## ortho-5-Methylfuran- and Benzofuran-Substituted $\eta^3$ -Allyl( $\alpha$ -diimine)nickel(II) Complexes: Syntheses, Structural Characterization, and the First Polymerization Results<sup>†</sup>

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Two representatives of a new family of *ortho*-furan-substituted N,N-phenyl  $\alpha$ -diimine ligands [(Ar-N=C(Me)-(Me)C=N-Ar)] Ar = 2,6-bis(5-methylfuran-2-yl)-4-phenylphenyl, 9; Ar = 2,6-bis(benzofuran-2-yl)phenyl, 17 have been synthesized by two alternative synthetic methodologies. 3,5-Bis(5-methylfuran-2-yl)biphenyl-4-ylamine (7) was prepared through a classical pyrylium salt approach. 2,6-Bis(5-methylfuran-2-yl)-4-phenylpyranylium tetrafluoroborate (4) was converted to 2,6-bis(5-methylfuran-2-yl)-4-phenylnitrobenzene (5) by reaction with nitromethane. Reduction of nitro compound 5 by zinc dust afforded aniline 7. The palladium-catalyzed cross-coupling reaction between 2,6-dibromophenylamine 13 and 2-benzofuranboronic acid 14 was used to prepare 2,6-bis(benzofuran-2-yl)phenylamine 15. The condensation of 2,2,3,3-tetramethoxybutane **8** with anilines **7** and **15** afforded  $\alpha$ -diimines **9** and 17. The reaction of  $\pi$ -allylnickel chloride dimer 10,  $\alpha$ -diimines 9 and 17, and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAF) (11) or silver hexafluoroantimonate 18 led to three complexes,  $[\eta^3-ally](Ar-N=C(Me)-(Me)C=N-Ar)Ni]^+X^-$  [Ar = 2,6-bis(5-methylfuran-2-yl)-4-phenylphenyl, X = BAF, **12**, Ar = 2,6-bis(benzofuran-2-yl)phenyl, X = BAF, **19**,  $X = SbF_{6}$ , **20**]. The steric repulsion of closely positioned benzofuran-2-yl groups in **20** caused distortion of the nickel square planar coordination by up to 11.4° according to X-ray analysis. Benzofuran-2-yl groups deviated up to 46.6° from the main planes of central phenyl rings in **20**. Complexes **12** and **19** were tested as ethylene polymerization catalysts. The benzofuran-substituted  $\eta^3$ -allyl ( $\alpha$ -diimine)Ni complexes **19** afforded polyethylene with ultrahigh molecular weights  $(M_w)$  and was about three time more productive than complex 12.

## Introduction

Late-metal catalysts for ethylene homo- and copolymerization based on Pd(II) and Ni(II)  $\alpha$ -diimine complexes (trademarked as the Versipol catalyst system by Du-Pont)<sup>1</sup> require moderately sterically hindered, *ortho*substituted anilines. Small deviations in the size and electronic properties of the *ortho*-substituent have a considerable impact on the amount of branching and molecular weight of the resulting polymer. The furyl group is comparable in size with the phenyl group, the presence of which in the *ortho*-position has a considerable effect on the molecular weight of the polymer.<sup>2</sup> Further modification of 2,6-diphenylaniline moieties by *para*-methoxy or *para-tert*-butyl groups had a profound effect on the polymerization process.<sup>3</sup> The palladium complexes with phosphine ligands bearing 2-furyl substituents have been found to be more efficient catalytic systems in the cross-coupling of alkylstannanes with aryl halogenides<sup>4,5</sup> and in the palladium-catalyzed alkoxycarbonylation of alkynes compared with the corresponding triphenylphosphine complexes.<sup>6</sup>

In this report, we describe two synthetic approaches for making *ortho*-substituted furyl  $\alpha$ -diimine ligands and the corresponding nickel(II) complexes with 5-methylfuran-2-yl and benzofuran-2-yl moieties. The 5-methyl substitution and benzo pattern of the furyl group substitutions were chosen to provide bulk in the axial sites of square planar nickel complexes and retard the rate of chain transfer.<sup>7</sup> The polymerization of ethylene by the *ortho*-5-methylfuran- and benzofuran-substituted  $\eta^3$ -allyl( $\alpha$ -diimine)nickel(II) complexes is also the subject of this report.

<sup>&</sup>lt;sup>†</sup> Dedicated to Professor Maurice Brookhart on the occasion of his 62nd birthday. This is DuPont contribution #8529.

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Scheme 1



## **Results and Discussion**

1.1. Synthesis of 5-Methylfuran-2-yl *ortho*-Substituted  $\alpha$ -Diimine Ligand and Corresponding Nickel(II) Complex. The classical approach through a pyrylium salt was used to introduce a 5-methylfuran-2-yl moiety in the structure of the desired  $\alpha$ -diimine ligand (Scheme 1).

