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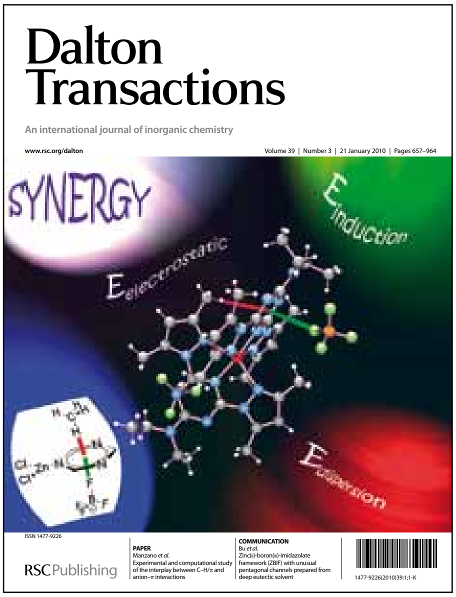

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Ni(II) and Fe(II) Complexes Based on Bis(imino)aryl Pincer Ligands: Synthesis, Structural Characterization and Catalytic Activities

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Bis(imino)aryl NCN pincer Ni(II) complexes 2,6-(ArN=CH)$_2$C$_6$H$_3$NiBr (**1**: Ar = 2,6-Me$_2$C$_6$H$_3$; **2**: Ar = 2,6-Et$_2$C$_6$H$_3$; **3**: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) were prepared *via* oxidative-addition of Ni(0)(Ph$_3$P)$_4$ with bis(N-aryl)-2-bromoisophthalaldimine. These nickel complexes were well characterized by NMR and elemental analyses. Their solid molecular structure were established by X-ray diffraction analyses. The nickel metal centers adopt distorted square planar geometries with the bromine atoms as one coordinate ligand. The NCN pincer Fe(II) complexes 2,6-(ArN=CH)$_2$C$_6$H$_3$Fe(μ-Cl)$_2$Li(THF)$_2$ (**4**: Ar = 2,6-Me$_2$C$_6$H$_3$; **5**: Ar = 2,6-Et$_2$C$_6$H$_3$; **6**: Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) were synthesized by lithium salt metathesis reactions of the ligand lithium salts with FeCl$_2$. X-ray structure analyses of **4** and **5** revealed that the Fe(II) complexes are hetero-dinuclear with the iron atoms in trigonal bipyramidal environments. When activated with MAO, the nickel complexes are active for norbornene vinyl polymerization but are inert for butadiene polymerization. The Fe(II) complexes show moderate activities in butadiene polymerization when activated with alkylaluminum affording the *cis*-1,4 enriched polymer.

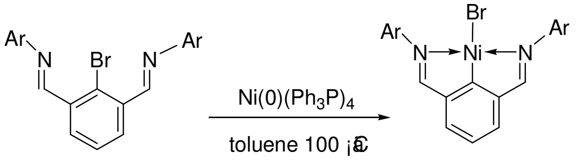
Introduction

In the past decades, late transition metal complexes have attracted considerable attentions in the olefin polymerization area for their low electrophilicity and more heteroatom tolerance.[1] Ever since the discovery of highly active Ni and Pd olefin polymerization catslysts bearing bidentate α-diimine ligands by Brookhart and co-workers in 1995,[2] a large amount of late-transition-metal based catalysts were synthesized and investigated. It is revealed that the bulky substituents of the ligands in the axial position play an important role in suppressing the β-H elimination, and therefore high molecular weight polymer were produced.[2] Three years later, Brookhart and Gibson reported respectively the Fe(II) and Co(II) complexes supported by bis(imine)pyridine ligands, which show high activities in ethylene polymerization.[3] The bis(imino)pyridine Ni(II) complexes show moderate to low activities in ethylene oligomerization/polymerization,[4, 5] but exhibit high activities in norbornene vinyl polymerization [6] and butadiene polymerization.[5] In these bis(imino)pyridine-based complexes, the metal centers were firmly chelated by the tridentate ligands. In addition, the dihedral angles between the two N-aryl moieties are relatively smaller than those in the bidentate α-diimine analogous and the metal centers were efficiently protected by the two N-aryl moieties during the activation and polymerization. Inspired by the pioneering works of Brookhart and Gibson, some tridentate ligands with similar frameworks were extensively explored.[7] Substituents with different steric and electronic effects were used and the influence of the steric and electronic properties of the substituents on the catalytic behaviour of the metal complexes were well inspected.[8]

