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The formation and polymerization behavior of Ni(II) α-diimine complexes using various aluminum activators

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Abstract

Several Ni(II) α-diimine complexes have been synthesized and examined for ethylene and propylene polymerization in combination with different aluminum co-catalysts. The precatalysts used in the study were [ArN=C(Nap)–C(Nap)=NAr]NiBr$_2$ (Nap = 1,8-naphthdiyl) (**1**, Ar = 2,4,6-trimethylphenyl; **2**, Ar = 2-^{t}Bu phenyl; **3**, Ar = 2-^{i}Pr phenyl). These complexes were synthesized via a one-pot reaction where the ligand is formed via an acid catalyzed condensation followed by direct addition of nickel(II) bromide. The complexes were also prepared by a two-step procedure where the ligand was first formed by condensation between the appropriate aniline and acenaphthoquinone, and the resulting ligand was then allowed to react with (1,2-dimethoxyethane) nickel(II) dibromide. X-ray structural studies of complexes **1** and **2** have been carried out. Diethylaluminum chloride (DEAC), and 1,3-dichloro-1,3-diisobutyldialuminoxane (DCDAO) show higher activities for ethylene and propylene polymerizations in combination with these Ni(II) α-diimine complexes than does polymethylaluminoxane (MAO). The molecular weight of the resulting polymers as well as their respective polydispersities and T_ms are also presented. The polypropylenes obtained with **1**/DEAC and **2**/DEAC at 0 °C show similar rr triad percentage as previously reported for polypropylenes generated by MAO activated Ni(II) α-diimine complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nickel; Polypropylene; Polyethylene; Diimine

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1. Introduction

Recently, late transition metal complexes have been shown to be useful in the field of Ziegler–Natta catalysis [1]. In particular, over the past decade cationic Ni(II) α-diimine complexes have gained considerable attention in this field [2]. These complexes have been shown to be primarily useful for ethylene polymerizations but are also known to promote homo- and copolymerizations of polar monomers [3]. Depending on the steric bulk of the nickel catalyst used, polymers with various microstructures have been produced [4].

It has also been shown that these Ni(II) α-diimine complexes can be activated via non-traditional polymethylaluminoxane (MAO) type co-catalysts. Kumar and Sivaram have shown that diethylaluminum chloride (DEAC) can be used in activating these systems to promote ethylene polymerizations [5]. Brookhart and coworkers have demonstrated that DEAC can be used in combination with these nickel catalyst systems to promote oligomerization of ethylene with longer chain lengths than was obtained with MAO [4a]. It was also shown that trialkylaluminum compounds in combination with these complexes could polymerize ethylene [6]. However, the uses of late transition metal complexes for propylene polymerizations are deficient in the literature [2,7]. Brookhart and coworkers discovered that living polymerization of propylene could be achieved when complex **2** was activated with MAO under optimal conditions [4d]. Pellecchia and coworkers have shown that a Ni(II) α-diimine complex in contact with MAO can promote syndiospecific propylene polymerizations at sub-ambient temperatures [8]. In addition, McCord et al. have published a detailed study on the microstructure of the polypropylenes produced with these nickel systems when activated by MAO [9]. Re-

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search continues to explore cationic Ni(II) α-diimine complexes in an attempt to mimic the dominance Group IV catalyst systems have shown in the field of Ziegler–Natta chemistry.

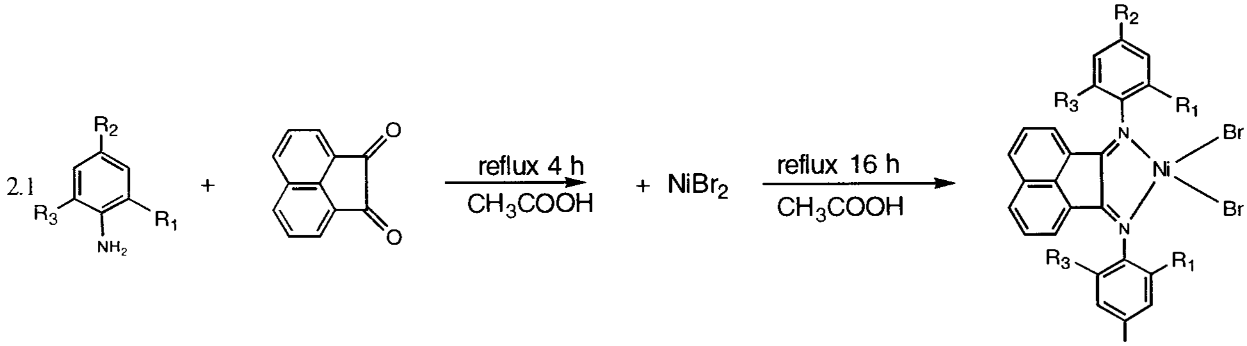
Herein, we report the synthesis and crystal structures of several Ni(II) α-diimine complexes (**1**–**3**). The synthesis of these complexes can be carried out via two procedures and these are detailed. The complexes have been examined as catalyst precursors for ethylene and propylene polymerizations in combination with various aluminum co-catalysts.

