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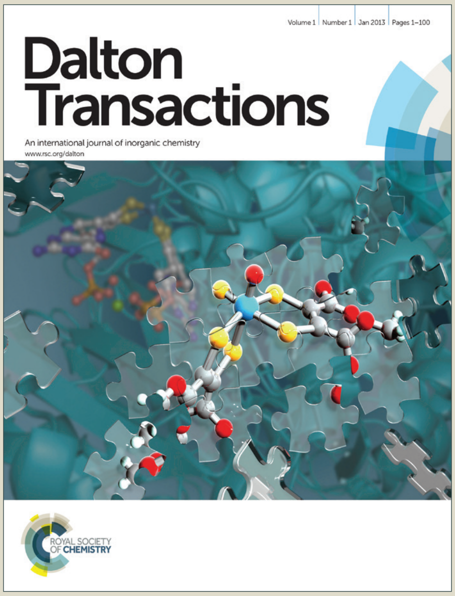

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ARTICLE TYPE

Ethylene Polymerisation and Ethylene/Norbornene Copolymerisation by Aryloxo-Modified Vanadium(V) Complexes Containing 2,6-Difluoro-, Dichloro-Phenylimido Complexes

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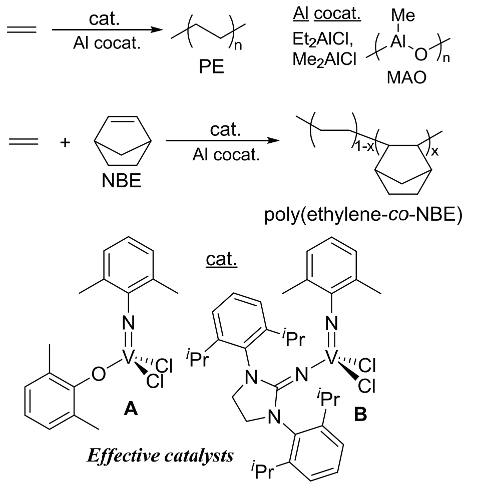
Aryloxo-modified vanadium(V) dichloride complexes containing dichloro- or difluoro-phenylimido ligand of type, $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)], showed remarkable catalytic activity in ethylene polymerisation and the copolymerisation with norbornene (NBE) in the presence of Et_2AlCl; the activities were higher than that by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ reported previously. Complex **1a** is a suitable catalyst precursor in terms not only of the activity, but also for synthesis of high molecular weight copolymers with both unimodal molecular weight distributions and uniform compositions.

Introduction

Due to a high reactivity toward olefins observed in olefin polymerisation using the classical Ziegler-type vanadium catalyst systems [e.g. consisting of $V(acac)_3$, $VOCl_3$ etc. and Et_2AlCl, $EtAlCl_2$, ^{n}BuLi etc.],[1-5] design and synthesis of the efficient vanadium complex pre-catalysts for olefin polymerisation attract considerable attention in the fields of catalysis, organometallic chemistry as well as polymer chemistry.[5-7] We have focused on (imido)vanadium(V) complexes containing anionic donor ligands of the type, $V(NAr)Cl_2(X)$ (X = aryloxo, ketimide, phenoxyimine, imidazolin-2-iminato, imidazolidin-2-iminato etc.),[5c,e,6,8] and demonstrated that these complexes, especially $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**A**) and $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2[1,3\text{-}(2,6\text{-}{}^iPr_2C_6H_3)_2(CH_2N)_2C{=}N]$ (**B**), exhibit remarkable catalytic activities for ethylene polymerisation in the presence of Al cocatalyst (Scheme 1).[6] In particular, the phenoxy analogue (**A**) showed remarkable catalytic activities for the ethylene/norbornene (NBE) copolymerisation with rather efficient NBE incorporation; both the activity and the NBE incorporation were strongly affected by Al cocatalyst (and solvent) employed.[6c-d] Moreover, we also demonstrated that (imido)vanadium(V) complexes containing (2-anilidomethyl)-pyridine ligand efficiently dimerize ethylene with both notable catalytic activity and high selectivity in the presence of methylaluminoxane (MAO).[8]

2,6-Dichlorophenylimido ligand was used in molybdenum-alkylidene complexes,[9] and these complexes showed unique reactivity especially in ring-closing metathesis reaction.[9] Two probable benefits to use this ligand is that (i) the dichloro-phenylimido ligand is smaller than the dimethylphenyl imido (less steric bulk) and (ii) placement of electron withdrawing group that may contribute to the unique reactivity toward olefins; these would affect nature of the coordinated olefins. We thus have an interest for syntheses of aryloxo-modified 2,6-dichlorophenyl and 2,6-difluorophenylimido analogues of type, $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)], and their use as the catalyst precursors for ethylene polymerisation and ethylene/norbornene copolymerisation.[10]

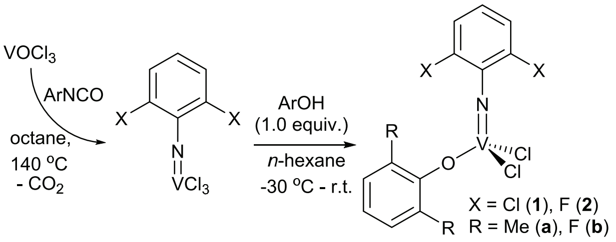


Scheme 1. Reported complexes as effective pre-catalysts for ethylene/ norbornene copolymerisation. (Complex **A** is also used **3a** in this text for comparison).