The bis(imino)aryl NCN pincer ligands, which have similar backbone to the bis(imine)pyridine, have been explored and widely investigated in the coordination chemistry and organometallic chemistry. The complexes based on such ligands exhibit some unique properties in balancing the stability *vs* reactivity *via* the ligand modification and variation of the metal center.[9] The Pd,[10,11] Pt,[11] Rh[11b,12] and Ir [11] complexes supported by such ligands were synthesized and investigated in catalysis on Heck-coupling and C–C bond formation *etc* reactions and material science. The lanthanide compelxes and chromium complexes bearing NCN pincer ligands, we have reported early, show high activities and high selectivities in dienes polymerization.[13] More recently we have reported the pincer aluminium and zinc complexes which show moderate activitites and good controllabilities in lactide polymerization.[14] In despite of some Ni(II) complexes based on the NCN pincer ligand have been reported,[15] their molecular-structure or catalytic behaviors were less explored. Moreover the Fe(II) complexes with NCN pincer ligands are not reported yet. Their structure and catalytic activities are also unknown so far. Herein we report the synthesis and structural characterization of the NCN pincer Ni(II) and Fe(II) complexes. The catalytic behavior of these complexes towards norbornene and butadiene polymerization were also presented.

Results and discussion

Synthesis and characterization of nickel complexes



1 Ar = 2,6-Me$_2$-C$_6$H$_3$
2 Ar = 2,6-Et$_2$-C$_6$H$_3$
3 Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$

Transmetallation, transcyclometallation and oxidative-addition are the main strategies for preparing pincer complexes.[13a] The oxidative-addition is the most convenient method and was widely used in the syntheses of the Pd, Pt, Ru and Ni pincer complexes. The nickel complexes were synthesized *via* the direct oxidative-addition of Ni(0)(Ph$_3$P)$_4$ with the corresponding bromine-substituted ligands in toluene at 100 °C. After evaporations of the toluene in vacuum, the residues were washed with hot hexane to remove the PPh$_3$. The products were obtained as orange powder in nearly quantative yields. All the nickel complexes are high soluble in toluene and dichloromethane. These complexes are very stable at room temperature and no apparent decomposition was found when open to the air for several days.

Complexes **1**–**3** were characterized with ^{1}H NMR and ^{13}C {^{1}H} NMR spectroscopy. The ^{1}H NMR spectra of these complexes show similar topology at low field and for all the complexes a singlet was observed within δ 7.89～7.90 ppm assignable to the C*H*=N proton which shifting to upfield when compared to that in the corresponding free ligands. At high field, complexe **1** and **2** show typical resonances for the methyl and ethyl groups attached to the ligands respectively. While in contrast to the free ligands, in which only one set of doublet for isopropyl methyl group was found, complex **3** shows two sets of doublets at 1.15 ppm and 1.36 ppm for non-equivalent isopropyl methyl groups, probably due to the restricted rotation about the N-C$_{\text{aryl}}$ bonds arising from the coordination of the ligand to the nickel metal center.[16]

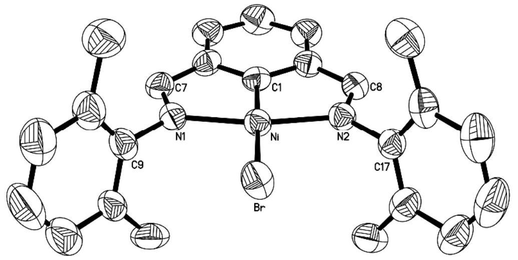


Figure 1. Perspective view of complex **1** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated Ph$_3$P are omitted for clarity.

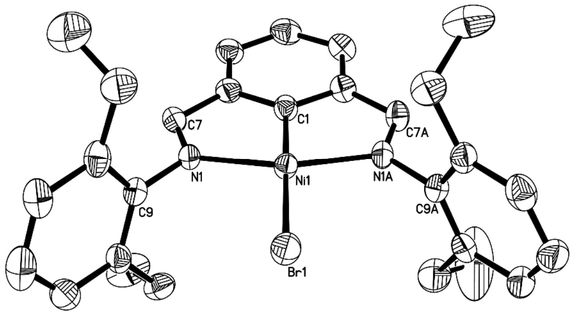


Figure 2. Perspective view of complex **2** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvents are omitted for clarity.

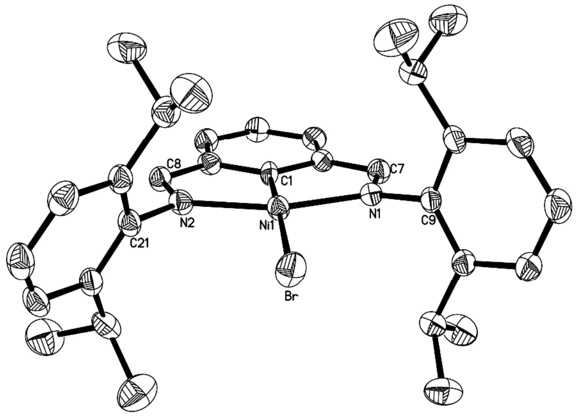
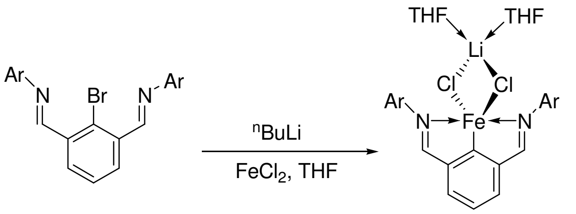


Figure 3. Perspective view of complex **3** with thermal ellipsoids drawn at 30% probability level. Hydrogens and uncoordinated solvents are omitted for clarity.

