metal are linked together through a dioxyoctamethylene bridge, was found to be completely inactive when treated with MAO. This result is indirect confirmation that, due to the structural requirements of **52e**, until a salicylaldiminate ligand is released from the metal center, no activation occurs, the MAO probably being not able to give an alkyl-metal species when a bis-bidentate ligand is firmly coordinated to the metal. [69]



53a: R=2,6-diisopropylphenyl
53b: R=Ph

Scheme 31 *N*,*O*-bi-dentate nickel complexes **53a-b** [70]

Carlini and his coworkers have investigated the homo-polymerization of ethylene by using different catalytic systems based on the dinitro-substituted bis(salicylaldiminate)nickel(II) precursors bis[3,5- dinitro-*N*(2,6-diisopropylphenyl)] nickel(II) **53a** (Scheme 31) and bis[3,5-dinitro-*N*(phenyl)]nickel(II) **53b** (Scheme 31) in combination with organoaluminium compounds.[70] The activities of the complexes **53a** and **53b** were high, up to 200 kg polyethylene/(mol Ni × h), affording linear high-molecular-weight polymer. The presence of electron withdrawing nitro groups on the phenoxy moiety of the ligand was a crucial requirement for obtaining high polymerization activity without the formation of oligomeric products. The absence of bulky groups in *ortho* positions at the *N*-aryl moiety of the ligand, contrary to what was observed for other nickel systems, not only did not cause the formation of oligomeric products but also did not largely reduce the molecular weight of the resulting PE, indeed, the only effect being a remarkable decrease of the polymerization activity.[70]

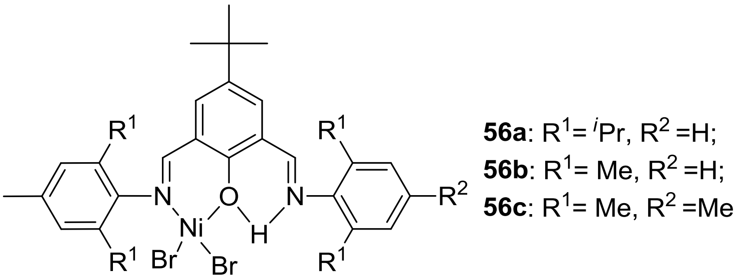


54a: R^1=Me, R=H;
54b: R^1=Et, R=H;
54c: R^1=^{i}Pr, R=H;
55a: R^1=Me, R=^{t}Bu;
55b: R^1=Et, R=^{t}Bu;
55c: R^1=^{i}Pr, R=^{t}Bu;

Scheme 32 *N*,*O*-bi-dentate nickel complexes **54a-c** and **55a-c** [71]

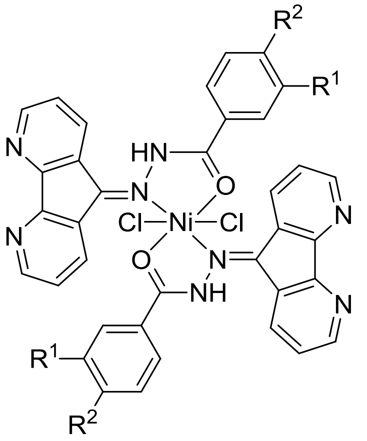
Kim and his coworkers have studied ethylene oligomerization by the complexes **54a-c** and **55a-c** (Scheme 32), which bear bi-dentate phenoxy-imine ligands. [71]

Indirect evidence of the formation of the active species in the presence of an EAS co-catalyst could be collected using UV–vis spectroscopy. The formation of an active species was observed at [Al]/[Ni] = 25, and this spectroscopic result was in good agreement with the actual polymerization result. All the nickel complexes in this study exhibited extremely high activities ((5.21 – 6.21) × 10^8 g oligomer/mol Ni h atm) under moderate conditions (30 °C, 1.3 atm) in the presence of 200 equivalents of aluminium sesquichloride in toluene solvent. The catalytic activity was almost independent of the catalyst structure. Variation of the catalyst bulk did not dramatically affect the α-olefin content or distribution of oligomers. Due to the low activation energy needed to produce the cationic active species, the **54c**/EAS catalyst system revealed a very high activity at low oligomerization temperatures (10 °C). Utilization of aliphatic hydrocarbon (hexane) and halogenated compounds (methylene chloride) as solvents resulted in sharp reductions in activity, compared to toluene. By changing the parameters such as co-catalyst concentration and temperature as well as reaction medium, the product distribution could be controlled to some degree, but they were not the decisive factors when it came to controlling the product distribution. [71]



Scheme 33 *N*,*O*-bi-dentate nickel complexes **56a-c** [72]

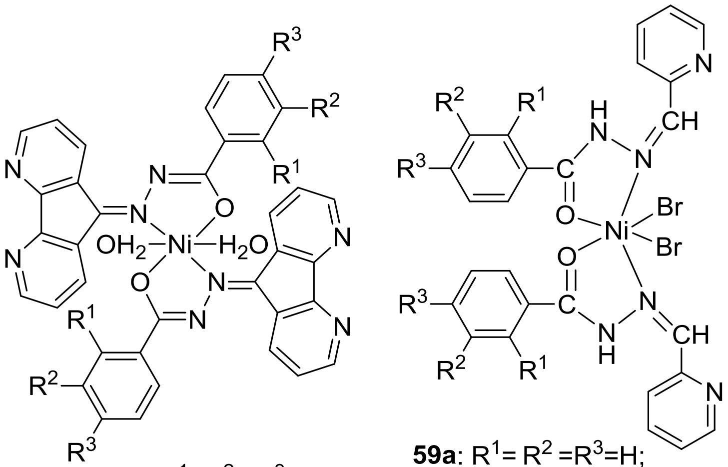
Our group has studied the characteristics of the ethylene oligomerization reaction using the complexes **56a-c** (Scheme 33) bearing 2,6-bis(imino)phenoxy ligands.[72] Upon treatment with methylaluminoxane (MAO), the complexes **56a-c** were active for ethylene oligomerization, and the most active was complex **56c**, which reached 2.1×10^5 g mol^{-1} h^{-1} atm^{-1} . The Ni complexes **56a-c** gave higher olefins such as 1-hexene and 1-octene along with 1-butylene. The stereochemistry of the ligands affected their catalytic activities. Furthermore, a reduction in the steric bulk at the *ortho*-aryl position resulted in an increase of activity. The complex **56a** contains isopropyl groups at the *ortho* positions of the aryl rings and displayed an activity of 1.2 × 10^5 g mol^{-1} atm^{-1} h^{-1}, whilst complex **56b** with dimethyl on the aryl ring had an activity of 1.9 × 10^5 g mol^{-1} atm^{-1} h^{-1}. Methyl substitution at the *para*-position of the aryl (**56c**) resulted in a slight increase of catalytic activity.[72]



57a: R^1= R^2 =H;
57b: R^1= H, R^2 =NO_2;
57c: R^1= NO_2, R^2 =H

Scheme 34 *N*,*O*-bi-dentate nickel complexes **57a-c** [73]

Our group has investigated ethylene oligomerization using the hydrazone nickel complexes **57a-c** (Scheme 34) when activated by methylaluminoxane (MAO) in toluene.[73] The catalytic complexes **57a-c** mainly assisted the dimerization of ethylene with moderate to high catalytic activities (10^5 to 10^4 gmol^{-1} h^{-1}) at ambient pressure. The nickel(II) complex **57a** without a nitro-substituent on its aryl ring exhibited a higher catalytic activity compared with the other two analogues. Due to electron-withdrawing nitro-group in the two precursors **57b** and **57c**, ethylene was firmly coordinated on the metal center and migratory insertion was also hindered. Therefore, catalyst **57a** performed the best activities among this grouping. [73]



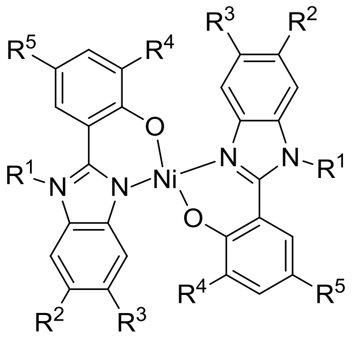
58a: R^1=R^2 =R^3=H;
58b: R^1= Me, R^2 =R^3=H;
58c: R^2= Me, R^1 =R^3=H;
59d: R^3=Me, R^1 =R^2=H

59a: R^1= R^2 =R^3=H;
59b: R^1=Cl, R^2 =R^3=H;
59c: R^1=Me, R^2 =R^3=H;
59d: R^2=MeO, R^1 =R^3=H;
59e: R^3=Me, R^1=R^2=H

Scheme 35 *N*,*O*-bi-dentate nickel complexes **58a-d** and **59a-e** [74]

We have synthesized two kinds of nickel complexes **58a-d** and **59a-e** (Scheme 35) bearing acylhydrazone and studied their properties in terms of ethylene oligomerization.[74] The nickel(II) centers are six-coordinate with two corresponding *N*,*O*-bi-dentate ligands and two coordinated solvent molecules for **58a-d**, while the geometry around the nickel atom of **59a-e** is distorted octahedral with two bi-dentate ligands and two bromides. Upon activation with methylaluminoxane, all nickel complexes revealed considerable activities for ethylene oligomerization at ambient pressure.[74]

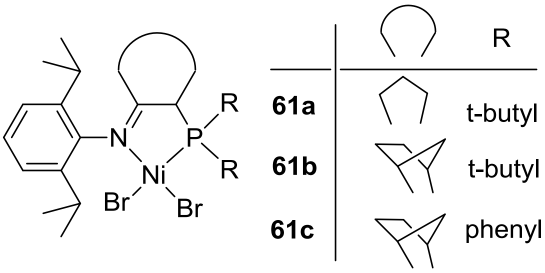
Complex **58d** showed the highest catalytic activity at 3.62 × 10^5 g mol^{-1} atm^{-1} h^{-1} for the Al/Ni molar ratio of 100:1 at 30 °C. The oligomerization products formed by **58a-d** and **59a-e** were mainly C_4 and C_6. Compared to the activity (1.23×10^5 g mol^{-1} h^{-1}, Al/Ni = 500) of nickel complexes **57a** (Scheme 34),[73] the complex **58a** showed a lower activity (8.56×10^4 g mol^{-1} h^{-1}, Al/Ni = 500).[74] The coordination model affected the coordination and insertion of ethylene. The variation of ligands clearly affected the activities of the corresponding complexes; i.e., the phenyl ring containing an additional alkyl substituent impaired the catalytic activity for ethylene oligomerization. Under mild catalytic conditions (Al/Ni = 100, 30 ◦C), **58d** with a 4-methyl group on the phenyl ring exhibited a catalytic activity of 3.62 × 10^5 g mol^{-1} h^{-1}, whilst **58b** with 2-methyl groups on the phenyl ring showed a relatively lower value of 5.09 × 10^4 g mol^{-1} h^{-1}. As for **59a-e**, the introduction of chloro and methyl-groups into the ligands affected the catalytic activities. The order of the activity was **59e** > **59a** > **59d** > **59b** > **59c**. From the two series of catalytic systems, it is concluded that the **58d**/MAO and **59e**/MAO systems, which contain a methyl substituent at the 4-position of the ligand phenyl ring show the highest catalytic activities.[74]