The Michaelis condensation between 2-acetyl-5-methylfuran 1 and benzaldehyde 2 led to the formation of 1,5-bis(5-methylfuran-2-yl)-3-phenylpentane-1,5-dione (3) with a 67% yield. The ring closure of the 1,5-diketone 3 was performed with triphenylcarbenium tetrafluoroborate in glacial acetic acid under reflux for 2 h. The pyrylium salts with 2,6-furyl substituents are difficult to isolate in a pure state due to the susceptibility of furan rings to electrophilic attack of triphenylcarbenium cation.<sup>8</sup> For this reason, the X-ray analysis of compound 4 was conducted. A crystal of 4 suitable for X-ray analysis was grown from acetic acid. An ORTEP drawing of 4 without any incorporation of trityl fragments in the molecule is shown in Figure 1.

The two 5-methylfuran-2-yl groups are almost planar (deviations are 9.7° and 10.8°) with the central pyrylium ring of compound **4**. This implies the participation of 5-methylfuran-2-yl groups in the  $\pi-\pi$  conjugation with the pyrylium core.

The reaction of 2,6-bis(5-methylfuran-2-yl)-4-phenylpyranylium tetrafluoroborate (**4**) and nitromethane in the presence of triethylamine resulted in the formation of compounds **5** and **6**. 2,6-Bis(5-methylfuran-2-yl)-4phenylnitrobenzene (**5**) was isolated as a major product with a 56% yield. 2,6-Bis(5-methylfuran-2-yl)-4-nitromethyl-4-phenyl-4*H*-pyran (**6**) was a product of the nucleophilic attack of nitromethane at the 4-position of



**Figure 1.** ORTEP drawing of 2,6-bis(5-methylfuran-2-yl)-4-phenylpyranylium tetrafluoroborate, **4**. Thermal ellipsoids are drawn at the 50% probability level.

pyrylium salt  $4.^{9-11}$  ORTEP drawings of **5** and **6** are shown in Figures 2 and 3.

The reduction of the nitro group in 2,6-bis(5-methylfuran-2-yl)-4-phenylnitrobenzene (**5**) in the amino group of substance **7** was accomplished by zinc dust in glacial acetic acid.<sup>12</sup> The condensation of 2,2,3,3-tetramethoxybutane<sup>13</sup> **8** with aniline **7** in the presence of an acid catalyst led to the desired 2,3-bis[2,6-bis(5-methylfuran-2-yl)-4-phenylphenylimino)]butane (**8**) (Scheme 2).<sup>14</sup> The ORTEP drawing of **9** (Figure 4) shows that C=N bonds

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Scheme 2





are in the *trans*-configuration. The methyl groups are pointed out in different directions, perhaps to minimize steric overlap. The 5-methylfuran-2-yl moiety forms angles of 30.6° and 27.0° with the central phenyl rings (Table 1). The  $\pi - \pi$  conjugation between them should be disrupted at those angles. Thus, any possible  $\pi$ -electronic effect of the oxygen atom on the furyl rings onto the  $\alpha$ -diimine core will be diminished and the steric impact of the 5-methylfuran-2-yl moiety will be predominant.

The reaction between the  $\pi$ -allylnickel chloride dimer<sup>15</sup> **10**,  $\alpha$ -diimine **9**, and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAF) **(11)** led to  $\eta^3$ -allyl( $\alpha$ -diimine)nickel complexes **12** (Scheme 2).



**Figure 3.** ORTEP drawing of 2,6-bis(5-methylfuran-2-yl)-4-nitromethyl-4-phenyl-4*H*-pyran, **6**. Thermal ellipsoids are drawn at the 50% probability level.

1.2. Synthesis of Benzofuran-2-yl ortho-Substituted  $\alpha$ -Diimine Ligand and Corresponding Nickel(II) Complexes. The palladium-catalyzed Suzuki cross-coupling reaction between 2,6-dibromophenylamine 13 and 2-benzofuranboronic acid 14 was used to prepare 2,6-bis(benzofuran-2-yl)phenylamine 15 (Scheme 3).

The catalytic protocol involves Pd<sub>2</sub>dba<sub>3</sub>/tri-*tert*-Bu<sub>3</sub>P as the catalyst<sup>16</sup> in the presence of cesium carbonate in 1,4-dioxane as solvent. 2,6-Bis(benzofuran-2-yl)phenyl-amine **15** was isolated with a 68% yield. [2,2']Bibenzo-furanyl **16** was a minor product of this reaction. The X-ray analysis of compound **15** reveals intramolecular hydrogen bonding of the amino hydrogen with the oxygen atoms of the furyl rings (Figure 5).