The solid molecular structure of complexes **1**–**3** were established by X-ray diffraction analysis. The molecular structures were depicted in Figures 1–3 respectively. Crystallographic data and selected bond distances and angles are given in Table 1 and 2. All the complexes **1**–**3** are isostructural, adopting a distorted square planar geometry around the nickel atom. The monoanionic NCN-pincer ligand coordinates to the central metal ion in a κC:κN:κN′ tridentate mode with the two N-aryl rings being perpendicular to the NCN plane. The nickel atoms are essentially coplanar with the NCN plane. The Ni–C bond lengths, 1.827(7) Å in **1**, 1.804(6) Å in **2** and 1.823(4) Å in **3** fall in a reasonable range for the linkage between nickel atom and a carbon atom.[15a] The C–N$_{\text{imine}}$ bond lengths ranging from 1.278(3) Å to 1.2898(4) Å are comparable to those in the analogous rhodium and platinum complexes.[10] The bond-length of Ni–Br of 2.3345(13) Å in **1**, 2.3486(10) Å in **2**, and 2.3549(10) Å in **3** are slightly shorter than that of 2.60 Å (av.) for Ni–Br in the literatures.[15a]

Synthesis and characterizaiton of pincer Fe(II) complexes



4 Ar = 2,6-Me$_2$-C$_6$H$_3$
5 Ar = 2,6-Et$_2$-C$_6$H$_3$
6 Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$

Attempts to synthesize the pincer Fe(II) complexes *via* oxidative-addition of the ligand with low value iron precursors, such as Fe(CO)$_5$ or Fe(0)(Me$_3$P)$_4$, in toluene failed. Unidentified mixture with gray metal powder were obtained. Alternatively, the lithium salt elimination reaction was used to synthesize the pincer Fe(II) complexes. The ligand lithium salts were prepared in THF at low temperature by addition of

^{n}BuLi to the ligands in THF solution. Reactions of the *in-situ* prepared ligand lithium salts with $FeCl_2$ in THF afford the corresponding NCN pincer Fe(II) complexes in moderate yields. No informative NMR spectra were obtained due to the paramagnetic nature of these compelxes. While these Fe(II) complexes were well characterized with IR, elemental analyses, and X-ray crystallography analysis as well. The molecular structure of **4**, and **5**, were shown in Figures 4–5 respectively.[17] It can be seen that both the pincer Fe(II) complexes are chlorine-bridged hetero-dinuclear. The Fe(II) atoms are in a trigonal bipyramidal environment and two additional THF ligands complementing the coordinated sphere of the lithium atoms. The Fe(II) atoms are essentially coplanar with the NCN plane and the two N-aryl rings are oriented basically orthogonal to the coordination plane. The Fe–Cl bond lengths (2.3972 Å (av) in **4** and 2.3967(16) Å in **5**) are similar to that of 2.375(2)–2.417(3) Å in the $[Fe(\mu\text{-}Cl)Ar']_2$ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$^iPr_2$)$_2$).[18] The Fe–C$_{ipso}$ bond distances (2.037(4) Å in **4** and 2.058(9) Å in **5**) are comparable to that of 2.0317(13) Å in [CpFe(C_6H_3-2,6-$^iPr_2$],[18] but slightly longer than that of 1.950(18)–1.979(3) Å in FeCl(PMe_3)$_3$(Ar-CH=N-R).[19] The N–Fe bond lengths of 2.170(2) Å and 2.181(2) Å are slightly shorter than those in the bis(imino)pyridine derivatives.[3a,c] All the iron complexes **4–6** are paramagnetic. The complex **4** and **5** exhibited a magnetic moment (determined with Evans method)[20] of 3.11 and 2.66 μ_B respectively, which are comparable to the spin-only value for an $S = 1$ state (2.83 μ_B). But, complex **6** is high spin species with a magnetic moment of 4.80 μ_B, which in good agreement with the spin-only value for high spin d^6 (Fe^{2+}) centers.[7c, 21a, 21b] The exact reason for the difference in magnetic moments was unknown yet, but we think the repulsions of the bulky moieties in the two N-aryl group may weaken the coordination of the N atoms to the Fe(II) center and afford smaller splitting energy which favors a high spin state. A similar phenomenon in which the electronic environment of the complexes varied with the bulkiness of the auxiliary aromatic groups was also observed in bis(imino)pyridine Fe(II) complexes.[21c]