Results and Discussion

1. Synthesis of $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (1), F (2); R = Me (a), F (b)].

$V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_3$ (X = Cl, F) could be prepared in high yields (70-80 %) from $VOCl_3$ with ArNCO (Ar = $2,6\text{-}X_2C_6H_3$) in *n*-octane at 140 ºC, established method for synthesis of a series of (imido)vanadium(V) trichloride analogues.[11] The resultant complexes were identified by ^{1}H, ^{13}C and ^{51}V (and ^{19}F) NMR spectra, and elemental analysis. A series of (arylimido)-vanadium(V) dichloride complexes containing aryloxo ligands, $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**), Scheme 2] could be prepared in moderate yields from the trichloride analogue, $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_3$ with 0.9 equiv. of $2,6\text{-}X_2C_6H_3OH$ in *n*-hexane at -30 ºC. The reactions with $2,6\text{-}F_2C_6H_3OH$ were carried out in the freezer in the drybox to eliminate by-production of the bis(phenoxide) complexes. The analytically pure samples were obtained by removing volatiles *in vacuo*. These complexes were identified on the basis of NMR spectra and elemental analysis.



Scheme 2. Synthesis of aryloxo-modified (arylimido)vanadium(V) dichloride complexes.

2. Ethylene Polymerisation by $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (1), F (2); R = Me (a), F (b)] – Al Cocatalyst Systems.

Ethylene polymerisations by $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)] were conducted in toluene in the presence of d-MAO [prepared by removing toluene and $AlMe_3$ from the commercially available samples, TMAO-212. 9.1 wt% (Al) toluene solution, Tosoh Finechem Co.] or Et_2AlCl. The results by $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**3a**)[6c] are also cited for comparison. The results are summarised in Tables 1-2. The resultant polymers are linear polyethylene (by NMR spectra, DSC thermograms) that are not sufficiently soluble in hot 1,2,4-trichlorobenzene (150 ºC) required for a GPC analysis. Since, as described below, prepared poly(ethylene-*co*-norbornene)s possessed uniform molecular weight distributions, formation of ultrahigh molecular weight polymers was thus highly assumed in this catalysis as reported previously in the polymerisation by **3a** and the derivatives.[6b-d]

It turned out that the catalytic activities in the presence of MAO were affected by the Al/V molar ratio (Table 1), and the activity by $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ under the optimised molar ratios conducted at 25 ºC increased in the order: 344 kg-PE/mol-V·h (**2b**, run 17) < 641 (**2a**, run 13), 643 (**1a**, run 2), 662 (**1b**, run 7) < 1770 (**3a**, X = Me, run 18[6c]). The activities by **1a**,**b** at 0 ºC were higher than those conducted at 25 ºC, whereas the activities by **3a**, $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ (**3c**) at 0 ºC were lower than those conducted at 25 ºC [activities by **3a**,**3c** were 1770 kg-PE/mol-V·h, 1050 (25 ºC) and 441, 758 (0 ºC), respectively].[6c] The activity decreased at 50 ºC, and these might be due to a stability of the active species in this catalysis, although we do not have any clear reasons at this moment.

Table 1. Ethylene polymerisation by $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (**1**), F (**2**), Me (**3**); R = Me (**a**), F (**b**)] - MAO catalysts.[a]

run	cat. (µmol)	Al/V [b]	temp. / ºC	yield / mg	activity[c]
1	**1a** (2.5)	500	25	237	569
2	**1a** (2.5)	1000	25	268	643
3	**1a** (2.5)	1500	25	248	595
4	**1a** (5.0)	1000	25	389	467
5	**1a** (3.0)	1000	25	263	526
6	**1b** (2.5)	500	25	218	523
7	**1b** (2.5)	1000	25	276	662
8	**1b** (2.5)	1500	25	226	543
9	**1b** (5.0)	1000	25	336	403
10	**2a** (2.5)	500	25	166	398
11	**2a** (2.5)	1000	25	206	494
12	**2a** (2.5)	1500	25	234	562
13	**2a** (2.5)	2000	25	267	641
14	**2a** (2.5)	2500	25	271	650
15	**2a** (2.5)	3000	25	274	658
16	**2a** (5.0)	1000	25	358	430
17	**2b** (5.0)	1000	25	286	344
18	**3a** (2.5)[d]	1000	25	737	1770
19	**3a** (1.0)[d]	2500	25	488	2930
20	**1a** (2.5)	1000	0	388	931
21	**1b** (2.5)	1000	0	473	1140
22	**2a** (2.5)	2000	0	224	538
2	**1a** (2.5)	1000	25	268	643
7	**1b** (2.5)	1000	25	276	662
13	**2a** (2.5)	2000	25	230	552
23	**1a** (2.5)	1000	50	122	293
24	**1b** (2.5)	1000	50	158	379
25	**2a** (2.5)	2000	50	157	377

[a] Conditions: toluene 30 mL, 10 min, ethylene 8 atm, d-MAO white solid [prepared by removing $AlMe_3$, toluene from TMAO-S]. [b] Al/V molar ratio. [c] Activity in kg-PE/mol-V·h. [d] $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**3a**) cited from reference 6c.