60a: $R^1 = R^2 = R^3 = R^4 = R^5 = H$;
60b: $R^1 = R^3 = R^4 = R^5 = H$; $R^2 = CH_3$;
60c: $R^1 = R^4 = R^5 = H$; $R^2 = R^3 = CH_3$;
60d: $R^1 = {}^iPr$, $R^2 = R^3 = R^4 = R^5 = H$;
60e: $R^1 = {}^iPr$, $R^2 = R^3 = H$; $R^4 = R^5 = Cl$;
60f: $R^1 = {}^iPr$, $R^2 = R^3 = R^4 = H$; $R^5 = CH_3O$

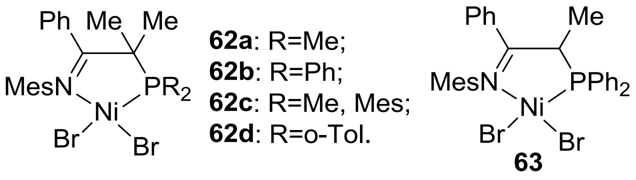
Scheme 36 *N*,*O*-bi-dentate nickel complexes **60a-f** [75]

We have also investigated the ethylene oligomerization behaviour of the nickel complexes **60a-f** (Scheme 36) containing 2-(1*H*-benzimidazol-2-yl)-phenoxy ligands.[75] When activated by Et_2AlCl, the nickel complexes **60a-f** exhibited considerably high catalytic activities for ethylene oligomerization with C_4-C_6 olefins as the main products. The ligand environment had a considerable effect on the catalyst behaviour, such as catalyst activity and the distribution of products. Under similar conditions, the activity decreased in the order **60c** < **60b** < **60a**, which indicated that the more substituted the phenyl group, the lower the ethylene reactivity. On the other hand, the incorporation of an isopropyl group on the N atom of the imidazole led to a decrease in ethylene reactivity. The complex **60d** showed lower activity than **60a**. Complexes **60a-60c**, containing N-H groups, showed relatively higher catalytic activities compared with other analogues. When PPh_3 was added as an auxiliary ligand to the catalytic system, an increased activity as high as 1.60×10^7 g mol^{-1} (Ni) h^{-1} was observed.[75]



Scheme 37 *N*,*P*-bi-dentate nickel complexes **61a-c** [76]

Guan and his coworkers have studied the ethylene polymerization behaviour of complexes **61a-c** (Scheme 37) bearing α-phosphine imine hybrid ligands.[76] Upon activation with MAO, the Ni(II) complexes were active for ethylene polymerization. Whereas the Ni(II)-P^N complexes are less productive than the Brookhart Ni(II)-α-bis(imine) complexes and form polyethylenes with relatively low molecular weight. The thermal stabilities of these complexes upon activation were significantly higher than those of the corresponding Ni(II)- α-bis(imine) complexes. In addtion, the polyethylenes obtained by the complexes **61a-c** were highly branched and had branch-on-branches.[76] The ligand structure influenced both the catalyst activity and the molecular weight of the polymer formed. Complex **61c** was much more active than **61a**,**b**, which was presumably due to the difference in the electronic structures between **61c** and **61a**,**b**. The phosphine in **61a**,**b** was much more electron rich than the phosphine in **61c** because the *tert*-butyl group has a stronger electron donating ability than the phenyl group. The lower molecular weight for the polyethylene obtained with complex **61c** was attributed to the decreased steric bulkiness of the diphenylphosphine in **61c** as compared to the di-*tert*-butylphosphine in **61a**,**b**. [76]

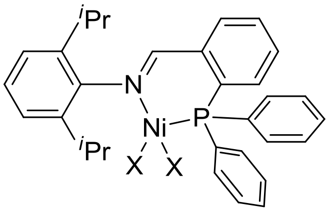


62a: R=Me; **62b**: R=Ph; **62c**: R=Me, Mes; **62d**: R=o-Tol.

63

Scheme 38 *N*,*P*-bi-dentate nickel complexes **62a-c** and **63**[77]

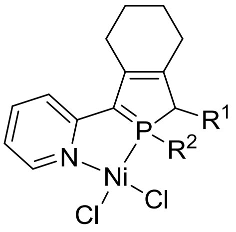
The Brookhart group have investigated the ethylene polymerization by the non-enolizable Ni(II) imine-phosphine complexes **62a-c** and **63** (Scheme 38).[77] The catalysts **62a-c** and **63** showed improved temperature stability with respect to the corresponding diimine complexes. Nickel imine-phosphine pre-catalysts containing a *gem*-dimethyl substituent α to the phosphorus displayed moderate activity and produced substantially higher molecular weight polyethylene compared to the corresponding enolizable complexes. A control experiment using non-enolizable pre-catalyst **62b** and enolizable pre-catalyst **63** revealed that under the same conditions the former produces more than 20 times higher molecular weight polyethylene than the latter, even though they differ only by a single methyl group in the backbone.[77]



64a:X=NCS; **64b**:X=Br

Scheme 39 *N*,*P*-bi-dentate nickel complexes **64a-b** [17]

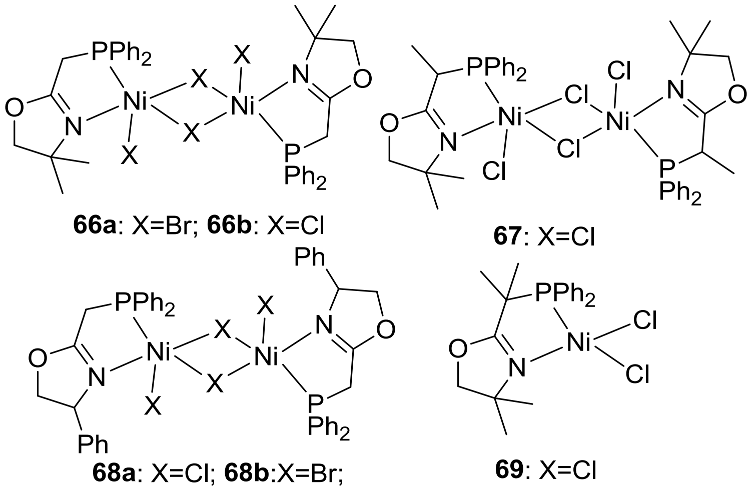
Crossetti and coworkers have studied the ethylene polymerization behaviour of the iminophosphine complexes **64a-b** (Scheme 39) activated by methylaluminoxane (MAO).[17] The activity of complex **64a** can reach 30 g PE/(g cat. h) with molecular weight 5.47 × 10^4, while the activity of complex **64b** is 8 g PE/(g cat. h) and the molecular weight 5.31 × 10^4 under the same polymerization conditions. Replacement of the halide for an NCS (pseudo halide) affected the activity and decreased the molecular weight of the polymer formed. The decrease in molecular weight caused by the presence of the isothiocyanate was more dramatic with the diphosphine complexes. The different activities and behaviour of the catalyst systems with halide versus NCS in the polymerization of ethylene and the characteristics of the final products suggested a modification in the active species caused by the non-chelating ligand.[17]



65a: R^1=phenyl, R^2=Ph;
65b: R^1=2-thienyl, R^2=Ph;
65c: R^1=phenyl, R^2=Cy;
65d: R^1=2-thienyl, R^2=Cy;

Scheme 40 *N,P*-bi-dentate nickel complexes **65a-d**[78]

The de Souza group has studied the ethylene oligomerization behaviour of the nickel complexes **65a-d** (Scheme 40) bearing the 2-(2-pyridyl)phospholes.[78] Under mild homogeneous reaction conditions, high catalytic activities (> 15 cycles per second) were recorded for the complexes **65b**. The selectivity depends on the ethylene pressure, and at 41 bar, high C_4 fraction contents (97 %) and high 1-butene selectivities (80 % of the C_4 fraction) were achieved. The C_6 fraction was mainly constituted by linear hexenes at high pressure. The total amount of the C6 fraction had very low variations. Complexes **65a** and **65b** gave low amounts of C_6 (3 to 11 %), but complexes **65c** and **65d**, at low ethylene pressure, gave 24 and 17 %, respectively. These results suggested that the higher steric hindrance of the complex containing the cyclohexyl fragment compared with the phenyl one, combined with the high steric hindrance of the pyridyl ligand, was responsible for a decrease in the amount of β-elimination process.[78]



66a: X=Br; **66b**: X=Cl

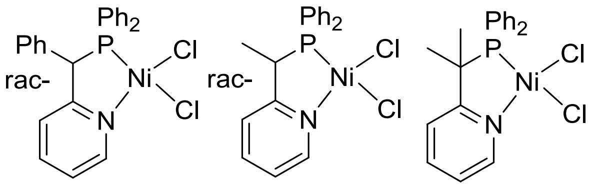
67: X=Cl

68a: X=Cl; **68b**:X=Br;

69: X=Cl

Scheme 41 *N*,*P*-bi-dentate nickel complexes **66a-69**[79]

Braunstein *et al* have researched the catalytic ethylene oligomerization behaviour of the nickel complexes **66a-69** (Scheme 41) bearing phosphinooxazoline ligands.[79] Whereas complexes **66a-68b** and $[NiCl_2(PCy_3)_2]$ were inactive for ethylene polymerization in the presence of methylaluminoxane (MAO), the mononuclear complex **69** gave a TOF of 7900 mol of C_2H_4/((mol of Ni) h) with a selectivity for 1-butene of 38 %. Complexes **66a,b** and **68a** were inactive for the oligomerization of ethylene in the presence of $NaBH_4$. However, with $AlEtCl_2$ as a co-catalyst, complexes **66a**, **67**, and **69** were active and activities and selectivities have been compared to those of $[NiCl_2(PCy_3)_2]$, a typical pre-catalyst used in the dimerization of α-olefins. Complex **66a** yielded a turnover frequency of 36300 mol of C_2H_4/((mol of Ni) h) in the presence of 14 equivalents of $AlEtCl_2$. In the presence of only 6 equivalents of co-catalyst, the nickel complexes **67** and **69** showed TOF values of 38100 and 45900 mol of C_2H_4/((mol of Ni) h), respectively, higher than that of 27 200 mol of C_2H_4/((mol of Ni) h) obtained with $[NiCl_2(PCy_3)_2]$.The dinuclear complexes **66a** and **67** led to selectivities for 1-butene within the C_4 fraction lower than the mononuclear complex **69**. The fact that the k_α value varies for a given catalyst as a function of the nature or quantity of co-catalyst used suggested that some incorporation of the butene formed occurs during chain growth (consecutive reaction).[79]