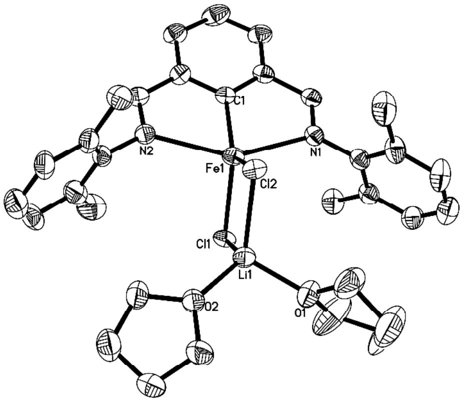


Figure 4. Perspective view of complex **4** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

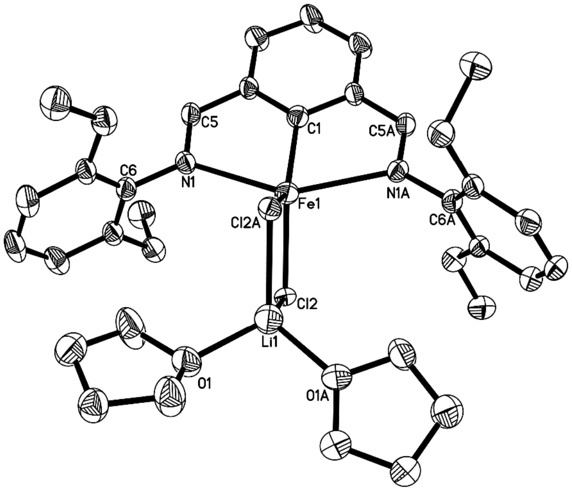


Figure 5. Perspective view of complex **5** with thermal ellipsoids drawn at 30% probability level. Hydrogens are omitted for clarity.

Table 1 Crystal Data and Structural Refinements Details for **1**, **2, 3, 4** and **5**

	1·1/3 PPh_3·0.1CH_2Cl_2	**2**	**3**	**4**	**5**
Formula	$C_{30}H_{28}BrN_2Ni(PPh_3)_{0.3}(CH_2Cl_2)_{0.1}$	$C_{29}H_{31}BrCl_2N_2Ni$	$C_{33}H_{41}BrCl_2N_2Ni$	$C_{32}H_{39}Cl_2FeLiN_2O_2$	$C_{36}H_{47}Cl_2FeLiN_2O_2$
Fw	572.73	617.08	675.20	617.34	673.45
Cryst. Syst.	Rhombohedral	Trigonal	Monoclinic	Monoclinic	Monoclinic
Space group	R-3	P4(3)2(1)2	C*c*	P2(1)/c	C2/c
a (Å)	26.515(7)	13.639(2)	11.756(5)	9.7112(9)	10.4769(19)
b (Å)	26.515(7)	13.639(2)	21.816(11)	21.3935(19)	17.050(3)
c (Å)	20.941(6)	16.039(4)	12.863(7)	15.7623(14)	20.291(4)
α (deg)	90.000	90.000	90.000	90.000	90.000
β (deg)	90.000	90.000	93.458(19)	93.5040(10)	98.088(3)
γ (deg)	120.000	90.000	90.000	90.000	90.000
V (Å^3)	12750(6)	2983.6(10)	3293(3)	3268.6(5)	3588.5
Z	18	4	4	4	4
D_{calcd} (g cm^{-3})	1.343	1.374	1.362	1.255	1.247
$F(000)$	5283	1264	1400	1296	1424
θ range for data collection	$3.05 \leq \theta \leq 27.48$	$2.99 \leq \theta \leq 27.47$	$3.17 \leq \theta \leq 27.48$	$1.61 \leq \theta \leq 26.06$	$2.03 \leq \theta \leq 25.06$
No. of reflns	39703	29441	15969	18242	9154
Unique	6542	3414	7129	6436	3167
Goodness-of-fit on F^2	0.949	1.019	1.081	1.068	1.075
R_1 ($I > 2\sigma$)	0.0824	0.0478	0.0435	0.0639	0.0726
R_w ($I > 2\sigma$)	0.2038	0.1245	0.0904	0.1909	0.1816
R_{int}	0.1423	0.0640	0.0457	0.0252	0.0743

Table 2 Selected bond lengths (Å) and angles (deg) for **1**, **2**, **3**, **4**, and **5**.