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Table 1. Selected Bond Lengths (Å) for 4–6, 9, 15–17, and 20

			0		
	C–O furanyl (inner)	C–O furanyl (outer)	fur-phen tors	C-N	C=N
4	O11-C7 = 1.367(6),	O11-C10 = 1.365(6),	9.7,		
	O17-C13 = 1.363(6)	O17 - C16 = 1.359(6)	10.8		
5	O10-C10 = 1.351(2),	O10-C13 = 1.357(2),	27.5,	N1-C1 = 1.452(2)	
	015-C15 = 1.356(2)	O15-C18 = 1.345(2)	18.4		
6	O15-C14 = 1.371(1),	O15-C16 = 1.377(1),	3.6,		
	O21-C20 = 1.374(1)	O21 - C22 = 1.383(1)	5.3		
9	O9-C9 = 1.384(2),	O9-C12 = 1.379(3),	30.6,	N1-C3 = 1.422(3)	N1-C1 = 1.271(3)
	O20-C20 = 1.387(3)	O20-C23 = 1.380(2)	27.0		
15	O1-C5 = 1.396(4)	O1 - C6 = 1.374(4)	35.6	N1-C1 = 1.381(7)	
16	O1-C1 = 1.389(2)	O1 - C4 = 1.377(2)			
17	O10-C9 = 1.388(6),	O10-C11 = 1.375(5),	5.1,	N1-C3 = 1.415(6)	N1-C1 = 1.293(6)
	O19-C18 = 1.401(5)	O19-C20 = 1.393(6)	21.6		
20	O1-C12 = 1.381(5),	O1 - C13 = 1.384(5),	31.1,	N1 - C6 = 1.432(5)	N1-C1 = 1.302(5)
	O2-C20 = 1.392(5),	O2-C21 = 1.375(4),	31.1,	N2-C28 = 1.435(5)	N2-C2 = 1.284(5)
	O3-C34 = 1.381(6),	O3-C35 = 1.375(6),	33.1,		
	O4 - C42 = 1.393(5)	O4-C43 = 1.381(6)	46.6		



**Figure 4.** ORTEP drawing of 2,3-bis[2,6-bis(5-methyl-furan-2-yl)-4-phenylphenylimino)]butane, **9**. Thermal ellipsoids are drawn at the 50% probability level.



**Figure 5.** ORTEP drawing of 2,6-bis(benzofuran-2-yl)-phenylamine, **15**. Thermal ellipsoids are drawn at the 50% probability level.



The condensation of 2,2,3,3-tetramethoxybutane **8** with aniline **15** and a few crystals of *para*-toluene-sulfonic acid led to the desired  $\alpha$ -diimine ligand **17** (Scheme 4).

The reaction between  $\pi$ -allylnickel chloride dimer **10**,  $\alpha$ -diimine **17**, and sodium tetrakis[3,5-bis(trifluorometh-



**Figure 6.** ORTEP drawing of nickel(1+), [*N*,*N*-(1,2-dimethyl-1,2-ethanediylidene) (2,6-bis(benzofuran-2-yl)phenyl-N],[( $\eta^3$ -2-propenyl]-, hexafluoroantimonate(1-), **20**. Thermal ellipsoids are drawn at the 50% probability level.

yl)phenyl]borate (NaBAF) (**11**) or silver hexafluoroantimonate **18** led to  $\eta^3$ -allyl( $\alpha$ -diimine)nickel complexes **19** and **20** (Scheme 4). The hexafluoroantimonate derivative **20** afforded single crystals suitable for X-ray analysis from chlorobenzene solution.

X-ray analysis of complex 20 reveals that the central nickel atom is four-coordinate with the bidentate  $\alpha$ -diimine and  $\pi$ -allyl ligands. The ORTEP drawing of **20** (Figure 6) shows that the nickel square planar coordination has been distorted. This distortion can be measured by the dihedral angle  $\Sigma$  between the two sets of planes defined by N1-Ni-N2 and C5-Ni-C3. The tetrahedral twist angles for the two independent molecules of 20 in the asymmetric unit are 5.2° and 11.4° (Figure 6). There are no short contacts between the oxygen atoms of the benzofuran-2-yl moieties and the nickel atom in complex 20. Benzofuran-2-yl groups deviated from the main planes of central phenyl rings in 20 from 31.1° to 46.6° (Table 1). Upon complexation the deviation of benzofuran-2-yl groups increased, because the starting ligand 17 has corresponding values at 21.6° and 5.1°. At these rotation angles between the central phenyl ring and the benzofura-2-yl groups, possible conjugation should be minimized. However,