2. Results and discussion

2.1. Synthesis of catalyst precursors

2.1.1. Synthesis of Ni(II) α-diimine complexes via one-pot reaction

The Ni(II) α-diimine complexes **1**–**3** investigated in this study were synthesized via a modification of a procedure described by Matei and Lixandru [10]. Acenaphthoquinone and the respective aniline were heated at reflux in glacial acetic acid for 4 h followed by addition of nickel(II) bromide, and the reflux was continued overnight (Eq. (1)).



(Eq. 1)

1: $R_{1,2,3} = CH_3$: 81% yield

2: R_1 = tBu ; $R_{2,3}$ = H : 77% yield (dimeric, see Figure 2)

3: R_1= iPr ; $R_{2,3}$ = H: 72% yield

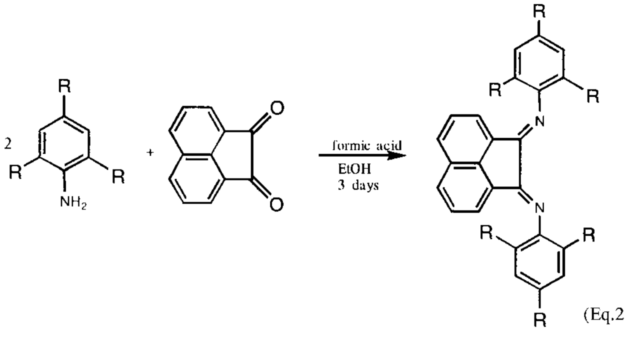
After removal of the glacial acetic acid in vacuo, compounds **1**–**3** were washed with diethyl ether to remove any remaining acetic acid and unreacted ligand. Further purification was also carried out by dissolving the nickel complex in methylene chloride, followed by slow layering of the subsequent solution with diethyl ether. Repeated layering techniques led to dark purple needles of complexes **1** and **2** suitable for X-ray studies.

Due to the paramagnetic nature of these α-diimine Ni(II) complexes, ^{1}H-NMR studies were not feasible. Elemental analysis of complex **2** fits the structure obtained by X-ray structural studies. We were not able to obtain elemental analysis for the solvated species of complex **1**. However, we were able to achieve an analytical sample for the anhydrous form of complex **1** by repeated Et_2O–CH_2Cl_2 recrystallizations, followed by drying in vacuo for several days. We were also able to obtain mass spectral data on **1** for the parent ion after bromine loss. This fragmentation pattern has been shown to occur for similar nickel systems [4c,8a]. X-ray structural analysis was not obtainable for complex **3** possibly due to the relative ease of solvent loss and its open nickel center relative to **1** and **2**.

Complexes **1**–**3** are all air stable complexes but do require moisture-free solvents during handling. However, the use of wet glacial acetic acid does not interfere with the formation of the nickel complex. This suggests that the resulting complexes are acid-stabilized with respect to decomposition.

2.1.2. Synthesis of Ni(II) α-diimine complexes via (DME)NiBr$_2$ route

Complexes **1**–**3** can also be prepared by a similar method previously described [4a,d,11] in which the respective ligand (**4**–**6**) was first formed via an acid catalyzed condensation between the aniline and the diketone (Eq. (2)), followed by subsequent displacement of 1,2-dimethoxyethane from (1,2-dimethoxyethane) nickel(II) bromide [$(DME)NiBr_2$] [12] (Eq. (3)).

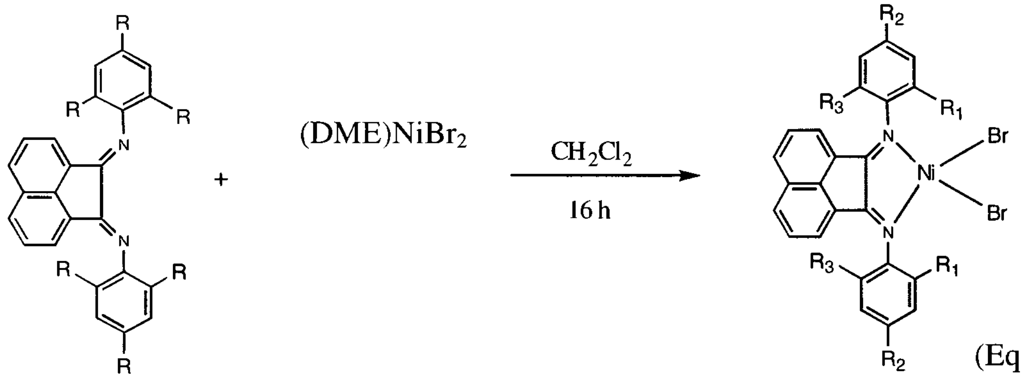


(Eq.2)

4: $R_{1,2,3} = CH_3$: 88% yield

5: R_1 = tBu ; $R_{2,3}$ = H : 85% yield

6: R_1= iPr ; $R_{2,3}$ = H : 83% yield



(Eq. 3)

1: $R_{1,2,3} = CH_3$: 94% yield

2: R_1 = tBu ; $R_{2,3}$ = H : 94% yield
(dimeric: see Figure 2)

3: R_1= iPr ; $R_{2,3}$ = H : 90% yield

Compounds **4**–**6** were recrystallized from diethyl ether to afford elementally pure ligands. These compounds were characterized by ^{1}H-NMR and were found to be free from impurities. Subsequent treatment of these ligands with $(DME)NiBr_2$ also produced the desired complexes **1**–**3**. The nickel complexes prepared by this route showed identical chemical characteristics and polymerization results as found for the complexes made via Eq. (1). The complexes are sparingly soluble in diethyl ether and hydrocarbons, are moderately soluble in toluene, and are soluble in methylene chloride and chloroform.