		1	
Ni(1)–C(1)	1.827(7)	Ni(1)–Br(1)	2.3345(13)
Ni(1)–N(1)	1.923(6)	N(2)–Ni(1)–N(1)	162.6(3)
Ni(1)–N(2)	1.918(6)	C(1)–Ni(1)–Br(1)	176.2(2)
		2	
Ni(1)–C(1)	1.840(6)	N(1)–Ni(1)–N(1A)	161.88(7)
Ni(1)–N(1)	1.947(3)	C(1)–Ni(1)–Br(1)	180.000(15)
Ni(1)–Br(1)	2.3486(10)		
		3	
Ni(1)–C(1)	1.823(4)	Ni(1)–Br(1)	2.3549(10)
Ni(1)–N(1)	1.938(4)	N(2)–Ni(1)–N(1)	161.13(15)
Ni(1)–N(2)	1.945(4)	C(1)–Ni(1)–Br(1)	174.25(13)
		4	
Fe(1)–C(1)	2.037(4)	Fe(1)–Cl(2)	2.3733(10)
Fe(1)–N(1)	2.438(3)	N(2)–Fe(1)–N(1)	147.54(11)
Fe(1)–N(2)	2.445(3)	Cl(1)–Fe(1)–Cl(2)	99.11(4)
Fe(1)–Cl(1)	2.3811(11)		
		5	
Fe(1)–C(1)	2.058(9)	N(2)–Fe(1)–N(1)	146.94(11)
Fe(1)–N(1)	2.463(5)	Cl(1)–Fe(1)–Cl(2)	98.45(9)
Fe(1)–Cl(1)	2.3967(16)		

Polymerization of norbornene

The nickel and iron complexes were tested to initiate the norbornene polymerization. The selective data were summarized in Table 3. The results showed that, activated with MAO, the nickel complexes are moderate active towards the vinylic polymerization of norbornene at room temperature and conversions of 32.6%–57.2% were obtained within 60 min (entry 1–3). Under the activation with MAO, the Fe(II) complexes are less active when compared to the nickel analogues. Complex **4** and **5** show very low activities and almost no polymer was obtained in these systems. Interestingly, complex **6** with bulky 2,6-diisopropyl group exhibits moderate activity (conversion of 70% in 60 min), affroding high molecular weight polymer. The are few reports about the vinyl polymerization of norbornene with Fe(II) complexes. The bis(imino)pyridine Fe(II) complexes show varied activities and remarkably, the activities is highly sensitive to the substitutes of the N-aryl moieties in ligands.[22] Some polynuclear carboxylate Fe(II) complexes were also reported to show poor activities in norbornene polymerization.[23] It is worth to note that, in the case of the nickel-based catalytic system, the *ortho* substituents of the ligands show strong influences on both of the activities and the molecular-weights of the resulted polymers. With increase in the size of the *ortho* substituents, the activities increased alongside dramatic decrease in the molecular weight of the resultant polymers. This might be ascribed probably to the differences in the activated-efficiency in the activation and the differences in the stabilities of the resulted active species during the polymerization. Complexes with bulky substituents at the axial position are more stable and can survive for long time. Complex **3** was used to study the effect of reaction conditions on vinyl polymerization of norbornene by changing the Al:Ni molar ratios, and reaction temperature. Variation of the ratio of MAO show significant effects on catalyst activity and the molecular-weight of the resultant polymers. As shown in Table 3. catalytic activity of precatalyst **3** increased rapidly first with increases in Al:Ni ratios, and then remained steady after the Al:Ni molar ratio reached about 2000:1. However, the molecular weights of the polymers gradually decreased with increasing in Al:Ni ratios. Catalyst activity and molecular weights for the resultant polymers were also dramatically influenced by the polymerization temperature. When the polymerization temperature increased from 15 ^{o}C to 45 ^{o}C, both catalyst activities and the molecular-weights of the polymer gradually increased. While further increase of the temperature resulted in dramatically decrease of the activity probably due the deactivation of the active species at high temperature. The FT-IR spectra of the resulted polymer show the characteristic peak of polynorbornene in the range of 940 cm^{-1} to 943 cm^{-1} which can be assigned to the vinyl addition polymer. No detectable absorption peaks at 960 cm^{-1} was found suggesting that the norbornene polymerization initiated by the nickel or ferrous complexes and MAO were performed in vinyl addition manner.[24]