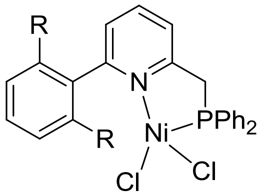


70a **70b** **70c**

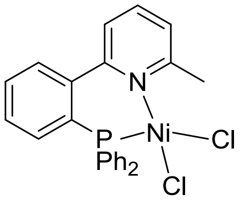
Scheme 42 *N,P*-bi-dentate nickel complexes **70a-c**[80]

The Braunstein group have also investigated ethylene oligomerization by the complexes **70a-c** (Scheme 42) bearing bi-dentate *P,N*-Phosphinopyridine ligands.[80] The Ni(II) complexes provided catalytic activities of up to 58100 mol

C_2H_4/mol Ni·h (**70c**) in the presence of 6 equivalents of $AlEtCl_2$. The selectivity for the C_4 olefins was as high as 81 % (**70a** in the presence of only 2 equivalents of $AlEtCl_2$). In the presence of 400 or 800 equivalents of MAO, complexes **70a-c** yielded lower activities but higher selectivities for 1-butene. A turnover frequency of 22800 mol C_2H_4/mol Ni·h was observed for **70c** in the presence of 800 equivalents of MAO. The selectivities for the C_4 olefins were in the range 70-85 %, with a maximum selectivity for 1-butene within the C_4 fraction of 38 % for **70b** with 400 equivalents of MAO or **70c** with 800 equivalents of MAO. It thus appears for these *P*,*N* ligands that an increase in the degree of alkyl substitution at the carbon α to P tends to lead to higher activities and more selective formation of α-olefins. [80] The influence of the nature of the *N*-heterocycle on the catalytic activity for ethylene oligomerization was shown by comparing the turnover frequencies of 58100 mol C_2H_4/mol Ni·h for **70c** and of 45900 mol C_2H_4/mol Ni·h for the related phosphinooxazoline complex **69**[79] in the presence of 6 equivalents of $AlEtCl_2$. This indicates a beneficial effect of an increased basicity of the nitrogen donor atom. When MAO was used as the co-catalyst (800 equivalents), a similar trend was observed, though the selectivities for 1-butene were similar to **70c** and **69**. [80]



71a: R=H; **71b**: R=CH_3
71c: R=^{i}Pr

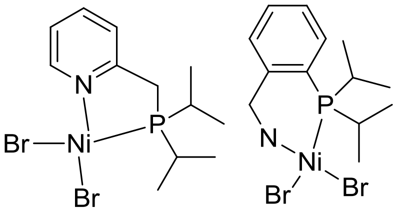


72

Scheme 43 *N*,*P*-bi-dentate nickel complexes **71a-c** and **72** [81]

Braunstein and coworkers have investigated the influence of the sterics and electronic properties of the *P*,*N*-phosphinopyridine ligands on the catalytic behaviour of the respective mononuclear nickel complexes **71a-c** and **72** (Scheme 43).[81] In the presence of MAO as a co-catalyst, complexes **71a-c** and **72** were inactive, however in the presence of six equivalents of $EtAlCl_2$, activities of up to 61000 mol of C_2H_4/((mol of Ni) h) (**71c**) were observed.

The selectivities for C_4 oligomers were as high as 92 % (for **72** in the presence of two equivalents of $AlEtCl_2$). [81] The k_α value varied for a given catalyst as a function of the nature or quantity of the co-catalyst suggesting that the C_6 products were formed by both ethylene oligomerization and incorporation of some of the 1-butene formed (C4 + C2, consecutive reaction). In general, the ligand basicity and the geometry of the coordination sphere of the metal center have an important influence on the catalytic properties. [81]

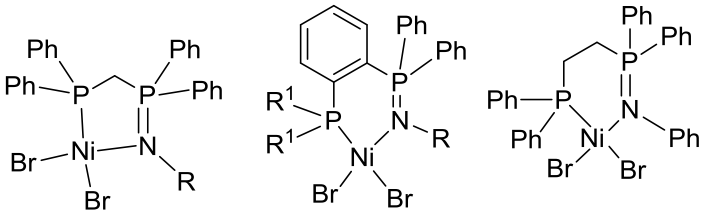


73a **73b**

Scheme 44 *N*,*P*-bi-dentate nickel complexes **73a-b** [82]

The Döring group have investigated the oligomerization behaviour of the

N,*P*-substituted nickel(II) complexes **73a-b** (Scheme 44).[82] Complexes **73a** and **73b** were active pre-catalysts when combined with the co-catalyst MAO for the oligomerization of ethylene, mainly favoring the production of butenes. The nickel(II) complex **73b** revealed a good selectivity at higher ethylene pressure for the production of 1-butene, for which the α-selectivity reached 77 %.[82]



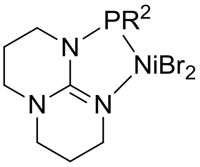
74a: R=CH_2-t-Bu
74b:R=p-CH_2-C_6H_4OMe
74c:R=Ph

75a: R^1=Ph, R=CH_2-*t*-Bu;
75b: R^1=Ph, R=^{i}Pr;
75c: R^1=Ph, R=*t*-Bu;
75d: R^1=^{i}Pr, R=*t*-Bu.

76

Scheme 45 *N*,*P*-bi-dentate nickel complexes **74a-76** [83]

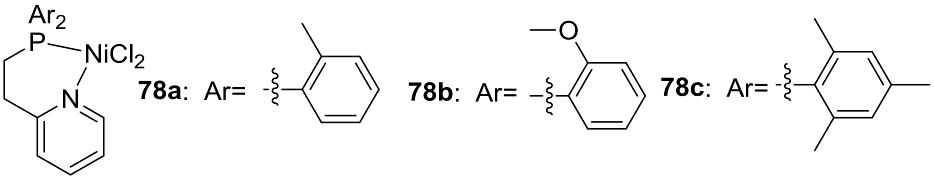
The Le Floch group have investigated the ethylene dimerisation of the *P*,*N*-nickel(II) complexes **74a-76** (Scheme 45).[83] The catalyst **75** features a rigid six-membered metallacycle and was more active than catalyst **74**. However, the increase of activity observed with complexes **75** was accompanied by a decrease in the selectivity for 1-butene (from 83.4 to 67.5 % with catalysts **74a** and **75a** which feature the same substitution pattern at the phosphorus and nitrogen). Interestingly, catalyst **76** despite its six-membered but flexible metallacycle gave only moderate results in term of both productivity and selectivity. Moreover, the nature of the functional group at the nitrogen atom seemed to affect the catalytic performances of complexes **74** only to a minor extent, while it played a more decisive role for complexes **75**. For example, the presence of a *t*Bu group dramatically reduced their catalytic activity. Besides, the phosphorus substituent had only a minor influence on the selectivity of the catalytic reaction. Overall, the most promising results were obtained with complex **75b** (TOF = 106 × 10^3 mol(C_2H_4) mol_{Ni} $^{-1}$ h^{-1}). [83]



77a: R=Ph; **77b**: R=Mes;
77c: R=^{i}Pr$_2$N; **77d**: R=Ph$_2$N

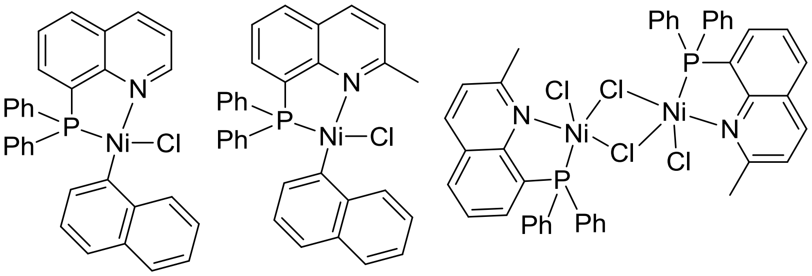
Scheme 46 *N,P*-bi-dentate nickel complexes **77a-d** [84]

Dyer *et al* have studied the ethylene oligomerization properties of the complexes **77a-d** (Scheme 46) bearing rigid bidentate *P*,*N*-ligands.[84] In combination with $EtAlCl_2$, the Ni(II) complexes **77b-d** were active ethylene oligomerization initiators (C_2H_4, 1 bar; Ni:Al) 1:14; toluene), affording varying mixtures of butenes, hexenes, and octenes (trace), depending on the nature of the *P*-donor, but with a reasonable selectivity toward C_4 for complex **77c**. In contrast, under identical reaction conditions complex **77a** gave rise to products resulting from a sequence of ethylene oligomerization and subsequent Friedel-Crafts alkylation of the toluene solvent. Notably, no activity toward ethylene (1 bar) was observed for **77**/MAO (Ni:Al) 1:15 or 1:500).[84]



Scheme 47 *N*,*P*-bi-dentate nickel complexes **78a-c** [85]

Flapper and coworkers have studied the properties of the ethylene oligomerization catalysis when using the nickel complexes **78a-c** (Scheme 47) upon MAO activation.[85] The bulky mesityl and 2-tolyl phosphorus substituents in **78a** and **78c** disfavoured isomerization of the oligomer chain, reflected in a high 1-butene selectivity. For the complex prepared from the ligand with the most bulky (mesityl) substituents, this selectivity was 90 %. The catalytic behaviour of the complex formed after activation of **78b**, containing the anisyl-substituted ligand, was different from that of the other complexes. Selectivity for 1-butene was lower, but the productivity was higher, with a turnover frequency of 65 × 10^3 (mol C_2H_4) · (mol $_{Ni}$ · h)$^{-1}$. [85]



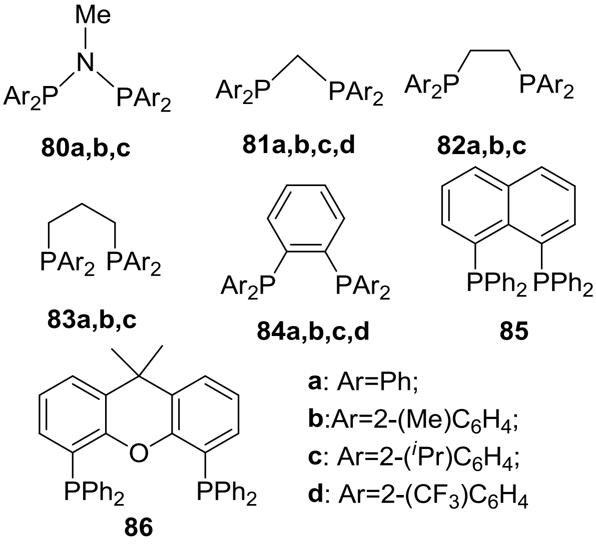
79a **79b** **79c**

Scheme 48 *N*,*P*-bi-dentate nickel complexes **79a-c** [86]