*2.2. Crystal and molecular structures of complexes **1** and **2***

Figs. 1 and 2 show ORTEP plots [13] and atom labeling for the structures of complexes **1** and **2**, while Table 1 gives details of the bond distances and angles for the geometry about the nickel atoms in each of the complexes. As can be seen, complex **2** contains five-coordinate nickel centers and is dimeric, the two halves of the dimer being related by a crystallographic inversion center, while complex **1** on the other hand, possesses crystallographic two-fold symmetry, the C_2 axis bisecting the α-diimine ligand.

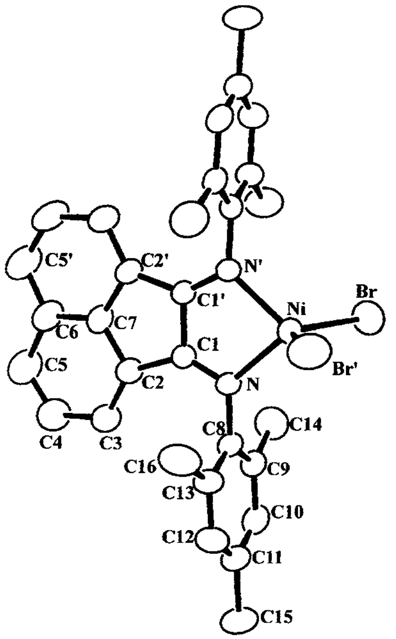


Fig. 1. ORTEP diagram of **1** with 40% ellipsoids. H atoms have been removed in drawings.

The pseudo-tetrahedral geometry about the nickel atom in **1** is very similar to that reported recently by Brookhart and coworkers [4c], for compound **4d** in their paper, namely, the complex bis(2-pentafluorophenyl-6-methylphenyl-imino)acenaphthene nickel dibromide. Thus the Ni–Br and Ni–N distances in **1**, of 2.318(1) and 2.021(3), compare closely with the averages of 2.306(1) and 2.024(3) reported for **4d**, and the bond angles at the nickel atom are likewise very similar.

Table 1
Selected bond lengths (Å) and bond angles (°) for compounds **1** and **2**

*Compound **1***			
Bond lengths			
Ni–N	2.021(3)	Ni–Br	2.318(1)
Bond angles			
N–Ni–N [a]	82.6(2)	Br–Ni–Br [a]	117.94(5)
N–Ni–Br	114.4(1)	N–Ni–Br [a]	111.3(1)
*Compound **2***			
Bond lengths			
Ni–N(1)	2.058(4)	Ni–N(2)	2.106(4)
Ni–Br(1)	2.380(1)	Ni–Br(2)	2.505(1)
Ni–Br(2) [b]	2.551(1)		
Bond angles			
N(1)–Ni–Br(1)	129.5(1)	N(1)–Ni–Br(2)	94.1(1)
Br(1)–Ni–Br(2)	136.36(3)	N(2)–Ni–Br(2) [b]	173.0(1)
N(2)–Ni–N(1)	80.4(2)	N(1)–Ni–Br(2) [b]	95.2(1)
N(2)–Ni–Br(1)	94.1(1)	Br(1)–Ni–Br(2) [b]	92.91(3)
N(2)–Ni–Br(2)	89.2(1)	Br(2)–Ni–Br(2) [b]	85.79(2)

[a] Two-fold related atoms.
[b] Inversion related atoms.

The compound **4d** differs from **1** principally by having the bulky pentafluorophenyl groups rather than methyl groups in one of the *ortho*-positions of the phenyl rings attached to the imine nitrogens. The crystallographically imposed two-fold symmetries for both of the two independent molecules in the unit cell of **4d** results in the pentafluorophenyl rings having an *anti*-conformation above and below the nickel imine coordination plane. With the more symmetrically substituted phenyl groups present in **1**, there is no such conformational difference, and both the diimine ligand, and the

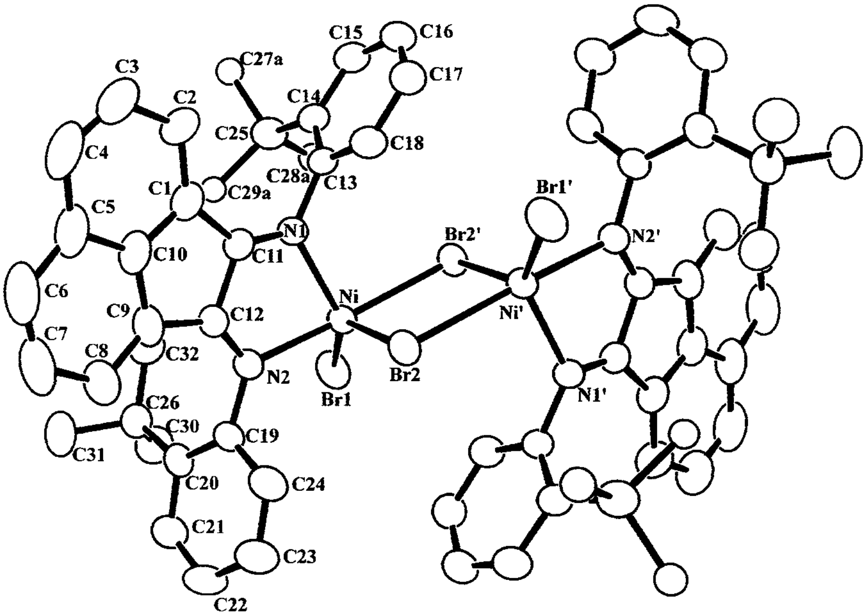


Fig. 2. ORTEP diagram of **2** with 40% ellipsoids. H atoms have been removed in drawings.