Polymerization of butadiene

Polybutadiene is the most widely used synthetic rubbers.[25] The most efficient catalysts for butadiene polymerization are homogeneous Ziegler-Natta catalyst systems composed of complexes of various transition metals such as Ti,[25, 26d] V,[26] Cr,[27] Co,[28] and Nd,[29] and co-activators aluminum alkyls or the aluminum alkyl chloride. Some nickel and ferrous complexes were also reported for the butadiene polymerization affording *cis*-1,4 enriched polybutadiene.[30] The complexes **1–6** were tested for butadiene polymerizations. The preliminary polymerization data are summarized in Table 4. It is worth to note that under the activation of MAO or alkylaluminum the nickel complexes (**1–3**) show very low activities in butadiene polymerization and almost no polymer were obtained. In contrast, under the same conditions, the pincer Fe(II) complexes (**4–6**) show moderate activities for butadiene polymerization. Up to 85.2% conversion was obtained with **6**/$AlMe_3$ at room temperature in 30 minutes affording the polybutadiene with 75.3% *cis*-1,4 unit. The activities and molecular-weight of the polymer show similar dependence on the *ortho* bulkyness as described in the polymerization of norbornene with nickel complexes. With complex **4**, 71.1% conversion were achieved affording the polymer with high molecular weight and broad PDI. While when **6** was used, high conversion was observed and the molecular weight of the resultant polymer is relatively low with narrow PDI (2.95). The activities also show strong dependence on the kind of co-activator used. When the $AlEt_3$ and $Al(^{i}Bu)_3$ were used low activities were observed. It is worth to note that, in all cases, the *cis*-1,4 selectivity of this system did not show strong dependence on the ligands and co-activators, and varied in a narrow range between 71.0% to 75.5%.

Table 3. Addition polymerization of norbornene with nickel and ferrous complexes activated by methylaluminoxane(MAO)[a]

entry	Cat	Al/M	Time，min	Temp, °C	Yield,[b] %	M_v,[c] ×10^5
1	**1**	500	60	15	32.6	13.5
2	**2**	500	60	15	42.2	7.8
3	**3**	500	60	15	57.2	4.3
4	**4**	500	60	15	–	–
5	**5**	500	60	15	trace	–
6	**6**	500	60	15	70.0	–
7	**3**	500	30	15	45.8	3.0
8	**3**	500	90	15	64.6	4.8
9	**3**	500	120	15	65.1	5.7
10	**3**	250	60	15	30.8	–
11	**3**	1000	60	15	65.9	2.9
12	**3**	1500	60	15	69.7	3.3
13	**3**	2000	60	15	75.0	3.1
14	**3**	3000	60	15	75.1	3.2
15	**3**	500	60	30	63.6	6.2
16	**3**	500	60	45	69.2	7.5
17	**3**	500	60	60	40.9	3.1

[a] Polymerization conditions: toluene 10 mL; catalyst, 10μmol; Norbornene/Cat = 2000; [b] Isolated yield. [c] Obtained by capillary viscosimetry using the Mark–Houwink coefficients $a = 0.56$, $K = 7.78 \times 10^{-4}$ dl/g.

Table 4. Summary of butadiene polymerization catalyzed by pincer Fe(II) complexes[a]

entry	cat	[BD]/[Fe]	Tp (°C)	time (min)	Conv (%)	M_n[b] (×10^4)	PDI	microstructure[c] (%)	
								cis-1,4	1,2-
1	**4**	500	20	30	71.1	86.0	5.03	72.6	27.4
2	**5**	500	20	30	78.9	116	7.15	73.2	26.8
3	**6**	500	20	30	85.2	5.54	2.95	73.5	26.5
4	**6**	1000	20	60	83.2	16.5	2.91	75.4	24.6
5	**6**	2000	20	60	75.8	29.1	2.89	75.5	24.5
6[d]	**6**	500	20	35	40.2	17.6	2.62	71.1	28.9
7[e]	**6**	500	20	180	44.6	64.7	5.67	73.0	27.0

[a] The polymerization reactions: toluene (10 mL), cat 20 μmol, Cat:$AlMe_3$ = 25. [b] Determined by gel permeation chromatography (GPC) with respect to a polystyrene standard. [c] Determined by NMR spectrum and IR. [d] $AlEt_3$ was used. [e] $Al(^iBu)_3$ was used.

Experimental

General considerations

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene and hexane were dried over sodium metal and distilled under nitrogen. 2,6-dimethylaniline, 2,6-diethylaniline (90%) and 2,6-diisopropylaniline were bought from Aldrich Chemical Co. and used without further purification. Elemental analyses were performed on a Varian EL microanalyzer. NMR spectra were carried out on Varian 300 Hz instrument at room temperature in $CDCl_3$ solution for ligands and complexes.

Synthesis of the complexes

Bis(*N*-2,6-dimethylphenyl)isophthalaldimin-2-yl nickel bromide (1) To a solution of bis(N-2,6-dimethylphenyl)-2-bromoisophthalaldimine (0.42 g, 1.00 mmol) in 20 mL toluene was added $Ni(Ph_3P)_4$ (1.10 g, 1.00 mmol), and the reaction mixture was stirred overnight at 100 °C. The solvent was evaporated to dryness under reduced pressure. The resulted residue was washed with hot hexane (50 mL) and filtered over Celite to yield orange powder (0.47 g, 98%). The crystal suitable for X-ray determination was obtained by recrystallization from mixed hexane and dichlormethane solution. ^1H NMR (300 MHz, $CDCl_3$): δ 2.37 (s, CH_3, 12H), 7.01–7.05 (mult, 6H), 7.20 (t, $J_{H–H}$ = 7.0 Hz, 1H, *p*-Ni-C_6H_3), 7.41 (d, $J_{H–H}$ = 7.0 Hz, 2H, *m*-Ni-C_6H_3), 7.90 (s, 2H, *H*C=N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.52 (s, 2C CH_3), 119.60, 121.56, 121.89, 122.95, 125.80, 139.23, 168.25(s, 2C, H*C*=N) ppm. Anal. Calcd for $C_{24}H_{23}BrN_2Ni$: C, 60.30; H, 4.85; N, 5.86. Found: C, 60.35; H, 4.88; N, 5.74.