Our group has investigated the ethylene oligomerization behaviour of the complexes **79a-c** (Scheme 48).[86] In the presence of MAO as co-catalyst, complexes **79a-c** displayed good catalytic activities for ethylene oligomerization in toluene, typically up to 2.45 × 10^5 g ethylene (mol Ni·h·atm)$^{-1}$ by complex **79c**. The complex **79a** showed moderate activity ((0.13–2.05) × 10^5 g C_2H_4 (mol Ni·h·atm)$^{-1}$) for ethylene oligomerization at 25 °C. The products were mainly C_4 and C_6 olefins, and the selectivity for 1-C_4 was very high, whilst appreciably lower for 1-C_6 . Complexes **79b** and **79c** showed higher catalytic activities than **79a**, probably the result of the greater stability of their cationic active centers in toluene. For complex **79c**, in contrast to **79a** and **79b**, the products were mainly C_4, C_6 and C_8.[86]

2.3 [P^P] bi-dentate nickel complex pre-catalysts

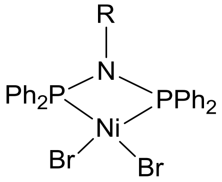
Extensive research on ethylene polymerization using bi-dentate Ni-based catalysts bearing *P^P* type ligation has been reported.



a: Ar=Ph;
b:Ar=2-(Me)C_6H_4;
c: Ar=2-(^{i}Pr)C_6H_4;
d: Ar=2-(CF_3)C_6H_4

Scheme 49 *P*,*P* Ligand **80a-86** [87,88]

The Wass group have explored the ethylene oligo-/polymerization behaviour of the nickel(II) complexes **80a-86** (Scheme 49).[87,88] The four membered nickel(II) chelates derived from the aminodiphosphines **80a-c** were very efficient catalysts for polymerization of ethylene, giving high molecular weight linear polymer.[87] The catalytic activity and polymer structure were very sensitive to the nature of the ligand backbone and the substituents at phosphorus. Nickel complexes of the bis(diarylphosphino)methane ligands **81a-d** were activated and screened for polyethylene catalysis under the same conditions. It was clear that these systems were active and the activity is a function of the *ortho* substituent. The activity increased in the order of increasing ligand steric bulk: **81a** < **81b** < **81c** < **81d**, and in this regard, the **81a-d** systems resemble the four-membered chelates formed by **80a-c**.[87,88] However, the low molecular weight, highly branched polymer formed by the **81a-d** systems contrasts sharply with the high molecular weight, substantially linear material formed by the **80a-c** systems. However, the five-membered chelates formed by dppe (**82a**) and the six-membered rings formed by dppp (**83a**) were completely inactive under the same conditions. Moreover, the larger rings were unresponsive to steric effects, and complexes of the sterically demanding ligands **82b**,**c** and **83b**,**c** were inactive under the same conditions. However, the five-membered nickel(II) chelates formed by the 1,2-phenylene diphosphines **84a**,**b** also gave active polymerization catalysts and revealed similar steric activation characteristics: i.e., **84a** < **84b**. The more bulky ligands utilized in **84c**,**d** gave polymer and the expected increase in molecular weight, but the activity was very low. Interestingly, the polymer formed by **84b-d** had high molecular weight and low branching: i.e., more akin to the polyethylene formed by the catalysts derived from **80a-c** than **81a-d**. Neither of the nickel complexes bearing the ligands **85** and **86** gave catalytically active systems under the same conditions.[88]



87a: $R=CH_2(C_6H_5)$;
87b: $R=CH_2(C_4H_3O)$;
87c: $R=CH_2(C_4H_3S)$
87d: $R=CH_2(C_5H_4N)$
87e: $R=CH_2CH_2(C_4H_3S)$

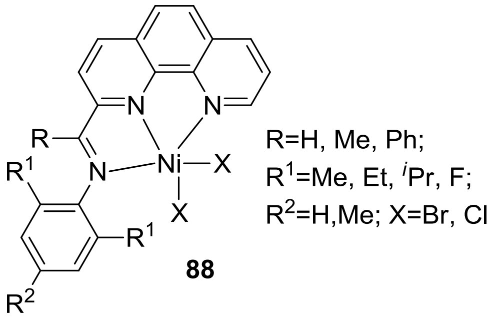
Scheme 50 *P*,*P*-bi-dentate nickel complexes **87a-e** [89]

The Wu group has studied the catalytic ethylene oligomerization behaviour of the bis(phosphanyl)amine nickel(II) complexes **87a-e** (Scheme 50) containing *N*-functionalized pendant groups.[89] In the presence of MAO or Et_2AlCl, these nickel complexes **87a-e** showed high activity for ethylene oligomerization, and the products obtained were mainly dimers, with a small amount of trimer with a high selectivity for linear α-olefins. However, a higher selectivity for α-olefins (1-C_4 or 1-C_6) was obtained when activated by MAO rather than Et_2AlCl. Both the catalytic activity and selectivity for α-olefin oligomers were mostly dependent on the structure of the complexes and the reaction temperatures.[89] Moreover, the activity increased in the order of increasing basicity of the *N*-functionalized pendant ligand: **87a** < **87b** < **87c** < **87d**. The catalysts afforded a higher C_4 content and better selectivity for linear α-olefins with decreasing reaction temperature. This was especially the case for complex **87e** with a thiophene-2-ethyl pendant group, the oligomerization products containing 95.9 mol-% C4 fraction with 100 mol-% 1-butene at -40 °C. However, at elevated temperatures (50 °C), the nickel complex/MAO systems decomposed rapidly and underwent Friedel–Crafts alkylation of toluene with ethylene and the olefin oligomers.[89]

3. Tri-dentate nickel complex pre-catalysts

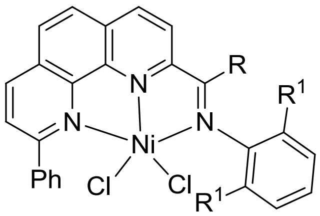
Although tri-dentate nickel complexes have tended to exhibited relatively lower activity for ethylene reactivity than the bi-dentate nickel complex pre-catalysts, much promising work has been conducted in recent years on new nickel systems bearing tri-dentate ligands.

3.1 [*N*^*N*^*N*] tri-dentate nickel complex pre-catalysts



Scheme 51 *N*,*N*,*N*-tri-dentate nickel complexes **88** [90,91]

Our group has investigated the properties of the ethylene oligomerization by the nickel complexes **88** (Scheme 51) bearing 2-imino-1,10-phenanthrolines.[90,91] The ligand environment and reaction conditions significantly affected the catalytic activity of such nickel complexes. Upon treatment with Et_2AlCl, the nickel(II) complexes **88** showed moderate activities of up to 3.3 × 10^6 g mol^{-1}(Ni) h^{-1} for ethylene oligomerization.[90,91] Both the R on the imino-C and the substituents on the *N*-aryl rings had an obvious influence on the catalytic activity and distribution of oligomers due to their different steric and electronic properties. In addition, the ethylene oligomerization activities increased up to 3.76×10^7 g mol^{-1}(Ni) h^{-1} when additional PPh$_3$ was employed as an auxiliary ligand.The activity of nickel complexes ligated by the methyl-ketimine (R = Me) or by phenyl-ketimine (R = Ph) was much better than those ligated by the aldimine (R = H). Furthermore, the R substituent had different influences for the methyl or phenyl-ketimine and aldimine analogues. For the methyl-ketimine and phenyl-ketimine complexes, it was observed that an increase in steric hindrance of the R^1 group led to an enhanced activity, but no significant effect was noticed for the aldimine complexes. The electronic effect of the substitution pattern of the phenyl ring connected with the imine nitrogen atom was not significant. Similarly, the halide anion linked to the nickel center had no obvious influence on the catalytic activity. [90,91]

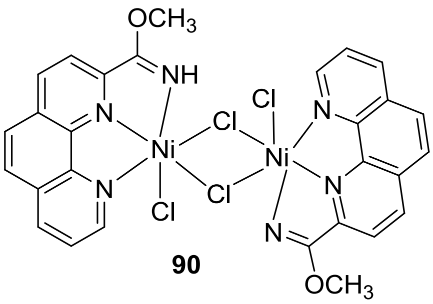


89

89a: R=Me, R^1=Me;
89b: R=Me, R^1=Et;
89c: R=Me, R^1=^{i}Pr;
89d: R=Ph, R^1=Me;
89e: R=Ph, R^1=Et;
89f: R=Ph, R^1=^{i}Pr.

Scheme 52 *N*,*N*,*N*-tri-dentate nickel complexes **89** [92]

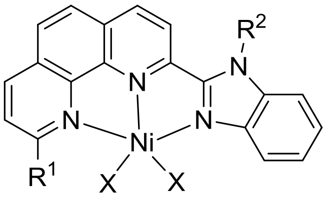
Our group has probed the ethylene oligomerization by the nickel complexes **89** (Scheme 52) bearing 2-imino-9-phenyl-1,10-phenanthrolines.[92] Et$_2$AlCl was a more effective co-catalyst for nickel complexes **89**, and the addition of PPh$_3$ significantly improved the catalytic activity and prolonged the catalyst lifetime. The addition of 20 equivalents of PPh_3 led to higher catalytic activities at 10 atm of ethylene pressure. Generally, the phenyl ketimine complexes displayed slightly higher activities than the methyl ketimine complexes bearing the same substituents on the aryl ring of the imino nitrogen. The catalytic properties of the methyl ketimine complexes after 30 min were found to be not greatly affected by the substituents on the aryl ring of the imino nitrogen, and the complexes **89a-c** showed comparable catalytic activity and similar selectivity for 1-butene. However, when the reaction time was prolonged to 60 min., a higher catalytic activity and slightly higher selectivity for 1-butene were achieved with the ethyl-substituted **89b** versus the methyl-substituted **89a** and the isopropyl-substituted **89c**. For the phenyl ketimine complexes, isopropyl-substituted **89f** showed the highest activity at 5.88 × 10^5 g $mol^{-1}(Ni)h^{-1}$ over 30 min. and the methyl substituted **89d** showed the highest activity at 4.71 × 10^5 $gmol^{-1}(Ni)h^{-1}$ over 60 min.[92]



90

Scheme 53 *N*,*N*,*N*-tri-dentate nickel complexes **90** [93]