Scheme 4



20 X=SbF6

Table 2. Ethylene Polymerization Results with Catalysts 12 and 19

entry	catalyst	temp (°C)	productivity <sup>a</sup>	<sup>1</sup> H NMR branching <sup>b</sup>	<i>M</i> <sup>c</sup>	M/M.	mp (°C), $(\Delta H^*)$ (I/g)
enery	cuturyst	( 0)	productivity	branching	111	171W/1711	(211) (0/8)
1	12	60	25.4	8.3	651	3.4	121.1
							(110.6)
2	12	90	15.7	21.2	318	3.3	97.9
							(84.6)
3	12	120	3.8	69.8	64	2.3	65.9
							(8.4)
4	19	60	90.0	7.4	3 050	111.1	127.5
						bimodal	(97.6)
						(insolubles)	
5	19	70	76.2	14.2	2 486	36.8	116.5
						(insolubles)	(75.6)
6	19	80	71.9	17.0	685	6.2	111.1
							(85.9)
7	19	90	59.3	26.3	765	4.9	94.9
							(41.5)
8	19	120	69.2	36.8	55	2.7	86.8
							(67.5)
9	19	150	20.3	59.9	23	3.2	89.6
							(1.2)

<sup>a</sup> kg polymer/g Ni. <sup>b</sup> Total CH<sub>3</sub> per 1000 CH<sub>2</sub>. <sup>c</sup> 10<sup>3</sup> g mol<sup>-1</sup>.

angles are not at 90°, which would prevent  $\pi$ -conjugation completely. Further analysis of bond lengths of oxygen atoms in the furanyl part of the molecules 17 and 20 (Table 1, second and third columns) did not reveal substantial differences, which could indicate limited, if any, conjugation between those moieties. The most flat molecules are the pyrylium salt 4 and 2,6bis(5-methylfuran-2-yl)-4-nitromethyl-4-phenyl-4H-pyran (6) with a potentially higher degree of  $\pi$ -conjugation between the central rings and the furanyl moieties. The bond lengths of the oxygen atoms in the furanyl part of these molecules can be used as an indicator of the conjugation. For example, C-O bonds have a tendency to be longer with smaller torsion angles between furanyl groups and central rings (compound 5 versus compound 6). It may be concluded from the above structural studies that benzofuran-2-yl moieties in 20 provide

considerable steric protection for the nickel above and below the square plane.

Table 1 summarizes the bond lengths of furanyl derivatives **4**–**6**, **9**, **15**–**17**, and **20** for the furan oxygen and  $\alpha$ -diimine cores of the molecules.

2.0. Ethylene Polymerization Activity of ortho-5-Methylfuran- and Benzofuran-Substituted  $\eta^3$ -Allyl( $\alpha$ -diimine)nickel(II) Complexes 12, 19, and 20. The general procedure for ethylene polymerization is as follows. In a nitrogen-purged drybox, a 20 mL glass insert was loaded with the nickel compound (0.001 mmol) and 20 equiv of cocatalyst (B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). Next, the solvent (*para*-xylene (10 mL)) was added to the glass insert. The glass insert was then loaded in a pressure tube inside the drybox. The pressure tube was then sealed, brought outside of the drybox, connected to the pressure reactor, placed under the desired ethylene

Table 3. Summary of Crystal Data, Data Collection, and Structure Refinement Parameters of 4-6 and 9

	4	5	6	9
empirical formula	$C_{23}H_{21}O_5B_1F_4$	$C_{22}H_{17}N_1O_4$	$C_{22}H_{19}N_1O_5$	$C_{48}H_{40}N_2O_4$
fw	464.21	718.73	377.38	473.78
cryst color, form	colorless needle	colorless needle	colorless block	gold rod
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	P21/c	P21/n	$P\overline{1}$	P21/n
a (Å)	7.477(1)	7.270(3)	9.931(1)	8.5187(8)
$b(\mathbf{\hat{A}})$	13.615(2)	23.042(5)	10.418(1)	14.515(2)
<i>c</i> (Å)	21.374(3)	20.403(4)	10.524(1)	18.523(2)
α (deg)			100.436(2)	
$\beta$ (deg)	92.363(3)	93.01(3)	93.297(2)	99.470(2)
$\gamma$ (deg)			117.185(2)	
$V(Å^3)$	2173.9(5)	3413.1(2)	940.2(2)	2265.2(4)
Ζ	4	4	2	4
density (g/cm <sup>3</sup> )	1.418	1.399	1.333	1.389
abs, $\mu$ (mm <sup>-1</sup> )	0.12	0.10	0.09	0.43
F(000)	960	1504	396	980
cryst size (mm)	$0.27\times0.04\times0.05$	$0.30\times0.005\times0.005$	0.40 imes 0.38 imes 0.23	$0.43 \times 0.16 \times 0.16$
temp (°C)	-100	-100	-100	-100
scan mode	ω	ω	ω	ω
detector	BrukerCCD	MarCCD	BrukerCCD	BrukerCCD
$\theta_{\rm max}$ (deg)	22.98	26.39	28.27	28.28
no. obsd reflns	8970	24 363	11 103	11 389
no. unique reflns	3007	6800	4422	5268
no. params	306	491	256	283
$S^b$	0.87	0.95	1.06	0.83
<i>R</i> indices $[I > 2\sigma(I)]^a$	R1 = 0.057	R1 = 0.053	R1 = 0.041	R1 = 0.045
	wR2 = 0.124	wR2 = 0.140	wR2 = 0.112	wR2 = 0.089
R indices (all data) <sup>a</sup>	R1 = 0.186	R1 = 0.066	R1 = 0.051	R1 = 0.108
-	wR2 = 0.167	wR2 = 0.146	wR2 = 0.120	wR2 = 0.103
max diff peak, hole (e/ų)	0.307, -0.243	0.643, -0.375	0.318, -0.228	0.339, -0.373