Bis(*N*-2,6-diethylphenyl)isophthalaldimin-2-yl nickel bromide (2) Using the same work-up procedure described for the preparation of **1**, treatment of bis(N-2,6-diethylphenyl)-2-bromoisophthalaldimine (0.47 g, 1.00 mmol) with $Ni(Ph_3P)_4$ yielded complex **2** as orange powder. (0.50 g, 94.6%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.19 (t, $J_{H–H}$ = 7.5 Hz, 12H, CH_2CH_3), 2.54 (q, $J_{H–H}$ = 7.5 Hz, 8H, CH_2CH_3), 7.03 (d, $J_{H–H}$ = 7.2 Hz, 4H, *m*-N-C_6H_3), 7.13–7.19 (m, 2H, *p*-N-C_6H_3), 7.20 (t, $J_{H–H}$ = 7.0 Hz, 1H, *p*-Ni-C_6H_3), 7.42 (d, $J_{H–H}$ = 7.2 Hz, 2H, *m*-Ni-C_6H_3), 7.90 (s, 2H, *H*C=N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.59 (s, 4C, CH_2CH_3), 25.37 (s, 4C, CH_2CH_3), 124.62, 125.76, 126.57, 127.18, 136.36, 144.09, 173.06 ppm. Anal. Calcd for $C_{28}H_{31}BrN_2Ni$: C, 62.96; H, 5.85; N, 5.24. Found: C, 63.02; H, 5.83; N, 5.20.

Bis(*N*-2,6-diisopropylphenyl)isophthalaldimi-n-2-yl nickel bromide (3) Using the same work-up procedure described for the preparation of **1**, treatment of bis(N-2,6-diisopropylphenyl)-2-bromoisophthalaldimine (0.53 g, 1.00 mmol) with Ni(Ph_3P)$_4$ yielded complex **3** as orange powder. (0.56, 95.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (d, J_{H-H} = 7.2 Hz, 12H, CH(CH_3)$_2$), 1.36 (d, J_{H-H} = 7.2 Hz, 12H; CH(CH_3)$_2$), 3.38 (sept, J_{H-H} = 7.2 Hz, 4H, C*H*(CH_3)$_2$), 7.06 (m, 2H, *p*-N-C_6H_3), 7.09 (m, 4H, *m*-N-C_6H_3), 7.20 (t, J_{H-H} = 7.2 Hz, 1H, *p*-Ni-C_6H_3), 7.45 (d, J_{H-H} = 7.2 Hz, 2H, *m*-Ni-C_6H_3), 7.89 (s, 2H, *H*C=N) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.57 (s, 4C, CH(CH_3)$_2$), 24.36 (s, 4C, CH(CH_3)$_2$), 28.75 (s, 4C, *C*H(CH_3)$_2$), 122.80, 124.28, 126.27, 127.17, 140.86, 143.80, 146.47, 172.15 ppm. Anal. Calcd for $C_{32}H_{39}BrN_2Ni$: C, 65.11; H, 6.66; N, 4.75. Found: C, 65.07; H, 6.68; N, 4.70.

[Bis(*N*-2,6-dimethylphenyl)isophthalaldimin-2-yl]Fe(*μ*-Cl)$_2$Li(THF)$_2$ (4) A hexane solution of ^{n}BuLi (0.66 mL, 1.05 mmol) was added dropwise to a THF (20 ml) solution of bis(N-2,6-dimethylphenyl)-2-bromoisophthalaldimine (0.42 g, 1.00 mmol) at –78°C. The mixture was stirred for 4 hours before the addition of $FeCl_2$ (0.14 g, 1.10 mmol). The mixture was allowed to warm to ambient temperature gradually and stirred overnight. The solvent was removed under reduce pressure and the residue was treated with toluene, after evaporation of the toluene to dryness, the product was obtained as purple powder (0.43 g, 70%). Crystals of **4** suitable for X-ray structural determination was grown in THF/hexane mixed solution. Anal. Calcd for $C_{32}H_{39}Cl_2FeLiN_2O_2$: C, 62.26; H, 6.37; N, 4.54. Found: C, 62.14; H, 6.31; N, 4.47. IR (KBr) *v* (cm^{-1}) 3420s, 1639w, 1473w, 1380w, 1349w, 1253w, 1203w, 1149w, 1091m, 852w, 802w,767s, 690w, 609w.