We have also studied the properties of ethylene oligomerization by the nickel complexes **90** (Scheme 53) bearing a 2-alkoxyimidate-1,10-phenanthroline at each metal.[93] In the presence of Et_2AlCl, the methoxyimidate nickel complex **90** gave moderate to good activities and produced butenes and hexenes. For instance, in the presence of 200 equivalents of Et_2AlCl at 1 atm of ethylene pressure, the nickel complex **90** exhibited the highest activity at 3.23×10^5 g mol^{-1} h^{-1} for ethylene oligomerization with a selectivity of 19.1 % for 1-butene. Increasing the Al/Ni molar ratio over the range of 100–500 resulted in an increase in the activity to 3.85×10^5 g mol^{-1} h^{-1} at the optimal Al/Ni molar ratio of 300 and then a gradual decrease; however, the distribution of oligomers and the selectivity for 1-butene did not change greatly. The reaction temperature was found to have a remarkable influence on the catalytic activity and the distribution of oligomers. The highest activity over 30 min. was obtained at 5 ^oC and 91.2 % of butanes were observed in the oligomeric products with a selectivity of 41.9 % for 1-butene. At lower temperature, the consumption of ethylene could last longer time, and the activity was slightly decreased over 60 min. with increasing amount of hexenes formed, whereas the selectivity for 1-butene decreased dramatically (2.0 %). An elevated reaction temperature led to a decrease of the catalytic activity and an increase of the butene content. When the reaction temperature was increased to 60 ^oC, the activity decreased to 1.28×10^4 g mol^{-1} h^{-1} including 93.2 % of butenes in the products with a selectivity of 42.3 % for 1-butene. The catalytic activity could also be improved with an increase of ethylene pressure. When the ethylene pressure was increased to 10 atm from 1 atm, the catalytic activity of complex **90** increased to 8.71×10^5 g mol^{-1} h^{-1} with 84.1 % selectivity for 1-butene.[93]

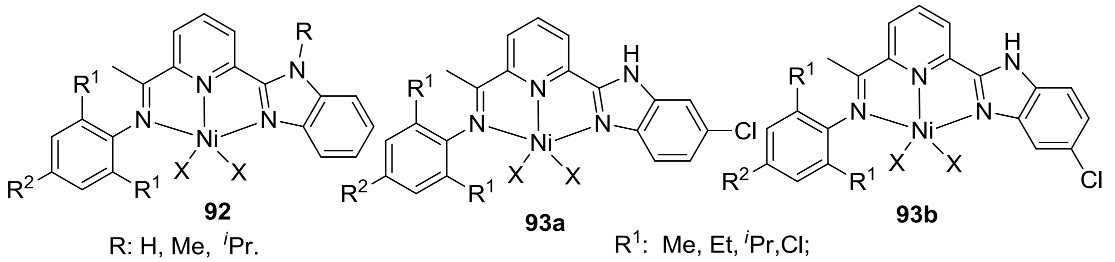


R^1=Me, H;
R^2=H, Me, Et, ^{i}Pr, Bn;
R^2=Cl, Br.

91

Scheme 54 *N*,*N*,*N*-tri-dentate nickel complexes **91** [94]

We have also investigated the properties of ethylene oligomerization by nickel complexes of the type **91** (Scheme 54) bearing 2-(benzimidazol-2-yl)-1,10-phenanthrolines.[94] Upon activation with diethylaluminum chloride (Et_2AlCl), high catalytic activity of up to 1.27×10^7 g•mol^{-1}(Ni)•h^{-1} and high selectivity for 1-butene (90.5 %) could be achieved. The ligand environment significantly influenced the catalytic properties of the complexes. Complexes **91** with a methyl group at the 9-position of the phenanthrolinyl ring (R^1 = Me), showed lower activities, but higher selectivities for α-olefins than did complexes with R^1 = H. The incorporation of an alkyl group (R^2) on the nitrogen atom of the benzimidazole led to a decrease in oligomerization activity and selectivity for 1-butene. In general, higher ethylene pressure and lower temperature resulted in higher activities and α-olefin selectivities of the catalysts. Additionally, in the presence of 20 equivalents1` of PPh_3, the activities of all investigated complexes increased dramatically with lower selectivities for 1-butene.[94]

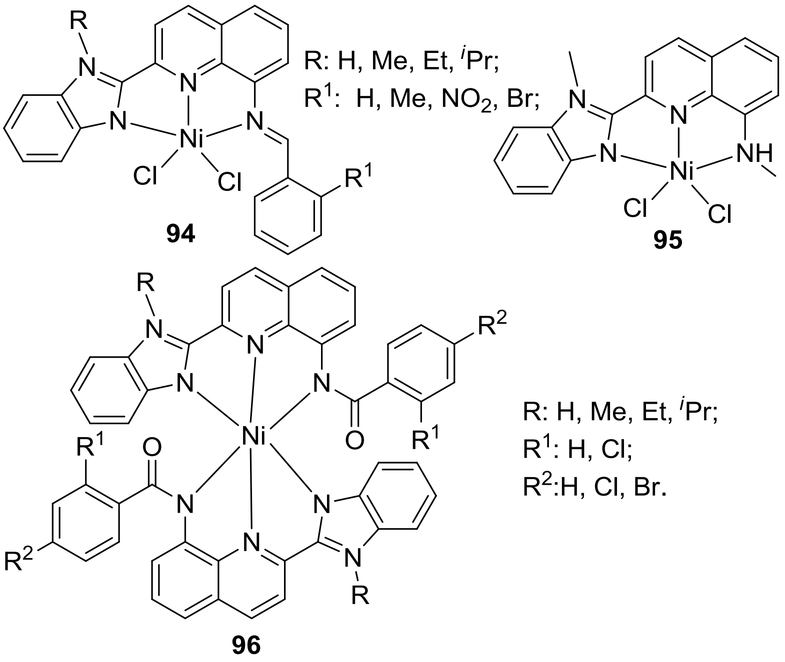


R: H, Me, ^{i}Pr.
R^1: Me, Et, ^{i}Pr,Cl, Br;
R^2: H, Me;
X: Cl, Br.

R^1: Me, Et, ^{i}Pr,Cl;
R^2: H, Me;
X: Cl, Br.

Scheme 55 *N*,*N*,*N*-tri-dentate nickel complexes **92** and **93a,b** [59,95-97]

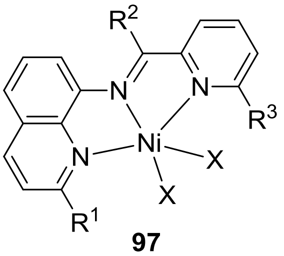
Our group has investigated the properties of the ethylene oligomerzation by the nickel complexes **92** and **93a,b** (Scheme 55) bearing a benzimidazolyl group.[59,95-97] With the addition of Et_2AlCl as co-catalyst, all the nickel complexes **92** and **93a,b** exhibited good catalytic activities of up to 10^6 g mol^{-1}(Ni) h^{-1} for ethylene oligomerization. The steric and electronic effects of the ligands had a significant influence on the catalytic activities of the nickel complexes.[59,95-97] The nickel complexes containing an isopropyl group on the benzimidazole instead of a methyl group performed with lower catalytic activities,[59,95] whilst the complexes that contain an N–H group on the benzimidazole exhibited a higher activity than those containing alkylated benzimidazoles.[59,95-97] Variation of the R^1 group at the *ortho* positions of the imino-*N* aryl ring resulted in a strong influence on the catalytic performance. An increase of the steric hindrance of the R^1 group led to decreased activity, but higher selectivity for α-olefins. Furthermore, the complex containing electron-withdrawing substituents at the aniline-derived group showed lower activity than that with an alkyl substituents.[59,95-97] In addition, the catalytic system containing the auxiliary ligand PPh_3 exhibited better catalytic activities toward ethylene oligomerization because of the protection of the phosphine group. [59,95,96] The nickel pre-catalysts **93** bearing chloro-modified ligands performed with higher activities at the elevated reaction temperature of 50 ^{o}C, whereas analogous pre-catalysts prefer to operate at room temperature.[59,95-97]



Scheme 56 *N*,*N*,*N*-tri-dentate nickel complexes **94-96**[98,99]

We have investigated the properties of the ethylene oligomerization using the nickel complexes **94-96** (Scheme 56) bearing ligands incorporating the quinoline group.[98,99] The complexes **94** form two kinds of complexes, depending on the reaction conditions. When activated by Et_2AlCl, the complexes $L\cdot NiCl_2$ of **94** exhibit high catalytic activities and selectivities for 1-C_4 during ethylene oligomerization, while the complexes $[L_2Ni]^{2+}\cdot 2Cl^{-}$ of **94** bearly showed any activity, which is attributable to the nickel coordination - the two ligands prevented ethylene from reaching the metal center. The substituents R^1 and R can affect the catalytic behaviour. The introduction of bromide at the R^1 position resulted in lower activity. On changing the R^1 to a strong electron withdrawing nitro group, an even lower activity was observed, which suggests that having an electron withdrawing substituent at the R^1 position was not favourable for high catalytic activities. The alkylation of the N–H of the benzimidazole fragment resulted in lower activity.[98]

Nickel complexes **96** exhibited high activities in ethylene oligomerization, with C_4 as the main product. The substituents also had a remarkable influence on the activities, whereas the influence on selectivity was not so obvious. The highest activity was obtained with the complexes having all substituents (R, R^1, R^2) as hydrogen. This implies that the less bulky R group was favourable for better activity. The electron withdrawing substituents at the R^1 or R^2 positions led to lower activities. Under the optimum conditions, the activity of **95** was as high as 7.63×10^6 g mol^{-1}(Ni) h^{-1}, which was even better than those by the catalysts **96**. However, the selectivity for 1-C4 was still moderate.[99]

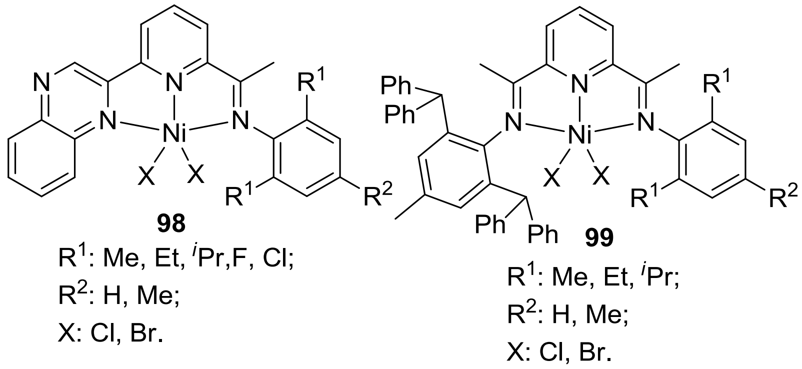


97

R^1: Me, ^{i}Pr, t-Bu, Cy;
R^2: H, Me, Ph;
R^3: H, Me;
X: Cl, Br.