complete complex approximate C_{2v} symmetry quite closely. The bis(imino)acenaphthene moiety is planar to within the estimated S.D.s and the dihedral angle it makes with the nitrogen bonded mesityl groups is 88.8(3)°, while the dihedral angle between the $NiBr_2$ unit and the nickel–nitrogen plane is 88.1(2)°.

The geometries for the nickel atoms in the two inversion related halves of the dimer in complex **2**, may be described as being basically trigonal bipyramidal, two such bipyramids sharing an apical edge. However, although the atoms defining the equatorial plane, namely Ni, N(1), Br(1) and Br(2), are planar to within the estimated S.D.s, the angles within the plane are far from 120°. The terminal Ni–Br(1) and the nickel–nitrogen distances are slightly longer than those in **1**, and there is a small, but significant difference between the 'axial' and 'equatorial' nickel–nitrogen and the nickel–bromine bond lengths, perhaps supporting the trigonal-bipyramidal description.

In contrast to other structurally confirmed examples, both of free α-diimine ligands [8a] and of their nickel and palladium complexes [4c,11a], the *tert*-butyl substituted phenyl rings in **2** take on the *syn*-conformation, so that both *tert*-butyl groups are on the same side of the coordination plane. In this instance the conformation is presumably dictated by the steric requirements arising from the dimerization of the complex to give a five-coordinate geometry for the nickel. In all other instances where asymmetrically substituted aryl rings are employed, and monomeric complexes are formed, the substituents on the ligand take up an *anti*-conformation with respect to the acenaphthene plane. However, in common with the other characterized examples, the phenyl rings are nearly perpendicular to the plane formed by the nickel and nitrogen atoms, the dihedral angles being 99.5° for the ring bonded to N(1), and 84.1° for that bonded to N(2).

2.3. Polymerization results

Polymerizations of ethylene were carried out using nickel systems **1**–**3** at 20 °C with MAO, DEAC, 1,3-dichloro-1,3-diisobutyldialuminoxane (DCDAO), trimethylaluminum (TMA), and triisobutylaluminum (TIBA). The results are reported in Table 2.

It is apparent from Table 2 that **1**/DEAC produces the highest amount of polyethylene compared to the other catalyst systems investigated. In our study, DEAC appears to be the best co-catalyst even when compared to MAO in generating the most polyethylene. This is in agreement with the previous studies by Marques et al. [14]. The trialkylaluminum activators (TMA and TIBA) in combination with **1**, **2** and **3** produce a factor of ten times lower amount of polymer when compared to DEAC, DCDAO and MAO. Catalyst precursor **3** generated the lowest amount of polymer compared to the other nickel systems. This may be due to the less bulky isopropyl moiety, thus causing oligomerization processes possibly to occur.

The molecular weights of the resulting polymers as well as their respective polydispersities are also reported in Table 2. In general, the polydispersities are relatively high and the T_ms are lower compared to single site, linear polyethylene obtained with metallocene catalyst systems. It is apparent from the table that these polyethylenes are more branched and have lower molecular weights compared to those reported by Brookhart and coworkers [4] possibly due to the lower steric hindrance of the aniline moiety in our study. It is well known that Ni(II) diimine complexes that lack bulky diisopropylaniline moieties generally favor chain transfer relative to chain propagation and thus produce lower molecular weight polymers [2].

It is seen from the table that the polydispersities are higher and the T_ms are lower with the use of trialkylaluminum activators (TMA and TIBA) than are obtained with the other co-catalyst systems (MAO, DEAC and DCDAO) in combination with **1**–**3**. This could result from the higher affinity of TMA and TIBA to undergo easier chain transfer processes due to a closer ion pair relative to the cationic species. Also, bridging alkyls would provide a closer ion pair relative to the Ni center, thus causing chain transfer processes to occur more readily. The melting points of the polymers obtained with TMA and TIBA in combination with **1** are much lower than those obtained with the other co-catalyst systems. It is likely that catalyst **1** would provide a more distant ion pair relative to **2** and **3** due to the increased steric bulk of the trimethylaniline moiety. The polydispersities are higher and the T_ms are lower for the resulting polymer obtained with **2** and **3** compared to **1**.

Propylene polymerizations were also carried out with the use of **1**–**3** in combination with DEAC, DCDAO and MAO and the results are tabulated in Table 3. Table 3 shows that both DEAC and DCDAO can activate α-diimine nickel complexes to produce a significant amount of polypropylene. In our study, the **1**/DEAC system gave the highest amount of polypropylene compared to the other systems. DCDAO was also shown to promote a higher degree of propylene polymerization compared to MAO. Catalyst precursor **2** gave a polymer with a slightly higher M_w compared to the polymers obtained with different co-catalyst systems. In general, the molecular weights of the polymers decrease as the polymerization temperature increases. Also, the polydispersities increase as the temperature increases. It is interesting to note that the M_w of the obtained polymers are fairly constant with respect to the co-catalyst used. The polypropylenes obtained with **1** and **2** were isolated as amorphous solids that showed no true melting point by DSC.