Note that the catalytic activities by **1a**,**b** and **2a** were higher than that by **3a**,[6d] when these ethylene polymerisations were conducted in the presence of Et_2AlCl in place of MAO at 0 ºC (Table 2). The observed activities on the basis of polymer yields were also affected by the Al/V molar ratios. The activity at 0 ºC under the optimised Al/V molar ratio increased in the order: 11700 kg-PE/mol-V·h (**3a**, run 38[6d]) < 17400 (**1b**, run 32) < 31900 (**2a**, run 35) < 55800 (**1a**, run 27). The trend observed here is an interesting contrast to that in the presence of MAO (shown in Table 1). Interestingly, activity at 25 ºC increased in the order: 15800 kg-PE/mol-V·h (**1a**, run 39) < 17300 (**1b**, run 40) < 22200 (**2a**, run 41), and the degree of decrease in the activity was somewhat dependent upon the ligand set employed, as shown in Figure 1. Moreover, the activity by **2a** at 50 ºC (13900 kg-PE/mol-V·h, run 44) was also higher than those by **1a**,**b** (runs 42-43). Although the activity decreased upon increasing the reaction temperature, **2a** seems to be rather suitable as the catalyst precursor in terms of catalytic activity at 50 ºC. This is also an interesting contrast because a rapid decrease in the activity was observed if $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ (**3c**) was employed as the catalyst precursor [the activity by **3c** in the presence of Et_2AlCl: 7100 kg-PE/mol-V·h (0 ºC), 3980 (25 ºC), 652 (40 ºC), plotted in Figure 1].[6b]

Table 2. Ethylene polymerisation by V(N-2,6-$X_2C_6H_3$)Cl_2(O-2,6-$R_2C_6H_3$) [X = Cl (**1**), F (**2**), Me (**3**); R = Me (**a**), F (**b**)] – Et_2AlCl catalysts.[a]

run	cat.(μmol)	Al/V [b]	temp. / ºC	yield / mg	activity[c]
26	**1a** (0.05)	1000	0	415	49800
27	**1a** (0.05)	2000	0	465	55800
28	**1a** (0.05)	3000	0	445	53400
29	**1a** (0.02)	1000	0	168	50400
30	**1a** (0.02)	2000	0	144	43200
31	**1b** (0.05)	500	0	129	15500
32	**1b** (0.05)	1000	0	145	17400
33	**1b** (0.05)	2000	0	132	15800
34	**2a** (0.05)	500	0	178	21400
35	**2a** (0.05)	1000	0	266	31900
36	**2a** (0.05)	2000	0	251	30100
37	**2a** (0.05)	3000	0	227	27200
38	**3a** (0.05)[d]	5000	0	97	11700
27	**1a** (0.05)	2000	0	465	55800
32	**1b** (0.05)	1000	0	145	17400
35	**2a** (0.05)	1000	0	266	31900
39	**1a** (0.02)	2000	25	132	15800
40	**1b** (0.05)	1000	25	144	17300
41	**2a** (0.05)	1000	25	185	22200
42	**1a** (0.02)	2000	50	59	7080
43	**1b** (0.05)	1000	50	49	5880
44	**2a** (0.05)	1000	50	116	13900

[a] Conditions: toluene 30 mL, 10 min, ethylene 8 atm. [b] Al/V molar ratio. [c] Activity in kg-PE/mol-V·h. [d] V(N-2,6-$Me_2C_6H_3$)Cl_2(O-2,6-$Me_2C_6H_3$) (**3a**) cited from reference 6d.

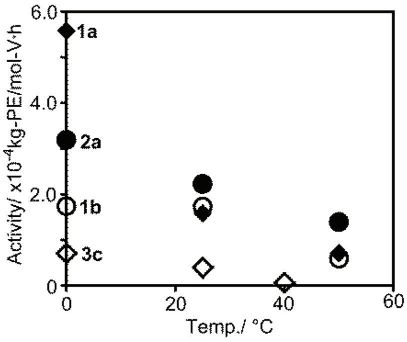


Figure 1. Temperature dependence toward the catalytic activity in ethylene polymerisation by V(N-2,6-$X_2C_6H_3$)Cl_2(O-2,6-$R_2C_6H_3$) [**1a**,**b**,**2a**; X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)] - Et_2AlCl catalyst systems. Data by V(N-2,6-$Me_2C_6H_3$)Cl_2(O-2,6-$^iPr_2C_6H_3$) (**3c**)[6b] were placed for comparison.

Figure 2 shows plots of the catalytic activity (under optimised conditions summarised in Table 3) against the chemical shifts (δ in ppm) in the ^{51}V NMR spectra in $CDCl_3$ (at 25 ºC), because we recently demonstrated a good relationship between the catalytic activity and the chemical shift in the ethylene polymerisation using (arylimido)vanadium complexes containing imidazolin-2-iminato or imidazolidin-2-iminato ligand in the presence of Et_2AlCl cocatalyst.[6h] It is interesting to note that a fairly good relationship was also observed in **1a**,**b** and **2a**. The fact might also suggest that a certain degree of electron donation plays a role toward the activity. As assumed in our previous report,[6h] one simple assumption which one might take into consideration on the basis of the results reported for the half-titanocenes such as Cp'Ti(OMe)$_3$ (Cp' = cyclopentadienyl group) in the syndio-specific styrene polymerisation[12] or Cp'TiCl$_2$(O-2,6-$^iPr_2C_6H_3$) in ethylene polymerisation[13] could be that a stabilization of the active site by more electron-donating substituents is important for the observation of high activity.[14]

Table 3. Summary in ethylene polymerisation by V(N-2,6-$X_2C_6H_3$)Cl_2(O-2,6-$R_2C_6H_3$) [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)] - Et_2AlCl catalysts (at 0 ºC).[a]

run	cat. (μmol)	Al/V [b]	activity[c]	δ (ppm) ^{51}V NMR
27	**1a** (0.05)	2000	55800	-19.4
32	**1b** (0.05)	1000	17400	-6.0
35	**2a** (0.05)	1000	31900	-13.0
38	**3a** (0.05)[b]	5000	11700	40.3

[a] Data cited from Table 2. [b] V(N-2,6-$Me_2C_6H_3$)Cl_2(O-2,6-$Me_2C_6H_3$) (**3a**) cited from reference 6d.