Scheme 57 *N,N,N*-tri-dentate nickel complexes **97** [100]

We also studied the ethylene oligomerization properties of the nickel complexes **97** (Scheme 57) ligated by *N*-((pyridin-2-yl)methylene)quinolin-8-amine derivatives.[100] Upon activation with Et_2AlCl, all such nickel complexes exhibited considerably high catalytic activity for ethylene oligomerization with dimers and trimers as the products; the selectivity for α-C4 was moderate to high. The steric and electronic influence of the substituents can affect the catalytic activities of nickel complexes **97**. The effect of the substitution pattern of the R^2 substituent on the imino-*C* of the ligands was significant. When varying the electron donating properties of R^2, the highest activities were observed when R^2 = H. However, with R^2 = Me, the observed activities decreased. On changing R^2 to a stronger electron donating phenyl group, the activity further decreased. The substituents R^1 and R^3 also had a considerable effect on the catalytic behaviour. The highest activities of 41.2 × 10^5 and 47.2 × 10^5 g mol^{-1}(Ni) h^{-1} were obtained with the least bulky complexes (R^1 = R^3= H). However, increasing the steric bulk to a methyl substituent resulted in a decreased activity. A possible explanation is that the active site of the catalyst is blocked through bulky substituents, leading to a decline in activities. Furthermore, on changing the R^1 substituent from Me to *i*Pr, *t*Bu, or Cy while keeping R^3= Me, higher activities were observed. A possible explanation could be found in two opposing effects. One is that the active site of the catalyst is blocked through bulky substituents, leading to a decline in activity, whilst on the other hand, these bulky substituents are protecting the active center against decomposition, thereby affording higher activities. Hence, the overall effect depends on the type of substituent. As to the product distribution, the substituents had a minimal influence. For the olefins formed in the oligomerization reactions, the C_4 content varied from 92.9 to 98.6 %. In addition, the dibromonickel complex exhibited higher activities than their dichloronickel analogues, which could be explained by the better solubility of the bromo compound versus the chloro analogue.[100]

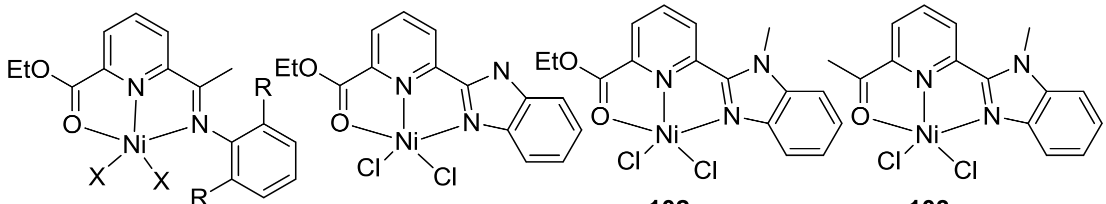


Scheme 58 *N*,*N*,*N*-tri-dentate nickel complexes **98** and **99** [101,102]

Ethylene oligomerization using the nickel complexes **98** and **99** (Scheme 58) bearing pyridine group was studied in our lab.[101,102] Upon activation with Et_2AlCl, the complexes **98** revealed moderate to good catalytic activity for the dimerization and trimerization of ethylene at low temperature and 10 atm ethylene. Due to the higher solubility of the nickel bromide precursors in toluene, their catalytic performance for ethylene oligomerization were slightly higher than the corresponding nickel chloride precursors.[101] With EASC as co-catalyst, the complexes **99** could be easily activated and showed high activities which can reach 2.5 $\times 10^6$ g $mol^{-1}(Ni)h^{-1}$ for ethylene oligomerization with moderate to good selectivities for 1-butene (54.2 - 99.1 %) at 10 atm ethylene pressure. However, the system **99** (R^1=Me, R^2=Me, X=Br)/EASC exhibited different oligomerization behaviour, and selectivity for hexenes, which substantially increased from 3.9 % to 54.1 %, when the reaction temperature was elevated from 25 to 100 ^{o}C. The catalytic activity for ethylene oligomerization and selectivity for butenes and hexenes could be easily controlled by altering the reaction conditions such as temperature and the molar ratio of Al/Ni. [102]

3.2 [*N*^*N*^*O*], [*N*^*N*^*P*]and [*P*^*P*^*N*] tri-dentate nickel complex pre-catalysts

Our group have designed numerous *N*^*N*^*O*, *N*^*N*^*P* and *P*^*P*^*N* tri-dentate ligand sets and employed them for nickel complex pre-catalysts for ethylene reactivity.



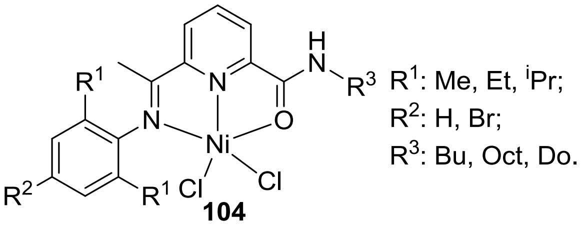
100a: R=Me, X=Cl;
100b: R=Et, X=Cl;
100c: R=F, X=Br.

101 **102** **103**

Scheme 59 *N*,*N*,*O*-tri-dentate nickel complexes **100-103** [59,62]

We investigated the properties of the ethylene oligomerzation using the nickel complexes **100a-103** (Scheme 59) bearing ligands incorporating a pyridine group.[59,62] Upon activation with MAO, the complexes **100** revealed moderate catalytic activity for ethylene oligomerization and polymerization. The ligand environment can play a role in dictating the catalytic behaviour. The complex **100c** with fluorine substituents in the ligand backbone just produced oligomers with a higher fraction of C_4 (87.86 %). The complexes **100a** and **100b** produced oligomers and a small amount of polymer. The activity of the complexes **100a** and **100b** was higher than the complex **100c** under identical reaction conditions.[62]

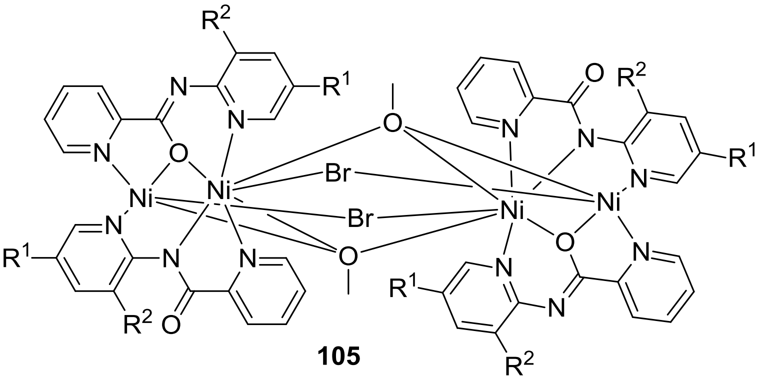
Comparing the nickel complexes **101** and **102** as catalysts, the activity associated with the complexes **101** was somewhat higher than **102**. These results can be attributed to the deprotonation of the N-H group to give an anionic amide ligand when activated by the co-catalyst to form N-Al species with increased catalytic activity.[103,104] The nickel complexes **101-103** (Scheme 59) exhibited lower catalytic reactivity than the nickel complexes **39a,b** (Scheme 22) containing *N*^*N* ligands. When the nickel complexes with ester groups were used as catalysts, the C_6 proportion in the products was higher than the C_4 proportion.[59]



Bu=n-butyl; Oct=n-octyl; Do=n-dodecyl

Scheme 60 *N*,*N*,*O*-tri-dentate nickel complexes **104** [105]

We have also studied the properties of the nickel complexes **104** (Scheme 60) ligated by2-(*N*-alkylcarboxamide)-6- iminopyridyl.[105] Upon activation with diethylaluminium chloride (Et_2AlCl), the nickel complexes **104** showed high activity for ethylene dimerization. The ligand environment had an influence on the observed catalytic behaviour, and the reactivity decreased with a shorter chain at the *N*-alkyl in these complexes under the same conditions, which was illustrated by the activity order of **104** (*i*Pr, Do) > **104** (*i*Pr, Oct) > **104** (*i*Pr, Bu) and **104** (Et, Do) > **104** (Et, Oct) >**104** (Et, Bu). However, the α-olefin selectivity increased when a shorter chain was present. These results are possibly due to the ability of the longer alkyl group to protect the active species and thereby lead to the higher observed activity. In contrast, bulkier substituents on the benzene ring resulted in lower activity, which led to the reactivity order of **104** (Me, Bu) >**104** (Et, Bu) > **104** (*i*Pr, Bu), **104** (Et, Oct) >**104** (*i*Pr, Oct) and **104**(Et, Do)>**104** (*i*Pr, Do). This is probably due to the substituents on the aryl ring being closer to the metal centre than the *N*imide−alkyl, and thus hindering the coordination of ethylene to the active species and thereby decreasing the reactivity. In contrast, the selectivity for 1-butene increased with bulkier substituents on the *ortho*-position of the aryl ring, as shown by the order **104**(Me, Bu) < **104** (Et, Bu) < **104** (*i*Pr, Bu). The reason is probably that the β-elimination barrier in the bulkier substituted catalyst systems is higher than that of those bearing smaller substituents, which will favour the generation of linear olefins.[45,106]

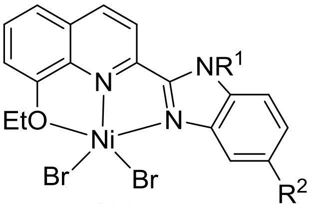


105

105a: R^1=H, R^2=H;**105b**:R^1=Br, R^2=Br;**105c**: R^1=CF_3, R^2=Cl.

Scheme 61 *N*,*N*,*O*-tri-dentate nickel complexes **105**[107]

We have studied the ethylene oligomerzation properties of the nickel complexes **105** (Scheme 60) ligated by *N*-(pyridin-2-yl)picolinamide derivatives.[107] The complexes **105** exhibited good activities in ethylene oligomerization with C_4 as the main product. The activity was as high as 2.7 × 10^6 g mol^{-1} (cat.) h^{-1}. The substituents had a remarkable influence on activity, however the influence on product distribution and selectivity for 1-C_4 was not as obvious. For example, catalyst **105b** exhibited lower activity than **105a**, indicating that introduction of bromide at the pyridine ring is not favourable for higher catalytic activities. Introduction of the more electron withdrawing substituents CF_3 and chloride, led to even lower activity.[107]

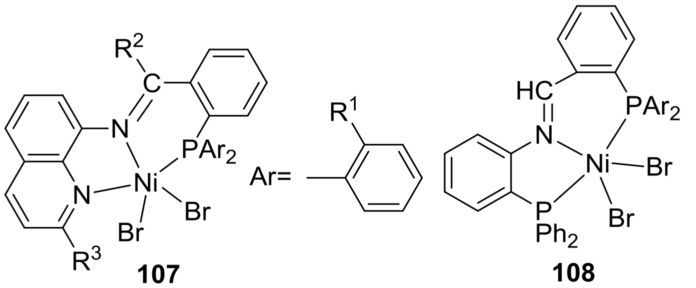


106

	106a	**106b**	**106c**	**106d**	**106e**	**106f**
R^1	Me	Et	^{i}Pr	Me	Et	^{i}Pr
R^2	H	H	H	Cl	Cl	Cl

Scheme 61 *N*,*N*,*O*-tri-dentate nickel complexes **106** [108]

We also investigated the ethylene oligomerization behaviour of the 2-benzoimidazol-8-ethoxyquinolylnickel dihalides **106** (Scheme 61).[108] Within this nickel chloride pre-catalysts series, the catalytic activities decreased with increasing electron-donating group ability of the R^1 on the *N*-atom of the imidazole. In the case of the nickel bromide pre-catalysts, the catalytic activities increased with enhanced electron-donating capability of group R^1 on the *N*-atom of the imidazole, however the catalytic activities decreased with enhanced electron-donating group R^1 at the *N*-atom of the 5-Cl-imidazole. The catalysts **106** had higher catalytic activities and better thermal stability.[108]



107

R^1: H, Me,OMe, Et, ^{i}Pr;
R^2: H, Me;
R^3: H, Me.