Table 2
Ethylene polymerizations [a] using nickel precursors **1**, **2** and **3** activated by various aluminum co-catalysts

Catalyst	Co-catalyst	P.E. (g)	A [b] ($\times 10^{-6}$)	M_w [c] ($\times 10^{-4}$)	M_n [c] ($\times 10^{-4}$)	M_w/M_n [c]	T_m [d] (°C)
1	TMA [e]	0.49	0.53	4.32	0.65	6.6	115
1	TMA [e]	0.52	0.56	–	–	–	–
1	TIBA [f]	0.43	0.46	4.71	0.77	6.1	117
1	TIBA [f]	0.47	0.51	–	–	–	–
1	DEAC [g]	3.29	3.55	4.87	1.50	3.2	127
1	DEAC [g]	3.21	3.46	–	–	–	–
1	MAO [h]	2.70	2.91	5.45	1.73	3.1	130
1	MAO [h]	2.69	2.90	–	–	–	–
1	DCDAO [i]	3.02	3.26	4.18	1.08	3.9	125
1	DCDAO [i]	3.08	3.32	–	–	–	–
2	TMA [e]	0.21	0.23	3.43	0.65	6.3	115
2	TMA [e]	0.17	0.18	–	–	–	–
2	TIBA [f]	0.22	0.24	3.97	0.76	5.2	118
2	TIBA [f]	0.22	0.24	–	–	–	–
2	DEAC [g]	2.71	2.92	3.16	0.53	6.0	122
2	DEAC [g]	2.65	2.86	–	–	–	–
2	MAO [h]	2.10	2.26	5.42	1.32	4.0	125
2	MAO [h]	2.14	2.31	–	–	–	–
2	DCDAO [i]	2.31	2.49	4.47	1.88	3.8	125
2	DCDAO [i]	2.29	2.47	–	–	–	–
3	TMA [e]	Trace	–	–	–	–	–
3	TMA [e]	Trace	–	–	–	–	–
3	TIBA [f]	Trace	–	–	–	–	–
3	TIBA [f]	Trace	–	–	–	–	–
3	DEAC [g]	1.62	1.75	3.98	0.66	6.0	110
3	DEAC [g]	1.68	1.81	–	–	–	–
3	MAO [h]	0.61	0.66	4.49	0.45	9.9	105
3	MAO [h]	0.55	0.59	–	–	–	–
3	DCDAO [i]	1.35	1.46	3.18	0.54	6.0	108
3	DCDAO [i]	1.30	1.40	–	–	–	–

[a] Polymerization conditions: [Ni], 50 μM in toluene; time of polymerization = 1 h, $T_p = 20$ °C, 15 PSIG ethylene.

[b] A (activity) = [g polymer/(mol Ni × conc. monomer × h)].

[c] M_w, M_n and M_w/M_n determined by GPC at 135 °C in 1,2,4-trichlorobenzene.

[d] T_m determined by DSC.

[e] TMA/Ni = 100:1.

[f] TIBA/Ni = 100:1.

[g] DEAC/Ni = 250:1.

[h] MAO/Ni = 500:1.

[i] DCDAO = 300:1.

Compound **3** in combination with DEAC and DCDAO gave polypropylene that was isolated as an oil which indicates that oligomerization processes were possibly occurring during the polymerization. Polymerizations were also attempted for propylene with the use of trialkylaluminum activators (TMA and TIBA) in contact with **1**–**3**. However, no polymer was obtained with any of these systems.

Triad analyses were performed on the polypropylenes obtained at 0 °C with **1**/DEAC and **2**/DEAC. The NMR spectra showed that polymers derived from **1**/DEAC gave the higher percentage syndiotacticity with a rr triad analysis of 87% while **2**/DEAC produced a syndiotacticity of 77%. Attempts to perform pentad analysis on the resulting polypropylenes were unsuccessful due to the poor resolution of the spectra as a result of high regioirregular content of the polymer (see Ref. [8a]).

In this study, we have outlined two different detailed routes for the synthesis of several Ni(II) α-diimine complexes. It was shown that these complexes could be activated by several aluminum activators to promote olefin polymerization. DEAC and DCDAO in combination with the Ni(II) α-diimine complexes were shown to be more effective towards ethylene and propylene polymerizations than MAO. Further modification of the co-catalyst used with these types of complexes could possibly lead to polypropylenes that resemble characteristics of those obtained with Group IV metallocene catalysts.