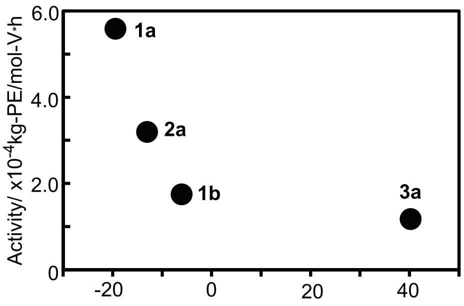
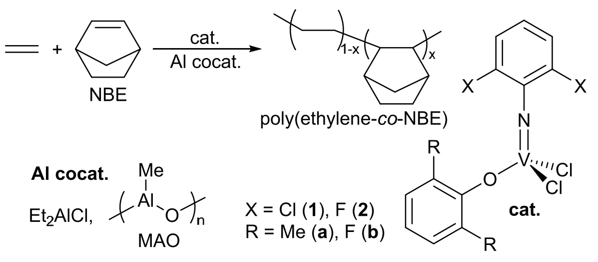


Figure 2. Plots of catalytic activity (kg-PE/mol-V·h) in ethylene polymerisation (in the presence of Et_2AlCl at 0 ºC) *vs* chemical shifts (δ in ppm) of the vanadium complexes (on the basis of data in Table 3).

3. Ethylene/Norbornene Copolymerisation by V(N-2,6-$X_2C_6H_3$)Cl_2(O-2,6-$R_2C_6H_3$) [X = Cl (1), F (2); R = Me (a), F (b)] – Al Cocatalyst Systems.

Certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV-Vis region along with humidity-, heat-resistance (high glass transition temperature, T_g),[15] and these polymers have been commercialized (as TOPAS®)[16] by using metallocene catalysts as ultra-pure (applicable to advanced pharma packaging, food contact films), crystal clear (glass clear, amorphous), high barrier (resistant to moisture, alcohols, acids) materials.[16-18] Since we previously reported that V(N-2,6-$Me_2C_6H_3$)Cl_2(O-2,6-$Me_2C_6H_3$) (**3a**) showed unique characteristics as the catalyst precursor in this copolymerisation, we thus explored possibilities for V(N-2,6-$X_2C_6H_3$)Cl_2(O-2,6-$R_2C_6H_3$) [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)] in the presence of Al cocatalysts. The results are summarised in Table 4.



Scheme 3. Copolymerisation of ethylene with norbornene (NBE) by V(N-2,6-$X_2C_6H_3$)Cl_2(O-2,6-$R_2C_6H_3$) [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)] – Al cocatalyst systems.

It turned out that these complexes (**1a**,**b**, **2a**,**b**) exhibited remarkable catalytic activities for the copolymerisation, affording high molecular weight polymers with uniform molecular weight distributions. As reported previously by **3a**, the activities in the presence of Et_2AlCl were higher than those in the presence of MAO. The activity in the presence of MAO (conditions: ethylene 8 atm, NBE 1.0 mmol/mL) increased in the order: 367 kg-polymer/mol-V·h (**3a**, run 54),[6d] 470 (**2a**, run 50) < 775 (**2b**, run 52) < 1540 (**1a**, run 46) < 2450 (**1b**, run 48). The activity in the presence of Et_2AlCl (conditions: ethylene 8 atm, NBE 1.0 mmol/mL) increased in the order: 24000 kg-polymer/mol-V·h (**3a**, run 64),[6d] 22600 (**2b**, run 62) < 33000 (**1b**, run 58) < 43200 (**2a**, run 60) < 44200 (**1a**, run 56). In terms of the activity, it thus seems likely that the 2,6-dichlorophenylimido analogue (**1a**) showed the higher catalytic activity than the 2,6-difluorophenylimido analogue (**2a**) and 2,6-dimethylphenylimido analogue (**3a**). These also indicate that an introduction of halogen (Cl, F) into 2,6-position in the phenylimido ligand is effective to increase the catalytic activity as observed in the ethylene polymerisation (Tables 1-2).

In contrast, the NBE contents in the resultant copolymer (estimated by ^{13}C NMR spectra according to the reported procedure[17-19]) prepared by these complexes (**1a**,**b** and **2a**,**b**) in the presence of Al cocatalyst (under the same conditions) were lower than those by **3a** in most cases [NBE content[19] under ethylene 8 atm, NBE 1.0 mmol/mL: (MAO cocatalyst) 15.8 mol% (**1a**), 16.3 (**1b**) < 22.9 (**2a**), 24.7 (**2b**) < 32.9 (**3a**); (Et_2AlCl cocatalyst) 12.1 mol% (**1a**) < 14.2 (**1b**), 14.3 (**2a**) < 16.8 (**2b**), 17.3 (**3a**)], whereas, as demonstrated previously,[6d,e] the NBE incorporation was affected by the Al cocatalyst employed.

Table 4. Copolymerisation of ethylene with norbornene (NBE) by $V(N-2,6-X_2C_6H_3)Cl_2(O-2,6-R_2C_6H_3)$ [X = Cl (**1**), F (**2**), Me (**3**); R = Me (**a**), F (**b**)] – Al cocatalyst systems.[a]