 ${}^{a}$  R1 =  $\sum ||F_{o}| - |F_{c}|/\sum |F_{o}|$ , wR2 =  $\{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]/\sum [w(F_{o}^{2})^{2}]\}^{1/2}$  (sometimes denoted as  $R_{w}^{2}$ ).  ${}^{b}$  GooF =  $S = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]/(n-p)\}^{1/2}$ , where *n* is the number of reflections, and *p* is the total number of refined parameters.

Table 4. Summary of Crystal Data, Data Collection, and Strue	cture Refinement Parameters of 15–17 and 20
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	15	16	17	20
empirical formula	$C_{22}H_{15}O_2N_1$	$C_{16}H_{10}O_2$	$C_{48}H_{32}N_2O_4$	$C_{60}H_{44.5}CL_{1.5}F_6N_2$
				$Ni_1O_4Sb_1$
fw	325.35	117.12	700.76	1205.11
cryst color, form	colorless plate	colorless parallelpiped	colorless prism	dark red wedge
cryst syst	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	Fdd2	P21/n	Pbca	P21/c
a (Å)	43.515(8)	9.4234(6)	10.1345(6)	18.768(4)
$b(\mathbf{A})$	6.263(1)	5.9391(3)	17.4948(4)	26.982(5)
<i>c</i> (Å)	11.651(3)	10.9880(6)	19.2433(6)	21.791(4)
α (deg)				
$\beta$ (deg)		114.399(2)		107.80(3)
$\gamma$ (deg)				
$V(Å^3)$	3175.6(1)	560.04(5)	3411.9(2)	10507(4)
Z	8	4	4	8
density (g/cm3)	1.361	1.389	1.364	1.524
abs, $\mu$ (mm <sup>-1</sup> )	0.09	0.09	0.09	1.02
<i>F</i> (000)	1360	244	1464	4872
cryst size (mm)	0.40 imes 0.38 imes 0.01	$0.31\times0.08\times0.01$	0.07 imes 0.05 imes 0.02	0.25 a 0.04 a 0.01
temp (°C)	-100	-100	-100	-173
scan mode	ω	ω	ω	ω
detector	BrukerCCD	Raxis-Image plate	Raxis-Image plate	MarCCD
$\theta_{\rm max}$ (deg)	23.77	24.09	24.09	28.28
no. obsd reflns	3432	2952	7934	91 307
no. unique reflns	1097	851	2333	25 003
no. params	145	102	245	1369
$S^b$	1.04	1.04	0.81	0.99
R indices $[I > 2\sigma(I)]^a$	R1 = 0	R1 = 0.039	R1 = 0.056	R1 = 0.072
	wR2 = 0	wR2 = 0.100	wR2 = 0.073	wR2 = 0.207
R indices (all data) <sup>a</sup>	R1 = 0	R1 = 0.044	R1 = 0.097	R1 = 0.080
	wR2 = 0	wR2 = 0.102	wR2 = 0.177	wR2 = 0.217
max diff peak, hole (e/ų)	0.135, -0.144	0.131, -0.174	0.184, -0.246	1.730, -1.594

 $^{a}$  R1 =  $\sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|$ , wR2 = { $\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]^{1/2}$  (sometimes denoted as  $R_{w}^{2}$ ).  $^{b}$  GooF =  $S = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / (n - p)\}^{1/2}$ , where *n* is the number of reflections, and *p* is the total number of refined parameters.

pressure (600 psig), and shaken mechanically. After the stated reaction time (18 h), the ethylene pressure was released and the glass insert was removed from the pressure tube. The polymer was precipitated by the

addition of MeOH ( $\sim$ 20 mL). The polymer was then collected on a fritted filter and rinsed with MeOH. The polymer was transferred to a preweighed vial and dried under vacuum overnight. Table 2 summarizes the

results on the ethylene polymerization catalyzed by nickel complexes **12** and **19**. Complex **20** was insoluble in *para*-xylene.