Table 3
Propylene polymerizations with nickel precursors **1**, **2** and **3** in combination with various aluminum activators at different temperatures

Catalyst	Co-catalyst	T_{p} [a]	P.P. (g)	A [b] ($\times 10^{-5}$)	M_{w} [c] ($\times 10^{-4}$)	M_{n} [c] ($\times 10^{-4}$)	$M_{\mathrm{w}}/M_{\mathrm{n}}$ [c] ($\times 10^{-4}$)
1	MAO [d]	−20	0.41	1.42	4.49	1.32	3.40
1	MAO [d]	−20	0.44	1.53	–	–	–
1	MAO [d]	0	0.55	2.42	4.11	0.99	4.15
1	MAO [d]	0	0.58	2.55	–	–	–
1	MAO [d]	20	0.63	3.80	3.93	0.905	4.35
1	MAO [d]	20	0.67	4.03	–	–	–
1	DCDAO [e]	−20	0.52	1.81	3.81	1.47	2.60
1	DCDAO [e]	−20	0.49	1.70	–	–	–
1	DCDAO [e]	0	0.68	2.99	3.77	1.10	3.42
1	DCDAO [e]	0	0.68	2.99	–	–	–
1	DCDAO [e]	20	0.74	4.45	3.64	0.881	4.13
1	DCDAO [e]	20	0.75	4.51	–	–	–
1	DEAC [f]	−20	0.72	2.51	4.42	1.16	3.80
1	DEAC [f]	−20	0.70	2.43	–	–	–
1	DEAC [f]	0	0.74	3.25	4.41	1.07	4.10
1	DEAC [f]	0	0.71	3.12	–	–	–
1	DEAC [f]	20	0.85	5.11	3.65	0.763	4.78
1	DEAC [f]	20	0.81	4.87	–	–	–
2	MAO [d]	−20	0.05	0.17	4.13	0.983	4.20
2	MAO [d]	−20	0.07	0.24	–	–	–
2	MAO [d]	0	0.09	0.39	3.88	0.87	4.45
2	MAO [d]	0	0.12	0.53	–	–	–
2	MAO [d]	20	0.16	0.96	3.54	0.65	5.44
2	MAO [d]	20	0.14	0.84	–	–	–
2	DCDAO [e]	−20	0.21	0.73	4.54	1.69	2.68
2	DCDAO [e]	−20	0.24	0.83	–	–	–
2	DCDAO [e]	0	0.35	1.54	4.10	1.43	2.9
2	DCDAO [e]	0	0.39	1.71	–	–	–
2	DCDAO [e]	20	0.45	2.71	3.77	1.20	3.1
2	DCDAO [e]	20	0.44	2.65	–	–	–
2	DEAC [f]	−20	0.29	1.00	6.34	1.55	4.09
2	DEAC [f]	−20	0.29	1.00	–	–	–
2	DEAC [f]	0	0.41	1.80	5.85	1.38	4.25
2	DEAC [f]	0	0.39	1.71	–	–	–
2	DEAC [f]	20	0.55	3.31	4.90	1.0	4.90
2	DEAC [f]	20	0.49	2.95	–	–	–
3	MAO [d]	−20	Trace	–	–	–	–
3	MAO [d]	−20	Trace	–	–	–	–
3	MAO [d]	0	Trace	–	–	–	–
3	MAO [d]	0	Trace	–	–	–	–
3	MAO [d]	20	Trace	–	–	–	–
3	MAO [d]	20	Trace	–	–	–	–
3	DCDAO [e]	−20	0.38	1.32	–	–	–
3	DCDAO [e]	−20	0.36	1.25	–	–	–
3	DCDAO [e]	0	0.42	1.85	–	–	–
3	DCDAO [e]	0	0.41	1.80	–	–	–
3	DCDAO [e]	20	0.55	3.31	–	–	–
3	DCDAO [e]	20	0.51	3.10	–	–	–
3	DEAC [f]	−20	0.42	1.45	–	–	–
3	DEAC [f]	−20	0.38	1.32	–	–	–
3	DEAC [f]	0	0.55	2.42	–	–	–
3	DEAC [f]	0	0.50	2.20	–	–	–
3	DEAC [f]	20	0.61	3.67	–	–	–
3	DEAC [f]	20	0.65	3.91	–	–	–

[a] Polymerization conditions: [Ni], 50 μM in toluene; time of polymerization = 1 h, 15 PSIG propylene.

[b] A (Activity) = [g polymer/(mol Ni × conc. monomer × h)].

[c] M_{w}, M_{n} and $M_{\mathrm{w}}/M_{\mathrm{n}}$ determined by GPC at 135 °C in 1,2,4-trichlorobenzene.

[d] MAO/Ni = 500:1.

[e] DCDAO/Ni = 250:1.

[f] DEAC/Ni = 250:1.

3. Experimental

All operations were carried out under Ar atmosphere using standard Schlenk techniques unless otherwise noted. Methylene chloride and 1,2-dimethoxyethane were distilled under Ar from CaH_2. Toluene, hexane, and Et_2O were each distilled under Ar from sodium–potassium alloy. Anhydrous $NiBr_2$, 2,4,6-trimethylaniline, 2-isopropylaniline, 2-*tert*-butylaniline and bromine were purchased from Aldrich and used without further purification. MAO was purchased from Akzo Nobel. DEAC, TIBA, DCDAO and TMA were purchased from Aldrich and used without further purification. (DME)$NiBr_2$ was synthesized via a literature procedure [12]. ^{1}H-NMR spectra were recorded on a Bruker-200 spectrometer. EIMS were obtained on a JMS-700 MStation high-resolution two-sector mass spectrometer using direct insertion. Molecular weights were determined by GPC in 1,2,4-trichlorobenzene. A calibration curve was established with polystyrene standards and universal calibration was applied using Mark–Houwink constants for polyethylene and polypropylene. Elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst, MA. ^{13}C-NMR triad analyses on the polypropylenes were performed for 2 h periods on a Bruker-500 MHz instrument at 80 °C with benzene-d_6/1,2,4-trichlorobenzene as the solvent.