run	cat. (μmol)	Al cocat.	Al/V [b]	NBE conc.[c]	temp. / °C	yield / mg	activity[d]	NBE[e] / mol %	$M_w \times 10^{-4}$	M_w/M_n[f]	T_g (T_m)[g]/ °C
45	**1a** (1.0)	d-MAO	2500	0.5	25	347	2080	9.6	20.3	2.98	-2.2 (63.4)
46	**1a** (1.0)	d-MAO	2500	1.0	25	257	1540	15.8	25.5	2.70	7.5
47	**1b** (0.5)	d-MAO	1500	0.5	25	265	3180	10.4	22.9	3.31	-4.6 (65.8)
48	**1b** (0.5)	d-MAO	1500	1.0	25	204	2450	16.3	26.3	2.69	5.5
49	**2a** (2.5)	d-MAO	2000	0.5	25	272	653	20.9	7.80	1.91	38.8
50	**2a** (2.5)	d-MAO	2000	1.0	25	196	470	22.9	7.00	1.53	44.9
51	**2b** (2.5)	d-MAO	1500	0.5	25	387	929	23.8	6.40	1.58	42.4
52	**2b** (2.5)	d-MAO	1500	1.0	25	323	775	24.7	7.40	1.56	83.6
53	**3a** (1.0)[h]	d-MAO	2500	0.5	25	146	875	23.9	53.5	1.79	
54	**3a** (2.5)[h]	d-MAO	1000	1.0	25	153	367	32.9	20.4	1.85	
55	**1a** (0.05)	Et_2AlCl	2000	0.5	0	416	49900	9.4	9.07	1.66	-4.0 (43.9)
56	**1a** (0.05)	Et_2AlCl	2000	1.0	0	368	44200	12.1	9.52	1.45	2.3
57	**1b** (0.05)	Et_2AlCl	1000	0.5	0	285	34200	8.0	15.1	1.63	-6.0 (57.5)
58	**1b** (0.05)	Et_2AlCl	1000	1.0	0	275	33000	14.2	13.7	1.57	6.1
59	**2a** (0.05)	Et_2AlCl	1000	0.5	0	354	42500	10.0	8.14	1.58	-2.8 (41.8)
60	**2a** (0.05)	Et_2AlCl	1000	1.0	0	360	43200	14.3	6.72	1.58	6.6
61	**2b** (0.05)	Et_2AlCl	1000	0.5	0	206	24700	11.6	13.7	1.69	-4.3 (46.2)
62	**2b** (0.05)	Et_2AlCl	1000	1.0	0	188	22600	16.8	13.1	1.51	8.5
63	**3a** (0.05)[h]	Et_2AlCl	5000	0.5	0	265	31700	10.4	58.2	1.29	
64	**3a** (0.05)[h]	Et_2AlCl	5000	1.0	0	200	24000	17.3	35.0	1.53	

[a]Conditions: toluene 30 mL, ethylene 8 atm, 10 min, d-MAO white solid [prepared by removing $AlMe_3$, toluene from TMAO-S] or Et_2AlCl. [b]Al/V molar ratio. [c]NBE concentration charged (mol/L). [d]Activity in kg-polymer/mol-V·h. [e]NBE content (mol %) estimated by ^{13}C NMR spectra. [f]GPC data in 1,2,4-trichlorobenzene *vs* polystyrene standards. [g]By DSC thermograms. [h]Data by $V(N-2,6-Me_2C_6H_3)Cl_2(O-2,6-Me_2C_6H_3)$ (**3a**) cited from reference 6d.

Table 5 summarizes results in the copolymerisation by **1b** – MAO and **1a** – Et_2AlCl conducted under rather high NBE concentration and/or low ethylene pressure conditions. The catalytic activity by **1b** – MAO catalyst system decreased upon increasing the NBE concentration charged, whereas increase in the NBE content in the resultant copolymer was observed without significant difference in the M_w values. The similar trend was observed in the copolymerisation by **1a** – Et_2AlCl catalyst system. The NBE contents prepared by **1b** – MAO catalyst system are apparently higher than those prepared by **1b** – Et_2AlCl catalyst system, due to effect of Al cocatalyst as observed in Table 4 as well as reported previously.[6d,e] No significant decreases in the M_w values in the resultant copolymers were observed even upon increasing the NBE concentration in the copolymerisation using **1a** – Et_2AlCl catalyst system. Although the observed fact is somewhat analogous to that in the copolymerisation by **3a** – Al cocatalyst systems, **1a** – Et_2AlCl catalyst system showed better catalyst performance in the copolymerisation especially in terms of catalytic activity *under high NBE concentrations* [for example, the activity by **3a** under NBE conc. of 2.0, 4.0 M were 2440 kg-polymer/mol-V·h, 792, respectively[6d] *vs* the activity by **1a** were 22700, 13900, respectively]. Moreover, it has been well known that the activities by ordinary metallocene and linked half-titanocene (exemplified as CGC) under these conditions were low.[18b] Therefore, using **1a** seems to be suitable for synthesis of high molecular weight copolymer with rather high NBE content.

The resultant polymers were high molecular weight poly(ethylene-*co*-NBE)s with uniform compositions (confirmed by DSC thermograms) as well as molecular weight distributions. On the basis of plots of glass transition temperature (T_g) *vs* the NBE contents (mol%), the T_g values increased linearly upon increasing the NBE contents (Figure 3), as demonstrated previously.[17,18] A high molecular weight copolymers with rather high T_g value as well as with uniform composition (and molecular weight distribution) could be thus prepared in this catalysis.

Figure 4 shows selected ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 °C) for poly(ethylene-*co*-NBE)s prepared by $V(N-2,6-Cl_2C_6H_3)Cl_2(O-2,6-Me_2C_6H_3)$ (**2a**) –

Et_2AlCl catalyst system (ethylene 8 atm, NBE 5.0 M, run 74, NBE content: 32.5 mol%, Table 5).[19] Resonances ascribed to alternating ethylene-NBE sequences as well as isolated NBE units (33.0-33.5 ppm) were observed and no resonances ascribed to NBE repeat units were observed.[17-19] Therefore, it seems difficult to prepare the copolymer with an NBE content higher than 50 mol% in this catalytic copolymerisation.