[Bis(*N*-2,6-diethylphenyl)isophthalaldimin-2-yl]Fe(*μ*-Cl)$_2$Li(THF)$_2$ (5) Following the same procedure described for the preparation of **4**, treatment of bis(N-2,6-diethylphenyl)-2-bromoisophthalaldimine (0.47 g, 1.00 mmol) with ^{n}BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then *in situ* adding $FeCl_2$ (0.14 g, 1.10 mmol) yielded complex **5** as purple powder (0.48 g, 72%). Crystals of **5** suitable for X-ray structural determination was grown in THF/hexane mixed solution. Anal. Calcd for $C_{36}H_{47}Cl_2FeLiN_2O_2$: C, 64.20; H, 7.03; N, 4.16. Found: C, 64.11; H, 7.08; N, 4.19. IR (KBr) *v* (cm^{-1}) 3421s, 2966m, 2942m, 2873m, 1635s, 1550m, 1454m, 1380m, 1373m, 1334m, 1230m, 1184m, 1164m, 1103m, 1049m, 871m, 798m, 759w, 690w, 505m.

[Bis(*N*-2,6-diisopropylphenyl)isophthalaldimin-2-yl]Fe(*μ*-Cl)$_2$Li(THF)$_2$ (6) Following the same procedure described for the preparation of **4**, treatment of bis(N-2,6-diisopropylphenyl)-2-bromoisophthalaldimine (0.53 g, 1.00 mmol) with ^{n}BuLi (1.6 M in hexane, 0.66 mL, 1.05 mmol) and then *in situ* adding $FeCl_2$ (0.14 g, 1.10 mmol) yielded complex **6** as purple powder (0.49 g, 68%). Crystals of **6** suitable for X-ray structural determination was grown in THF/hexane mixed solution. Anal. Calcd for $C_{40}H_{55}Cl_2FeLiN_2O_2$: C, 65.85; H, 7.60; N, 3.84. Found: C, 65.78; H, 7.57; N, 3.75. IR (KBr) *v* (cm^{-1}) 3421s, 3062w, 2962s, 2869m, 1623s, 1550s, 1461m, 1434m, 1384m, 1361m, 1326m, 1253w, 1226w, 1180m, 1160w, 1103w, 1045m, 933w, 883w, 844w, 798w, 775m, 755m, 613w, 520m, 512w.

General procedure for butadiene polymerization

In a typical polymerization experiment butadiene solution of toluene and 500 mmol alkylaluminum were added into a 25 mL flask. Then 25 *μ*mol complex **6** was added to initiate the polymerization. After a designated time, methanol was injected into the system to quench the polymerization. The mixture was poured into a large quantity of methanol to precipitate the white solids. Filtered and dried under vacuum at 40 °C for 24 h polybutadiene was given at a constant weight.

General procedure for norbornene polymerization

A 0.5 ml aliquot of a fresh catalyst solution (toluene, 10 μmol catalyst), 4.0 ml of a solution of norbornene (20 mmol) in toluene and 10.5 ml toluene were added under inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by the addition of 5 ml of a MAO solution (5 mmol MAO in toluene). The total reaction volume was 20 ml, which was achieved by variation of the amount of toluene if necessary. After 10 min, acidic ethanol was injected into the Schlenk flask to end the reaction and the reaction mixture was poured into 200 ml of acidic ethanol. The polymer was isolated by filtration, washed with acetone and dried under vacuum at 80 ºC for 24 h.

X-ray crystallography

Single crystals of **1, 2, 3, 4,** and **5** suitable for X-ray structural analysis were obtained from CH_2Cl_2/hexane or THF/hexane mixed solution. Diffraction data were collected at 293K with a Bruker SMART-CCD diffractometer equipped with graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073Å). Diffraction data of **1**, and **3** were collected at 293 K on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 2. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL[31] crystallographic software packages.

Conclusions

In conclusion, A series of Ni(II) and Fe(II) complexes based on bis(imino)aryl [NCN]$^-$ ligands were synthesized and characterized. With MAO as cocatalyst, the nickel complexes (**1**–**3**) and iron complex (**6**) show moderate activities towards vinyl polymerization of norbornene, while the iron complexe with less bulky substituents show very low activities. Under the activation of alkylaluminum, the Fe(II) complexes show moderate activities in butadiene polymerization affording *cis*-1,4 enriched polymer.

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Notes and references

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Ni(II) and Fe(II) Complexes Based on Bis(imino)aryl Pincer Ligands: Synthesis, Structural Characterization and Catalytic Activities

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Bis(imino)aryl $[NCN]^-$ Ni(II) and Fe(II) complexes are synthesized and investigate as catalysts for norbornene and butadiene polymerization in the presence of MAO or alkylaluminum.