*3.1. Synthesis of Ni(II) α-diimine complexes **1–3** via one-pot reaction*

Acenaphthoquinone (1.00 g, 5.55 mmol) was placed in a Schlenk tube followed by 100 ml glacial AcOH. The resulting suspension was allowed to warm to 50 °C and then a slight excess of the respective aniline (13 mmol) was introduced, forming a burgundy–red solution within minutes. This mixture was warmed to 120 °C and allowed to reflux for 4 h. Anhydrous $NiBr_2$ (1.20 g, 5.55 mmol) was added as a solid to the subsequent mixture and the reaction was allowed to reflux overnight. The solvent was removed in vacuo and the resulting solid was washed with Et_2O (20 ml × 3). Alternatively, the solid can also be conveniently washed with Et_2O via Soxhlet extraction. The residue was extracted with CH_2Cl_2 and the resulting deep red solution was filtered via a cannula to another Schlenk tube. This process was repeated twice and the solvent was removed in vacuo to give **1–3** that were suitable for polymerization use. Crystals of complexes **1** and **2** suitable for X-ray studies were obtained by dissolving a small amount of the compound in CH_2Cl_2 (100 ml), followed by slow addition of Et_2O (20 ml), forming two layers. The mixture was allowed to sit undisturbed overnight. Resulting crystals formed at the sides of the tube and the filtrate was decanted via a cannula. The crystals were washed with a small amount of Et_2O (5 ml) and were used immediately for X-ray analysis.

Compound **1** (2.82 g, 4.45 mmol, 81%) was obtained as a red solid after Et_2O washings and drying in vacuo. EIMS; *m*/*z* (%): 558, 557, 556, 555, 554, 553 [12, 36, 35, 100, 24, 71 $M^+ - Br$]]. Anal. Calc. for $C_{30}H_{28}N_2NiBr_2$: C, 56.74; H, 4.44; N, 4.41. Found: C, 56.44; H, 4.58; N, 4.22%.

Compound **2** (2.80 g, 4.23 mmol, 77%) was obtained as a orange solid after CH_2Cl_2 extraction and Et_2O washings. Anal. Calc. for $C_{32}H_{32}N_2NiBr_2 \cdot CH_2Cl_2$ solvate: C, 52.98; H, 4.58; N, 3.74. Found: C, 52.70; H, 4.38; N, 3.62%.

Compound **3** (2.51 g, 3.96 mmol, 72%) was obtained as a yellow solid after CH_2Cl_2 extraction and Et_2O washings. Attempts to prepare a sample of elemental analytical purity were not successful.

*3.2. Synthesis of α-diimine ligands **4–6***

Acenaphthoquinone (1.00 g, 5.55 mmol), 100 ml of MeOH and a slight excess of the respective aniline (13 mmol) were placed in a 250 ml beaker and allowed to stir for 3 days in the presence of formic acid (1 ml). Methylene chloride and water were added and the layers were separated. The resulting organic layer was dried with $MgSO_4$, filtered and the solvent was removed to give the crude ligands as red oils. The impure ligands were recrystallized from Et_2O to give **4–6** in high yield.

Compound **4** (2.01 g, 4.83 mmol, 88%) was obtained as red crystals (melting point (m.p.) 170 °C) after recrystallization from Et_2O. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 2.09$ (s, 12H), 2.38 (s, 6H), 6.75 (d, 2H), 6.97 (s, 4H), 7.44 (t, 2H), 7.91 (d, 2H). Anal. Calc. for $C_{30}H_{28}N_2$: C, 86.50; H, 6.77; N, 6.73. Found: C, 86.35; H, 6.84; N, 6.57%.

Compound **5** (2.07 g, 4.67 mmol, 85%) was obtained as orange crystals (m.p. 175 °C) after recrystallization from Et_2O. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.39$ (s, 18H), 6.84 (d, 2H), 6.96 (d, 2H), 7.51–7.20 (m, 8H), 7.89 (d, 2H). Anal. Calc. for $C_{32}H_{32}N_2$: C, 86.45; H, 7.25; N, 6.30. Found: C, 86.30; H, 7.30; N, 6.20%.

Compound **6** (1.90 g, 4.56 mmol, 83%) was obtained as orange crystals (m.p. 170 °C) after recrystallization from Et_2O. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 1.26$ (m, 12H), 3.18 (m, 2H), 6.84 (m, 4H), 7.20 (m, 4H), 7.44 (t, 2H), 7.91 (m, 2H), 8.20 (m, 2H). Anal. Calc. for $C_{30}H_{28}N_2$: C, 86.50; H, 6.77; N, 6.73. Found: C, 86.35; H, 6.81; N, 6.57%.

*3.3. Synthesis of nickel complexes **1–3** via (DME)$NiBr_2$ reaction*

(DME)$NiBr_2$ (1.00 g, 3.25 mmol), the respective ligands **4–6** (3.3 mmol) and CH_2Cl_2 (50 ml) were combined in a Schlenk flask and stirred at room temperature (r.t.) for 16 h. The resulting suspension was filtered and the filtrate was collected in another Schlenk flask. The solvent was removed and the residue was washed with Et_2O (3 × 20 ml) to give complexes **1**–**3** in high yields.