108

108a: R^1=H; **108b**:R^1=Me; **108c**:R^1=OMe;
108d: R^1=Et; **108e**:R^1=^{i}Pr

Scheme 62 *N,N,P and P,P,N*-tri-dentate nickel complexes **107** and **108** [109]

Finally, our group have investigated the tri-dentate nickel complexes **107** and **108** (Scheme 62) bearing *P*^*N*^*N* and *P*^*N*^*P* ligands.[109] Upon activation with MAO or AlEtCl$_2$, the complexes **107** and **108** exhibited considerably high activity (up to 1.34×10^6 g.mol^{-1}(Ni).h^{-1}) for ethylene oligomerization. The bulkiness of the ligands in the complexes **107** affected the catalytic activity of the ethylene oligomerization. Amongst the complexes **107**, that with an isopropyl group at the *ortho*-position of the phenyl ring showed the highest activity, and the activity decreases in the order *i*Pr > Et > OMe > Me > H under identical reaction conditions. The introduction of steric hindrance at the phosphorus atom had little influence on the selectivity for α-olefin formation. Increased substitution at the carbon β to phosphorus led to poor selectivities for α-olefin in the oligomerization of ethylene in the presence of 1000 equivalents of MAO. The ketimine-derived catalyst **107** was more active than the aldimine-derived catalysts, which produced oligomers ranging from C$_6$ to C$_{22}$ with a low selectivity for α-olefins (50-80 %).[109]

The bulkiness of the ligand in the nickel complexes **108** slightly affected the ethylene oligomerization activity. The selectivity for α-olefins with the catalytic system comprising complexes**108**/MAO was generally high. The main products formed during the oligomerization reactions were C_4 and C_6. The complex **108e**, with an isopropyl substituent on the phenyl ring, showed the highest activity under identical reaction conditions. Pre-catalyst **108c** generated a large quantity of octenes, while the selectivity for α-olefins was poor. The activity increases in the order of increased ligand bulk: **108e** > **108d** > **108c** > **108b** > **108a**.[109]

Outlook

The discovery of nickel(II) aryl-substituted α-diimine catalysts by Brookhart and co-workers proved to be a milestone in the development of nickel-based catalysts for the ethylene reactivity. Much effort has been devoted to catalyst modification with a view to enhancing both activity and control of the microstructure of the resulting polyethylene and the fractions of the oligomerization process. Some encouraging results has been achieved, for example, the new *N*,*N*-bi-dentate model comprising pyridine-amine designed by the Wu group, the new ligand skeleton of quinoxaline and phenanthroline, new substituents utilizing the benzimidazolyl and bulky unsymmetrical aniline have all been designed by our group. In order to achieve better control of the microstructure of the polyethylene and the fractions of the oligomerzation, further exploration is needed on these promising nickel-based catalyst systems.

Acknowledgements: **Acknowledgments:** This work is supported by NSFC No. 20904059. The RSC is thanked for the awarded of a travel grant (to CR)

References

(1) Johnson, L. K.; Killian, C.M.; Brookhart, M. *J. Am. Chem. Soc.***1995**, *117*, 6414-6415.

(2) Britovsek, G.J.P.; Gibson, V.C.; Wass, D.F. *Angew. Chem. Int. Ed.* **1999**, *38*, 428-447.

(3) Ittel, S.D.; Johnson, L.K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169-1203.

(4) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325-351.

(5) Mecking, S. *Angew. Chem. Int. Ed.* **2001**, *40*, 534-540.

(6) Coates, C. W.; Hustad, P.D.; Reinartz, S. *Angew. Chem. Int. Ed.* **2002**, *41*, 2236-2257.

(7) Gobson, V.C.; Spitzmesser, S. K. *Chem. Rev.* **2003**,*103*, 283-315.

(8) Zhang, J.; Wang, X.; Jin, G. -X. *Coord. Chem. Rev.* **2006**, *250*, 95-109.

(9) Domskia, G.J.; Rosea, J.M.; Coatesa, G.W.; Bolig, A.D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30-92.

(10) Anselment, T.M.J.; Vagin, S. -I.; Rieger, B. *Dalton Trans.*, **2008**, 4537-4548

(11) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics*,**1997**, *16*, 2005-2007.

(12) Svefda, S. A.; Brookhart, M. *Organometallics*, **1999**, *18*, 65-74.

(13) Helldörfer, M.; Backhus, J.; Alt, H. G. *Inorg. Chim. Acta* **2003**, *351*, 34-42.

(14) Liimatta, J.O.; Löfgren, B.; Miettinen, M.; Ahlgren, M.; Haukka, M.; Pakkanen, T. T. *J. Polym. Sci., Part A: Polym. Chem.***2001**, *39*, 1426-1434.

(15) Maldanis, R. J.; Wood, J.S.; Chandrasekaran, A.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **2002**, *645*, 158-167.

(16) Fassina, W.; Ramminger, C.; Seferin, M.; Mauler, R. S.; Souza, F. R.; Monteiro, A. L. *Macromol. Rapid Commun*. **2003**, *24*, 667-670.

(17) Crossetti, G. L.; Dias, M. L.; Queiroz, B.T.; Silva, L. P.; Ziglio, C. M.; Bomfim, J. A. S.; Filgueiras, C. A. L. *Appl. Organometal. Chem.* **2004**, *18*, 331-336.

(18) Liu, H.-R.; Gomes, P. T.; Costa, S. I.; Duarte, M. T.; Branquinho, R.; Fernandes, A. C.; Chien, J. C. W.; Singh, R. P.; Marques, M. M. *J. Organomet. Chem.* **2005**, *690*, 1314-1323.

(19) Zou, H.; Zhu, F. M.; Wu, Q.; Ai, J. Y.; Lin, S. A. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1325-1330.

(20) Son, G. W.; Bijal, K. B.; Park, D. -W.; Ha, C.-S.; Kim, I. *Catal. Today* **2006**, *111*, 412-416.

(21) Souza, C.G.; Souza, F. R.; Bernardo-Gusmo, K. *Appl. Catal. A: Gen.* 2007, *325*, 87-90.

(22) Brasse, M.; Cámpora, J.; Davies, M.; Teuma, E.; Palma, P.; Álvarez, E.; Sanz, E.; Reyes, M. L. Adv. Synth. Catal. 2007, *349*, 2111-2120.

(23) Zou, H.; Hu, S.; Huang, H.H.; Zhu, F.; Wu, Q. *Eur. Polym. J.* **2007**,*43*, 3882-3891.

(24) Bahuleyan, B. K.; Son, G. W.; Park, D. -W.; Ha, C.-S.; Kim, I. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1066-1082.

(25) Liu, J.; Li, Y.; Y. Li.; Hu, N. *J. Appl. Polym. Sci.* **2008**, *109*, 700-707.

(26) Martini, D.S.; Souza, F. R. *Polym. Bull.* **2008**, *60*, 237-242.

(27) Leung, D. H.; Ziller, J. W.; Guan, Z. *J. Am. Chem. Soc.* **2008**, *130*, 7538-7539.

(28) Budagumpi, S.; Kim, K.-H.; Kim, II. *Coord. Chem. Rev.*, **2011**, *255*, 2785-2809.

(29) Gao, R.; Sun, W.-H.; Redshaw, C. *Catal. Sci. Technol.*, **2013**, *3*, 1172-1179.

(30) Galli, P.; Vecellio, G. *Prog. Polym. Sci.*, **2001**, *26*, 1287-1336.

(31) Bubeck, R. A. *Mater. Sci. Eng. R*, **2002**, *39*, 1-28.

(32) Longo, P.; Oliva, L.; Grassi, A.; Pellecchia, C. *Makromol. Chem.* **1989**, *190*, 2357-2361.

(33) Laine, T. V.; Lappalainen, K.; Liimatta, J.; Aitola1, E.; Löfgren, B.; Leskelä, M. *Macromol. Rapid Commun.* 1999, *20*, 487-491.

(34) Gates, D.P.; Svejda, S.A.; Oñate, E.; Killian, C. M.; Lynda, Johnson, L.K.; White, P.S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320-2334.

(35) Laine, T. V.; Piironen,U.; Lappalainen, K.; Klinga, M.; Aitola1, E.; Leskelä, M. *J. Organomet. Chem.* **2000**, *606*, 112-124.

(36) Kinnunen, T.-J. J.; Haukka, M.; Pakkanen, T. T.; Pakkanen, T. A. *J. Organomet. Chem.* **2000**, *613*, 257-262.

(37) Schmid, M.; Eberhardt, R.; Klinga, M.; Leskelä, M.; Rieger, B. *Organometallics,* **2001,** *20*, 2321-2330.

(38) Helldörfer, M.; Backhaus, J.; Milius, W.; Alt, H. G. *J. Mol. Catal. A. Chem.* **2003**, *193*, 59-70.

(39) Helldörfer, M.; Milius, W.; Alt, H. G. *J. Mol. Catal. A. Chem.* **2003**, *197*, 1-13.

(40) Liu, F.; Hu, H.; Xu, Y.;Guo, L.; Zai, S.; Song, K.; Gao, H.; Zhang, L.; Zhu, F.; Wu, Q. *Macromolecules*, **2009**, *42*, 7789-7796.

(41) Deng, L.; Woo, T. K.; Cavallo, L.; Margl, P. M.; Ziegler, T. *J. Am.Chem. Soc.* **1997**, *119*, 6177-6186.

(42) Popeney, C.; Guan,Z. *Organometallics* **2005**, *24*, 1145-1155.

(43) Camacho, D. H.; Salo, E. V.; Ziller, J. W.; Guan, Z. *Angew. Chem. Int. Ed.* **2004**, *43*, 1821-1825.

(44) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059-2062.

(45) Leatherman, M. D.; Svejda, S. A.; Johnson, L. K.; Brookhart, M. *J. Am. Chem. Soc.* **2003**, *125*, 3068-3081.

(46) Rose, J. M.; Cherian, A. E.; Coates, G. W. *J. Am. Chem. Soc.* **2006**, *128*, 4186-4187.

(47) Song, C.-L.; Tang, L.-M.; Li, Y.-G.; Li, X.-F.; Chen,J.; Li, Y.-S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1964-1974.