Substantial differences in the productivity, the molecular weight average of the polyethylene formed, and the thermal stability of the 5-methylfuran-2-yl-substituted catalyst 12 and benzofuran-substituted catalyst 19 were observed. The nickel catalyst 19 was about 3 times more productive than catalyst 12 within the tested temperature range (fourth column). The benzofuran-substituted catalyst 19 produced ultrahigh molecular weight ethylene polymers in the runs at 60 °C and 70 °C (sixth column, entries 4 and 5). Broad, bimodal molecular weight distributions were observed in those cases. Ultrahigh molecular weight ethylene polymers were observed for the *para-tert*-butylphenylsubstituted catalysts of Rieger's research.<sup>3</sup> The 5-methylfuran-2-yl-substituted catalyst 12 produced polyethylenes having a molecular weight somewhat higher than ortho-methyl-substituted nickel catalysts,1 but below ortho-phenyl-substituted nickel catalysts.<sup>1</sup> The thermal stability of the catalyst 19 is noteworthy. It is still active up to temperatures as high as 150 °C. The catalyst 12 is less thermally stable; it deactivates around 120 °C. The molecular weight and catalyst productivity decrease upon increasing the temperatures of polymerization. The branching is low, but it increases at higher temperatures. The polyethylene produced at 60 and 70 °C is crystalline (eighth column, entries 1, 4, and 5). The crystallinity of the polymers declines at higher temperatures. These observations would constitute normal dependencies in the Versipol polymerization technology.1

In conclusion, 5-methylfuran-2-yl-substituted catalyst **12** and benzofuran-substituted catalyst **19** were found to be robust catalysts for ethylene polymerization. The catalyst **19** shows superior thermal stability and productivity and led to polyethylene with ultrahigh molecular weights. This could be attributed to steric protection, created by the four benzofuranyl moieties of the ligand, for the nickel atom above and below the square plane.

## **Experimental Section**

**General Procedures.** All the operations related to catalysts were carried out under an argon atmosphere using standard Schlenk techniques. Anhydrous solvents were used in the reactions. Solvents were distilled from drying agents or passed through alumina columns under an argon or nitrogen atmosphere. 2,6-Dibromophenylamine, 2-benzofuranboronic acid,  $Pd_2dba_3$ , silver hexafluoroantimonate, benzaldehyde, 2-acetyl-5-methylfuran, and triphenylcarbenium tetrafluoroborate were purchased from Aldrich. Sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (NaBAF) was purchased from Boulder Scientific.

**1,5-Bis(5-methylfuran-2-yl)-3-phenylpentane-1,5-dione (3).** Benzaldehyde **2** (5.3 g, 0.05 mol), 18.60 g (0.15 mol) of 2-acetyl-5-methylfuran **1**, 2.07 g (0.038 mol) of sodium methylate, and 50 mL of dry methanol were stirred at room temperature for 3 days. The precipitate was filtered and recrystallized from ethanol. The yield of 1,5-bis(5-methylfuran-2-yl)-3-phenylpentane-1,5-dione (**3**) was 11.29 g (67%) with mp 110 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.34 (s, 6H), 3.20 (m, 4H), 3.95 (m, 1H), 6.17–7.49 (broad lines, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub> selected bond):  $\delta$  186.73 ppm. LC/MS MW is 337 (M + H). Anal. Calcd for C<sub>21</sub>H<sub>20</sub>O<sub>4</sub>: C, 74.98; H, 5.99. Found: C, 74.87; H, 5.79.

**2,6-Bis(5-methylfuran-2-yl)-4-phenylpyranylium; tetrafluoroborate (4).** 1,5-Bis(5-methylfuran-2-yl)-3-phenylpentane-1,5-dione (**3**) (2.6 g, 0.0077 mol), 3.06 g (0.0093 mol) of triphenylcarbenium tetrafluoroborate, and 20 mL of glacial acetic acid were refluxed for 2 h. The reaction mixture was allowed to cool to ambient temperature and diluted with 200 mL of ethyl ether. The precipitate was collected and recrystallized from acetic acid. Yield of 2,6-bis(5-methylfuran-2-yl)-4phenylpyranylium tetrafluoroborate (**3**) was 0.89 g (29%) with mp 91 °C. Anal. Calcd for C<sub>21</sub>H<sub>17</sub>BF<sub>4</sub>O<sub>3</sub> (*M*<sub>w</sub> 404.16): C, 62.41; H, 4.24. Found: C, 62.22; H, 4.23. <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  2.21 (s, 6H), 5.90–7.50 (m, 11H). The structure was proven by X-ray analysis (Figure 1).