Compound **1** (1.81 g, 3.05 mmol, 94%) was obtained as dark-red microcrystals after CH_2Cl_2 extraction and Et_2O washings.

Compound **2** (2.02 g, 3.05 mmol, 94%) was obtained as an orange powder after CH_2Cl_2 extraction and Et_2O washings.

Compound **3** (1.74 g, 3.05 mmol, 90%) was obtained as an yellow powder after CH_2Cl_2 extraction and Et_2O washings.

3.4. Crystal structure determination

The X-ray crystallographic studies of compounds **1** and **2** were carried out on an Enraf–Nonius Kappa CCD diffractometer using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Data were collected at 296(2) K for a range in θ up to 25°. For compound **2**, this gave a total of 10 228 reflections, yielding 5747 independent values ($R_{int} = 0.026$), and for compound **1**, 5469 reflections yielding 2960 independent values ($R_{int} = 0.029$). The structures were solved by direct methods and difference Fourier techniques and were refined by full-matrix least-squares. Refinements were based on F^2 and were carried out using all the independent data. All of the non-hydrogen atoms, apart from those of the solvent molecules of crystallization, were refined anisotropically. The hydrogen atoms were included in the refinements as isotropic scatterers, riding in either idealized positions (C–H = 1.05 Å), or in the case of the methyl hydrogens, with torsional refinement on the respective bonded atoms. Pertinent crystallographic data are summarized in Table 4, the final agreement factors listed being based on reflections for which $I > 2\sigma(I)$.

Both compounds **1** and **2** possess crystallographic symmetry, an inversion center in the case of **2** and a two-fold axis in the case of **1**, so that in each instance, only one-half of a molecule comprises the asymmetric unit. The crystals of both complexes also contain solvent molecules of crystallization: CH_2Cl_2, to the extent of four molecules per unit cell for compound **2**, and, as indicated by the best refinement model, one-quarter of a molecule of Et_2O per molecule of complex (or one complete molecule per cell), in the case of **1**. The CH_2Cl_2 molecules are positionally disordered, and the chlorine atoms were refined in a total of five partially occupied positions, while the Et_2O molecule in **1**, is located on a two-fold axis.

The computations involved were carried out using SHELXS-86 [15] for the structure solution and SHELXL-97 for the refinement [16]. Neutral atom scattering factors for non-hydrogen atoms were taken from International Tables [17], and anomalous dispersion corrections were included [18]. The hydrogen atom scattering factor used is that tabulated by Stewart et al. [19].

Table 4
Crystal data and structure refinement parameters for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{30}H_{28}Br_2N_2Ni\cdot 0.25(C_2H_5)_2O$	$C_{64}H_{64}Br_4N_4Ni_2\cdot 2CH_2Cl_2$
Formula weight	653.6	1496.1
Crystal system	Orthorhombic	Monoclinic
Space group	*Pcca* (no. 54)	$P2_1/n$ (no. 14)
Unit cell dimensions		
a (Å)	16.6977(5)	12.3065(2)
b (Å)	11.4432(3)	22.0991(4)
c (Å)	17.6565(6)	12.3293(2)
β (°)	–	100.28(1)
V (Å^3)	3373.7(2)	3299.3(1)
Z	4	2
D_{calc} (g cm^{-3})	1.287	1.506
μ (Mo–K_α) (cm^{-1})	29.6	32.0
Crystal size (mm)	0.50 × 0.25 × 0.20	0.75 × 0.18 × 0.15
Total independent reflections	2960	5747
Reflections with $I > 2\sigma(I)$	2119	4419
$R(F_o)$ [a]	0.0545	0.048
$R_w(F_o^2)$ [b]	0.136	0.114
Goodness-of-fit on F_o^2	1.14	1.05

[a] $R(F_o) = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.

[b] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2}$.

3.5. Procedure of polymerizations

Polymerizations of ethylene and propylene were carried out in a flame dried 250 ml crown capped pressure bottle sealed under Ar atmosphere. After drying the polymerization bottle under an inert atmosphere, 50 ml of dry toluene was added to the polymerization bottle. The resulting solvent was then saturated with 15 PSIG monomer pressure and maintained through the course of the polymerization. The desired co-catalyst was then added in the proper Al–Ni ratio to the polymerization bottle via a syringe. If the amount of co-catalyst was too small to be measured out neatly by a syringe, a 10 ml toluene solution of the co-catalyst was made, and then 1 ml of the subsequent solution was added to the polymerization bottle. At this time, the solutions were brought to the desired temperatures and allowed to equilibrate for 15 min. Subsequently, 1 ml of a 50 μM toluene solution of the Ni catalyst was added to the polymerization reactors. The polymerizations were terminated after 1 h by quenching the mixture with 100 ml of a 2% HCl–MeOH solution. The obtained polymers were then filtered, washed with several 50 ml portions of 2% HCl–MeOH solution and dried in vacuo at

45 °C for several hours. After quenching, if the polymers remained in solution, the mixture was extracted with several portions of hexane, and the organic layers were collected, dried with $MgSO_4$ and filtered. After rotary evaporation of the solvent and drying in vacuo at 45 °C, an oily polymer was obtained.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 171422 and 171423 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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