Table 5. Copolymerisation of ethylene with norbornene (NBE) by $V(N\text{-}2,6\text{-}Cl_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [R = Me (**1a**), F (**1b**)] – Al cocatalyst systems.[a]

run	cat. (μmol)	ethylene / atm	NBE conc.[b]	Al cocat.	yield/ mg	activity[c]	NBE[d] / mol %	M_w[e] $\times 10^{-5}$	M_w/M_n[e]	T_g (T_m)[f] / ºC
47	**1b** (0.5)	8	0.5	d-MAO	265	3180	10.4	2.29	3.31	-4.6 (65.8)
48	**1b** (0.5)	8	1.0	d-MAO	204	2450	16.3	2.63	2.69	5.5
65	**1b** (1.0)	8	2.0	d-MAO	269	1610	25.5	1.79	1.92	41.7
66	**1b** (2.0)	8	3.0	d-MAO	456	1370	27.9	2.59	1.88	71.1
67	**1b** (2.0)	8	4.0	d-MAO	427	1280	30.1	insoluble		75.6
68	**1b** (2.5)	8	5.0	d-MAO	468	1120	34.4	insoluble		82.9
69	**1b** (2.5)	4	5.0	d-MAO	153	367	35.7	insoluble		104.5
70	**1b** (2.5)	2	5.0	d-MAO	81	194	41.1	insoluble		112.4
55	**1a** (0.05)	8	0.5	Et_2AlCl	416	49900	9.4	0.91	1.66	-4.0 (43.9)
56	**1a** (0.05)	8	1.0	Et_2AlCl	368	44200	12.1	0.95	1.45	2.3
71	**1a** (0.05)	8	2.0	Et_2AlCl	189	22700	16.4	16.4	1.57	19.7
72	**1a** (0.10)	8	3.0	Et_2AlCl	298	17900	21.2	12.1	1.45	39.8
73	**1a** (0.20)	8	4.0	Et_2AlCl	462	13900	29.7	12.6	1.74	66.8
74	**1a** (0.30)	8	5.0	Et_2AlCl	284	5680	32.5	13.2	1.77	65.0
75	**1a** (0.30)	2	5.0	Et_2AlCl	86	1720	38.8	1.71	1.59	107.2

[a] Conditions: toluene 30 mL, 10 min, ethylene 8 atm, 25 ºC (d-MAO, Al/V = 1500, molar ratio) or 0 ºC (Et_2AlCl, Al/V = 2000, molar ratio). [b] Norbornene (NBE) concentration charged (mol/L). [c] Activity in kg-polymer/mol-V·h. [d] NBE content (mol %) estimated by ^{13}C NMR spectra.[19] [e] GPC data in -1,2,4-trichlorobenzene vs polystyrene standards. [f] By DSC thermograms.

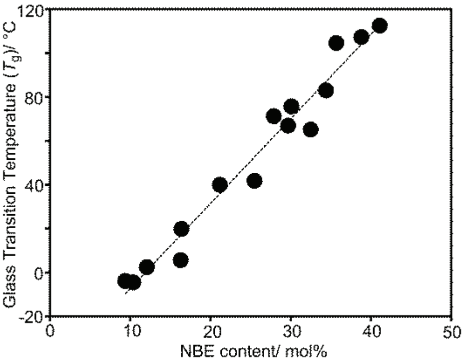


Figure 3. Plots of glass transition temperature (T_g) *vs* NBE contents.[19]

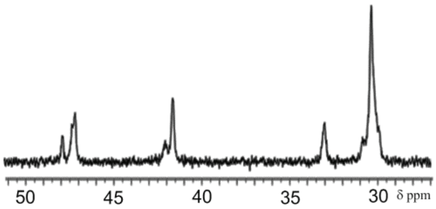


Figure 4. ^{13}C NMR spectrum (in 1,2-dichlorobenzene-d_4 at 120 ºC) for poly(ethylene-*co*-norbornene)s prepared by $V(N\text{-}2,6\text{-}Cl_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**2a**) – Et_2AlCl catalyst system (ethylene 8 atm, NBE 5.0 M, run 74, NBE content: 32.5 mol%, Table 5).[19]

Conclusions

In summary we have shown that $V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [X = Cl (**1**), F (**2**); R = Me (**a**), F (**b**)] – Al cocatalyst systems showed remarkable catalytic activity in ethylene polymerisation, and the activities by **1a**,**b**,**2a** in the presence of Et_2AlCl were higher than $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**3a**). Complex **2a** seems to be rather suitable as the catalyst precursor in terms of the activity at 50 ºC. These complexes also showed higher catalytic activities in the ethylene copolymerisation with norbornene (NBE) than **3a**, affording high molecular weight copolymer with unimodal molecular weight distributions as well as uniform compositions (confirmed by DSC thermograms). In terms of the activity under high NBE concentration, **1a** is the suitable catalyst precursor for synthesis of high molecular weight copolymer with rather high NBE content. We highly believe that this is a promising characteristics for using 2,6-dichlorophenylimido and 2,6-difluorophenylimido analogues as the catalyst precursor for olefin polymerisation, and the fact observed here should be promising for better design of efficient catalyst precursors for precise olefin polymerisation.

Experimental Section

General procedure.