2,6-Bis(5-methylfuran-2-yl)-4-phenylnitrobenzene (5) and 2,6-Bis(5-methylfuran-2-yl)-4-nitromethyl-4-phenyl-4H-pyran (6). 2,6-Bis(5-methyl-2-furyl)-4-phenylpyrylium tetrafluoroborate (4) (0.75 g, 0.00186 mol), 2.0 g (0.033 mol) of nitromethane, 2.0 g (0.020 mol) of triethylamine, and 2 mL of ethyl alcohol were stirred at ambient temperature for 3 days. The solvent was removed in a vacuum (0.1 mm) at room temperature, and the residue was purified by chromatography on silica with petroleum ether/ethyl ether (10:2) as eluent. Compound 5 was eluted from the column first. Yield of 2,6bis(5-methylfuran-2-yl)-4-phenylnitrobenzene (5) was 0.37 g (56%) with mp 107 °C. Anal. Calcd for  $C_{22}H_{17}NO_4$  ( $M_w$ 359.37): C, 73.53; H, 4.77; N, 3.90. Found: C, 73.30, H, 4.70; N, 3.80. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.30 (s, 6H), 6.01 (m, 2H), 6.51 (m, 2H), 7.20-7.75 (br, 7H). The structure of 5 was proved by X-ray analysis (Figure 2). Yield of 2,6-bis(5-methylfuran-2-yl)-4-nitromethyl-4-phenyl-4*H*-pyran (6) was 0.033 g (5%), mp 153 °C. Anal. Calcd for C<sub>22</sub>H<sub>19</sub>NO<sub>5</sub> (M<sub>w</sub> 377.39): C, 70.02; H, 5.07; N, 3.71. Found: C, 70.22; H, 5.16; N, 3.72. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.32 (s, 6H), 4.90 (s, 2H), 5.60 (s, 2H), 6.03 (m, 2H), 6.50 (m, 2H), 7.10-7.55 (br, 5H). The structure of 6 was proved by X-ray analysis (Figure 3).

**3,5-Bis(5-methylfuran-2-yl)biphenyl-4-ylamine (7).** 2,6-Bis(5-methylfuran-2-yl)-4-phenylnitrobenzene (5) (1.84 g, 0.00512 mol), 5.0 g (0.077 mol) of zinc dust, and 70 mL of glacial acetic acid were stirred at room temperature for 24 h. The reaction mixture was filtered, and the liquid part was washed with water and extracted with ethyl ether. After removal of the solvent, the residue was purified by chromatography on silica with petroleum ether/ethyl ether (10:2) as eluent. Yield of 3,5-bis(5-methylfuran-2-yl)biphenyl-4-ylamine (7) was 0.79 g (45%) with mp 54 °C. Anal. Calcd for C<sub>22</sub>H<sub>19</sub>-NO<sub>2</sub> ( $M_w$  329.39): C, 80.22; H, 5.81; N, 4.25. Found: C, 80.37; H, 5.82; N, 4.16. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.31 (s, 6H), 6.03 (m, 2H), 6.50 (m, 2H), 7.19–7.65 (broad lines, 7H).

**2,3-Bis[2,6-bis(5-methylfuran-2-yl)-4-phenylphenylimino)]butane (9).** 3,5-Bis(5-methylfuran-2-yl)biphenyl-4-ylamine (7) (0.79 g, 0.0024 mol), 0.21 g (0.0011 mol) of 2,2,3,3tetramethoxybutane (**8**), 20 mL of toluene, and a few crystals of *para*-toluenesulfonic acid were refluxed under nitrogen for 18 h. The solvent and formed methanol were removed under vacuum. The resulting yellow solid was recrystallzed from ethanol. Yield of 2,3-bis[2,6-bis(5-methylfuran-2-yl)-4-phenylphenylimino)]butane (**9**) was 0.47 g (55%) with mp 310 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.20 (s, 6H), 2.40 (s, 12H), 6.01 (m, 4H), 6.30 (m, 4H), 7.15–8.10 (m, 14H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) (assignment only for selected bonds due to complexity of spectra):  $\delta$  170.55 ppm (C=N bonds). Anal. Calcd for C<sub>48</sub>H<sub>40</sub>-N<sub>2</sub>O<sub>4</sub> (*M*<sub>w</sub> 708.84): C, 81.33; H, 5.69; N, 3.95. Found: C, 81.28; H, 5.77; N, 3.59. The structure was proven by X-ray analysis.

Nickel(1+), [*N*,*N*-(1,2-Dimethyl-1,2-ethanediylidene)-(3,5-bis(5-methylfuran-2-yl)biphenyl-4-ylamine ],  $[(\eta^3-2-$ propenyl]-, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1-) (12). 2,3-Bis[2,6-bis(5-methylfuran-2-yl)-4-phenylphenylimino)]butane (9) (0.025 g, 0.000035 mol), 0.0047 g (0.000017 mol) of allyl nickel chloride dimer 10, 0.031 g (0.000035 mol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate 11, and 20 mL of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite, and the solvent was evaporated in a vacuum. The residue was washed with 10 mL of pentane and dried, affording 0.050 g (85%) of nickel compound **12** as a brown powder. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.10 (s, 6H, CH<sub>3</sub>), 1.79 (br, 2-allyl-H), 2.10 (s, 12 H, CH<sub>3</sub>), 2.55 (br, 2-allyl-H), 4.95 (br, 1H central allyl-H), 5.45–7.50 (m, arom. and furyl 30H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) (selected signals):  $\delta$  177.86 (s, C=N). Anal. Calcd for C<sub>83</sub>H<sub>57</sub>BF<sub>24</sub>N<sub>2</sub>NiO<sub>4</sub> ( $M_w$  1671.82): C, 59.63; H, 3.44; N, 1.68. Found: C, 59.85; H, 3.61; N, 1.79.