(48) Liu, H.; Zhao, W.; Hao, X.; Redshaw, C.; Huang, W.; Sun, W.-H. *Organometallics* **2011**, *30*, 2418-2424.

(49) Liu, H.; Zhao, W.; Yu, J.; Yang, W.; Hao, X.; Redshaw, C.; Chen, L.; Sun, W.-H. *Catal. Sci. Technol.*, **2012**, *2*, 415-422.

(50) Kong, S.; Guo, C. -Y.; Yang, W.; Wang, L.; Sun, W.-H.; Glaser, R. *J. Organomet. Chem.* **2013**, *725*, 37-45.

(51) Shao, C.; Sun, W.-H.; Li, Z.; Hu, Y.; Han, L. *Catal. Commun.* **2002**, *3*, 405-410.

(52) Song, S.; Xiao, T.; Liang, T.; Wang, F.; Redshaw, C.; Sun, W.-H. *Catal. Sci. Technol.*, **2011**, *1*, 69-75.

(53) Song, S.; Li, Y.; Redshaw, C.; Wang, F.; Sun, W.-H. *J. Organomet. Chem.* **2011**, *696*, 3772-3778.

(54) Yu, J.; Hu, X.; Zeng, Y.; Zhang, L.; Ni, C.; Hao, X.; Sun, W.-H. *New J. Chem.*, **2011**, *35*, 178-183.

(55) Chai, W.; Yu, J.; Wang, L.; Hua, X.; Redshaw, C.; Sun, W.-H. *Inorg. Chim. Acta*, **2012**, *385*, 21-26.

(56) Yu, J.; Zeng, Y.; Huang, W.; Hao, X.; Sun, W.-H. *Dalton Trans.*, **2011**, *40*, 8436-8443.

(57) Hou, X.; Cai, Z.; Chen, X.; Wang, L.; Redshaw, C.; Sun, W.-H. *Dalton Trans.*, **2012**, *41*, 1617-1623.

(58) Du, J.; Li, L. -J.; Li, Y. *Inorg. Chem. Commun.*, **2005**, *8*, 246-248.

(59) Hao, P.; Zhang, S.; Sun, W.-H.; Shi, Q.; Adewuyi, S.; Lu, X.; Li, P. *Organometallics* **2007,** *26*, 2439-2446.

(60) Gao, R.; Xiao, L.; Hao, X.; Sun, W.-H.; Wang, F. *Dalton Trans.*, **2008**, 5645-5651.

(61) Spencer, L. P.; Altwer, R.; Wei, P.; Gelmini, L.; Gauld, J.; Stephan, D. W. *Organometallics* **2003,** *22*, 3841-3854.

(62) Tang, X.; Sun, W.-H.; Gao, T.; Hou, J.; Chen, J.; Chen, W. *J. Organomet. Chem.* **2005**, *690*, 1570-1580.

(63) Sun, W.-H.; Song, S.; Li, B.; Redshaw, C.; Hao, X.; Li, Y. -S.; Wang, F. *Dalton Trans.*, **2012**, *41*, 11999-12010.

(64) Huang, Z.; Song, K.; Liu, F.; Long, J.; Hu, H.; Gao, H.; Wu, Q. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 1618-1628.

(65) Zai, S.; Liu, F.; Gao, H.; Li, C.; Zhou, G.; Cheng, S.; Guo, L.; Zhang, L.; Zhua, F.; Wu, Q. *Chem. Commun.*, **2010**, *46*, 4321-4323.

(66) Zai, S.; Gao, H.; Huang, Z.; Hu, H.; Wu, H.; Wu, Q. *ACS Catal*. **2012**, *2*, 433-440.

(67) Li, L.; Jeon, M.; Kim, Y.S. *J. Mol. Catal. A. Chem.* **2009**, *303*, 110-116.

(68) Song, K.; Yang, W.; Li, B.; Liu, Q.; Redshaw, C.; Li, Y.; Sun, W.-H. *Dalton Trans.*, **2013**, DOI: 10.1039/c2dt32343e.

(69) Carlini, C.; Isola, M.; Liuzzo, V.; Galletti, A. M. R.; Sbrana, G. *Appl. Catal., A.* **2002**, *231*, 307-320.

(70) Carlini, C.; Macinai, A.; Masi, F. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 2534-2542.

(71) Kim, I.; Kwak, C. H. K.; Kim, J. S.; Ha, C. -S. *Appl. Catal., A.* **2005**, *287*, 98-107.

(72) Wang, L.; Sun, W.-H.; Han, L.; Li, Z.; Hu, Y.; He, C.; Yan, C. *J. Organomet. Chem.* **2002**, *650*, 59-64.

(73) Chen, L.; Hou, J.; Sun, W. -H. *Appl. Catal., A.* **2003**, *246*, 11-16.

(74) Hou, J.; Sun, W. -H. Zhang, D.; Chen, L.; Li, W.; Zhao, D.; Song, H. *J. Mol. Catal. A. Chem.* **2005**, *231*, 221-233.

(75) Shi, Q.; Zhang, S.; Chang, F.; Hao, P.; Sun, W. -H. *C. R. Chimie*. **2007**, *10*, 1200-1208.

(76) Guan, Z.; Marshall, W. J. *Organometallics*, **2002**, *21*, 3580-3586.

(77) Daugulis, O.; Brookhart, M. *Organometallics*, **2002,** *21*, 5926-5934.

(78) Souza, R.F.; Bernardo-Gusmão, K.; Cunha, G.A.; Loup, C.; Leca, F.; Réau, R. *J. Catal.* **2004**, *226*, 235-239.

(79) Speiser, F.; Braunstein, P. *Organometallics* **2004,** *23*, 2613-2624.

(80) Speiser, F.; Braunstein, P. *Organometallics* **2004,** *23,* 2625-2632.

(81) Speiser, F.; Braunstein, P. *Organometallics* **2004,** *23,* 2633-2640.

(82) Bluhm, M.E.; Folli, C.; Walter, O.; Döring, M. *J. Mol. Catal. A. Chem.* **2005**, *229*, 177-181.

(83) Buchard, A.; Auffrant, A.; Klemps, C.; Vu-Do, L.; Boubekeur, L.; Goff, X. F. L.; Floch, P. L. *Chem. Commun.*, **2007**, 1502-1504.

(84) Dyer, P. W.; Fawcett, J.; Hanton, M. *Organometallics* **2008,** *27,* 5082-5087.

(85) Flapper, J.; Kooijman, H.; Lutz, M.; Spek, A. L.; Leeuwen, P. W. N. M.; Elsevier,C. J.; Kamer, P. C. J. *Organometallics* **2009,** *28,* 3272-3281.

(86) Sun, W. -H., Li, Z.; Hu, H.; Wu, B.; Yang, H.; Zhu, N.; Leng, X.; Wang, H. *New J. Chem*., **2002**, *26*, 1474-1478.

(87) Cooley, N.A.; Green, S. M.; Wass, S. F. *Organometallics*, **2001**, *20*, 4769-4771.

(88) Dennett, J. N. L.; Gillon, A. L.; Heslop, K.; Hyett, D.J.; Fleming, J.S.; Emma, L. J.; Orpen, A.G.; Pringle, P.G.; Wass, D. F. *Organometallics*, **2004**, *23*, 6077-6079.

(89) Song, K.; Gao, H.; Liu, F.; Pan, J.; Guo, L.; Zai, S.; Wu, Q. *Eur. J. Inorg. Chem.* **2009**, 3016-3024.

(90) Wang, L.; Sun, W.-H.; Han, L.; Yang, H.; Hu, Y.; Jin, X. *J. Organomet. Chem.*, **2002**, *658*, 62-70.

(91) Sun, W.-H.; Zhang, S.; Jie, S.; Zhang, W.; Li, Y.; Ma, H.; Chen, J.; Wedeking, K.; Fröhlich, R. *J. Organomet. Chem.*, **2006**, *691*, 4196-4203.

(92) Jie, S.; Zhang, S.; Sun, W.-H. *Eur. J. Inorg. Chem.* **2007**, 5584-5598.

(93) Xiao, L.; Jie, S.; Song, Y.; Cao, X.; Sun, W.-H. *J. Organomet. Chem.*, **2008**, *693*, 3858-3866.

(94) Zhang, M.; Zhang, S.; Hao, P.; Jie, S.; Sun, W.-H.; Li, P.; Lu, X. *Eur. J. Inorg. Chem.*, **2007**, 3816-3826.

(95) Chen,Y.; Hao, P.; Zuo, W.; Gao, K.; Sun, W.-H. *J. Organomet. Chem.*, **2008**, *693*, 1829-1840.

(96) Xiao, L.; Zhang, M.; Gao, R.; Cao, X.; Sun, W.-H. *Aust. J. Chem.* **2010**, *63*, 109-115.

(97) Chen, X.; Zhang, l.; Yu, J.; Hao, X.; Liu, H.; Sun, W.-H. *Inorg. Chim. Acta.*, **2011**, *370*, 156-163.

(98) Wang, K.; Gao, R.; Hao, X.; Sun, W.-H. *Catal. Commun.* **2009**, *10*, 1730-1733.

(99) Wang, K.; Shen, M.; Sun, W.-H. *Dalton Trans.*, **2009**, 4085-4095.

(100) Sun, W.-H.; Wang, K.; Wedeking, K.; Zhang, D.; Zhang, S.; Cai, J.; Li, Y. *Organometallics* **2007,** *26,* 4781-4790.

(101) Adewuyi, S.; Li, G.; Zhang, S.; Wang, W.; Hao, P.; Sun, W.-H.;Tang, N.; Yi, J. *J. Organomet. Chem.*, **2007**, *692*, 3532-3541.

(102) Lai, J.; Hou, X.; Liu, Y.; Redshaw, C.; Sun, W.-H. *J. Organomet. Chem.*, **2012**, *702*, 52-58.

(103) Zhang, W.; Sun, W.-H.; Zhang, S.; Hou, J.; Wedeking, K.; Schultz, S.; Fröhlich, R.; Song, H. *Organometallics* **2006**, *25*, 1961-1969.

(104) McGuinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552-556.

(105) Zhang, W.; Wang, Y.; Yu, J.; Redshaw, C.; Hao, X.; Sun, W.-H. *Dalton Trans.*, **2011**, *40*, 12856-12865.

(106) Schrekker, H. S.; Kotov, V.; Preishuber-Pflugl, P.; White, P.; Brookhart, M. *Macromolecules*,**2006**, *39*, 6341-6354.

(107) Wang, K.; Shen, M.; Sun, W.-H. *Polyhedron*, **2010**, *29*, 564-568.

(108) Liu, H.; Zhang, L.; Chen, L.; Redshaw, C.; Li, Y.; Sun, W.-H. *Dalton Trans.*, **2011**, *40*, 2614-2621.

(109) Hou, J.; Sun, W.-H.; Zhang, S.; Ma, H.; Deng, Y.; Lu, X. *Organometallics* **2006,** *25*, 236-244.