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. Anhydrous grade toluene, benzene, *n*-hexane, and dichloromethane (Kanto Kagaku Co., Ltd.) were transferred into a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 and were passed through a short alumina column under a N_2 stream prior to use. All chemicals used were of reagent grades and were purified by standard purification procedures. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [TMAO-212. 9.1 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, $AlMe_3$ and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Ethylene for polymerisation was of polymerisation grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received. Elemental analyses were performed by using EAI CE-440 CHN/O/S

Elemental Analyzer (Exeter Analytical, Inc.). All ^{1}H, ^{13}C, ^{19}F, and ^{51}V NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^{1}H, 125.95 MHz for ^{13}C, 470.40 MHz for ^{19}F, and 131.55 MHz for ^{51}V). All spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00 ppm, ^{1}H, ^{13}C), $CFCl_3$ (δ 0.00, ^{19}F), and $VOCl_3$ (δ 0.00, ^{51}V). Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00 ppm, ^{1}H, ^{13}C) and $VOCl_3$ (δ 0.00 ppm, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in Hz. ^{13}C NMR data of the polymers were obtained on a Varian Unity-400 MHz spectrometer at 125 °C, with o-$C_6D_4Cl_2$ as a solvent, and the NMR spectra were recorded with proton decoupling, and the pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients accumulated was ca. 6000.

Molecular weights and molecular weight distributions for the resultant polymers were determined at 150 ºC by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10-μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd). The melting temperatures (T_m) and glass transition temperatures (T_g) of the polymers were measured by differential scanning calorimetry (DSC) using a TA Instruments Q2000 calorimeter equipped with an automated sampler. The data were collected with the heat/cool/heat cycle at a heating rate of 20 °C/min under N_2 atmosphere.

Synthesis of V(N-2,6-$Cl_2C_6H_3$)Cl_3.

Into an n-octane solution (20 mL) containing 2,6-$Cl_2C_6H_3NCO$ (2.00 g, 10.7 mmol) was added $VOCl_3$ (2.78 g, 16.1 mmol). The reaction mixture was stirred at 140 ºC for overnight and CO_2 gas was released during the reaction time. After the reaction, the mixture was then filtered through a Celite pad using CH_2Cl_2 as solvent. The solvent was removed *in vacuo* to give a green solid. The solid was then dissolved in a small amount of CH_2Cl_2 layered by n-hexane. The solution was placed in the freezer at –30 ºC to obtain green solid. Yield: 2.44 g (72%). ^{1}H NMR (C_6D_6): δ 6.29 (d, J = 10.0 Hz, 2H, Ar-H), 5.81 (t, J = 7.5 Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 135.8, 131.8, 128.3. ^{51}V NMR (C_6D_6): δ 262.3 ($\Delta\nu_{1/2}$ = 358 Hz). Anal. Calcd. for $C_6H_3Cl_5NV$: C, 22.71; H, 0.95; N, 4.41. Found: C, 22.69; H, 0.71; N, 4.36.

Synthesis of V(N-2,6-$F_2C_6H_3$)Cl_3.

Into an n-octane solution (20 mL) containing 2,6-$F_2C_6H_3NCO$ (2.00 g, 12.89 mmol) was added $VOCl_3$ (3.35 g, 19.34 mmol). The reaction mixture was stirred at 140 ºC for overnight and CO_2 gas was released during the reaction time. After the reaction, the mixture was then filtered through a Celite pad using CH_2Cl_2 as solvent. The solvent was removed *in vacuo* to give a green solid. The solid was then dissolved in a small amount of CH_2Cl_2 layered by n-hexane. The solution was placed in the freezer at –30 ºC to obtain green solid. Yield: 2.97 g (81 %). ^{1}H NMR (C_6D_6): δ 5.93 (m, 1H, Ar-H), 5.87 (m, 2H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 133.1, 111.8, 111.6. ^{19}F NMR (C_6D_6): δ -113.3. ^{51}V NMR (C_6D_6): δ 262.7 ($\Delta\nu_{1/2}$ = 371 Hz). Anal. Calcd. for $C_6H_3Cl_3F_2NV$: C, 25.34; H, 1.06; N, 4.93. Found: C, 25.49; H, 0.95; N, 4.94.

Synthesis of V(N-2,6-$Cl_2C_6H_3$)Cl_2(O-2,6-$Me_2C_6H_3$) (1a).

Into a n-hexane solution (50 mL) containing V(N-2,6-$Cl_2C_6H_3$)Cl_3 (0.349 g, 1.10 mmol), a n-hexane solution (15 mL) of 2,6-$Me_2C_6H_3OH$ (0.122 g, 1.00 mmol) was added in a dropwise manner at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was then stirred for 24 h. The solvent was removed *in vacuo*. The resultant dark purple residue was dissolved in n-hexane (ca. 10 mL). The solution was then placed in the freezer at -30 °C to obtain dark purple solid and was washed quickly with a small amount of cold hexane and dried *in vacuo*. Yield: 0.32 g (79 %). ^{1}H NMR (C_6D_6): δ 6.72-6.66 (m, 3H, Ar-H), 6.28 (d, J = 3.6 Hz, 2H, Ar-H), 5.76 (t, J = 8.2 Hz, 1H, Ar-H), 2.20 (s, 6H, -CH_3). ^{13}C NMR ($CDCl_3$): δ 129.6, 128.2, 127.8, 126.3, 125.9, 17.1. ^{51}V NMR (C_6D_6): δ -19.4 ($\Delta\nu_{1/2}$ = 362 Hz). Anal. Calcd. for $C_{14}H_{12}Cl_4NOV$: C, 41.72; H, 3.00; N, 3.48. Found: C, 41.34; H, 2.85; N, 3.40.

Synthesis of V(N-2,6-$Cl_2C_6H_3$)Cl_2(O-2,6-$F_2C_6H_3$) (1b).

Into a toluene solution (50 mL) containing V(N-2,6-$Cl_2C_6H_3$)Cl_3 (0.333 g, 1.05 mmol) was added dropwise an toluene solution containing 2,6-$F_2C_6H_3OH$ (0.130 g, 1.0 mmol) at –30 ºC. The reaction mixture was warmed slowly to room temperature, and then the mixture was stirred for 24 h. After the reaction, the solvent was removed *in vacuo* to give brown solid. The brown solid was dissolved in a small amount of n-hexane. The solution was placed in the freezer at –30 ºC to obtain green microcrystal. Yield: 16 mg (52 %). ^{1}H NMR (C_6D_6): δ 6.39-6.29 (m, 2H, Ar-H), 6.26 (d, J = 8.1 Hz, 2H, Ar-H), 6.20-6.14 (m, 1H, Ar-H), 5.76 (t, J = 7.9 Hz, 1H, Ar-H). ^{13}C NMR ($CDCl_3$): δ 127.8, 111.6 (dd, J = 17.2, 4.9 Hz). ^{19}F NMR (C_6D_6): δ -127.2. ^{51}V NMR (C_6D_6): δ -6.0 ($\Delta\nu_{1/2}$ = 342 Hz). Anal. Calcd. for $C_{12}H_6Cl_4F_2NOV$: C, 35.07; H, 1.47; N, 3.41. Found: C, 34.81; H, 1.43; N, 3.37.

Synthesis of V(N-2,6-$F_2C_6H_3$)Cl_2(O-2,6-$Me_2C_6H_3$) (2a).

Into a toluene solution (40 mL) containing V(N-2,6-$F_2C_6H_3$)Cl_3 (0.171 g, 0.60 mmol), a toluene solution (15 mL) of 2,6-$Me_2C_6H_3OH$ (61.0 mg, 0.50 mmol) was added dropwise at -30 °C. The reaction mixture was then warmed slowly to room temperature, and was stirred for 24 h. The solvent was removed *in vacuo*, and the resultant red purple residue was dissolved in n-hexane (ca. 8 mL). The solution was then placed in the freezer at -30 °C to obtain red purple microcrystals and was washed quickly with a small amount of cold hexane and dried *in vacuo*. Yield: 0.11 g (59 %). ^{1}H NMR (C_6D_6): δ 6.77-6.69 (m, 3H, Ar-H), 5.87-5.76 (m, 3H, Ar-H), 2.22 (s, 6H, -CH_3). ^{13}C NMR: δ 130.45 (t, J = 9.2 Hz), 128.19, 126.34, 125.39, 111.23 (dd, J = 19.0, 3.6 Hz), 16.92. ^{19}F NMR (C_6D_6): δ -115.2. ^{51}V NMR (C_6D_6): δ -13.0 ($\Delta\nu_{1/2}$ = 331 Hz). Anal. Calcd. for $C_{14}H_{12}Cl_4NOV$: C, 45.43; H, 3.27; N, 3.78. Found: C, 45.35; H, 3.25; N, 3.82.

Synthesis of V(N-2,6-$F_2C_6H_3$)Cl_2(O-2,6-$F_2C_6H_3$) (2b).

Into a n-hexane solution (45 mL) containing V(N-2,6-$F_2C_6H_3$)Cl_3 (0.171 g, 0.60 mmol), a n-hexane solution (15 mL) of 2,6-$F_2C_6H_3OH$ (65 mg, 0.50 mmol) was added dropwise at -30 °C. The reaction mixture was stirred at -30 °C for 24 h. The solvent was removed *in vacuo*, and the resultant dark brown residue was dissolved in toluene (ca. 1.5 mL), and layered with n-hexane (ca. 8 mL). The solution was then placed in the freezer at -30 °C to obtain dark brown microcrystals and was washed quickly with a small amount of cold *n*-hexane and dried *in vacuo*. ^{1}H NMR (C_6D_6): δ 6.43-6.35 (m, 2H, Ar-*H*), 6.26-6.20 (m, 1H, Ar-*H*), 5.84 (q, *J* = 8.9 Hz, 3H, Ar-*H*). ^{13}C NMR ($CDCl_3$): 111.59 (dd, *J* = 17.1, 5.0 Hz), 111.27 (dd, *J* = 18.9, 3.1 Hz). ^{19}F NMR (C_6D_6): δ -114.6, -127.7. ^{51}V NMR (C_6D_6): δ 3.8 ($\Delta\nu_{1/2}$ = 370 Hz). Anal. Calcd. for $C_{14}H_6Cl_2F_4NOV$: C, 38.13 (34.96 + vanadium carbide); H, 1.60; N, 3.71. Found: C, 35.31; H, 1.48; N, 3.84.

Ethylene polymerisation and copolymerisation of ethylene with norbornene (NBE).

Ethylene polymerisations were conducted in toluene by using a 100 mL scale autoclave. The solvent and the prescribed amount of cocatalyst (total solvent volume = 30 mL) were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of the vanadium pre-catalyst via a syringe, the reaction apparatus was immediately pressurized to 8, 4 or 2 atm and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resulting polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo*. Experimental procedures for the copolymerisation of ethylene with NBE were the same as those for the ethylene polymerisation described above except that prescribed amounts of NBE were added into an autoclave.

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Notes and references

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19 Selected ^{13}C NMR spectra and DSC thermograms in the poly(ethylene-*co*-norbornene)s are shown in the Electronic Supplementary Information (ESI).

Contents Abstract

Ethylene Polymerisation and Ethylene/Norbornene Copolymerisation by Aryloxo-Modified Vanadium(V) Complexes Containing 2,6-Difluoro-, Dichloro-Phenylimido Complexes

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$V(N\text{-}2,6\text{-}X_2C_6H_3)Cl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ (X = Cl, F; R = Me, F), showed remarkable activity in ethylene polymerisation and the copolymerisation with norbornene in the presence of Et_2AlCl.