2,6-Bis(benzofuran-2-yl)phenylamine (15) and [2,2']-Bibenzofuranyl (16). 2-Benzofuranboronic acid 14 (10.0 g, 0.0617 mol), 6.97 g (0.0278 mol) of 2,6-dibromoaniline 13, 24.14 g (0.069 mol) of cesium carbonate, 0.848 g (0.00093 mol) of tris(dibenzylideneacetone)dipalladium, 0.45 g (0.0022 mol) of tri-tert-butylphosphane, and 120 mL of dioxane were stirred at room temperature for 24 h under argon. The reaction mixture was filtered, and the solvent was removed under vacuum. The resulting mixture was purified by chromatography on silica with petroleum ether/ethyl ether (10:2) as eluent. The yield of the 2,6-bis(benzofuran-2-yl)phenylamine 15 was 6.1 g (68%) with mp 128 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  5.30 (br, 2H), 6.60-7.80 (m, 13H). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>NO<sub>2</sub> (M<sub>w</sub> 325.36): C, 81.21; H, 4.65; N, 4.30. Found: C, 80.97; H, 4.41; N, 4.12. The structure of 15 was proved by X-ray analysis (Figure 5). The yield of [2,2'] bibenzofuranyl **16**<sup>17</sup> was 0.20 g (3% on 2-benzofuranboronic acid). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.10–7.70 (m, 10H). Anal. Calcd for  $C_{16}H_{10}O_2$  ( $M_w$  234.25): C, 82.04; H, 4.30. Found: C, 81.87; H, 4.38.

**2,3-Bis(2,6-bis(benzofuran-2-yl)phenylimino)butane (17).** 2,6-Bis(benzofuran-2-yl)phenylamine (**15**) (2.20 g, 0.0068 mol), 0.60 g (0.0034 mol) of 2,2,3,3-tetramethoxybutane **8**, 30 mL of xylenes, and a few crystals of *para*-toluenesulfonic acid were refluxed under nitrogen for 3.5 h. The resulting yellow precipitate was filtered, washed with 20 mL of ethyl ether, and dried in a vacuum. Yield of 2,3-bis(2,6-bis(benzofuran-2-yl)phenylimino)butane (**17**) was 0.31 g (13%) with mp 316 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  0.95 (s, 6H), 6.50–8.60 (m, 26H). Anal. Calcd for C<sub>48</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub> (*M*<sub>w</sub> 700.78): C, 82.27; H, 4.60; N, 4.00. Found: C, 82.12; H, 4.58; N, 4.11. The structure of 2,3-bis-(2,6-bis(benzofuran-2-yl)phenylimino)butane was proved by X-ray analysis.

Nickel(1+), [*N*,*N*-(1,2-dimethyl-1,2-ethanediylidene)-(2,6-bis-benzofuran-2-yl-phenyl-*N*], [( $\eta^{3}$ -2-propenyl]-, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate(1-) (19). 2,3-Bis(2,6-bis(benzofuran-2-yl)phenylimino)butane (17) (0.20 g, 0.00029 mol), 0.0039 g (0.000144 mol) of allyl nickel chloride dimer 10, 0.25 g (0.00028 mol) of sodium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate 11, and 20 mL of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite, and the solvent was evaporated in a vacuum. The residue was washed with 10 mL of pentane and dried, affording 0.43 g (91%) of nickel compound **19** as a brown powder. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.50 (br, 2-allyl-H), 2.05 (s, 6H, CH<sub>3</sub>), 2.40 (br, 2-allyl-H), 4.35 (br, 1H central allyl-H); 6.50–8.00 (m, arom. 38H). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>) (selected signals):  $\delta$  177.79 (s, C=N). Anal. Calcd for C<sub>85</sub>H<sub>55</sub>BF<sub>24</sub>N<sub>2</sub>NiO<sub>4</sub> ( $M_w$  1693.82): C, 60.27; H, 3.27; N, 1.65. Found: C, 60.42; H, 3.50; N, 1.74.

Nickel(1+), [N,N-(1,2-dimethyl-1,2-ethanediylidene)-(2,6-bis(benzofuran-2-yl)phenyl-N],[( $\eta^3$ -2-propenyl]-, hexafluoroantimonate(1-) (20). 2,3-Bis(2,6-bis(benzofuran-2yl)phenylimino)butane (17) (0.21 g, 0.00030 mol), 0.0445 g (0.000168 mol) of allyl nickel chloride dimer 10, 0.113 g (0.000379 mol) of silver hexafluoride 18, and 20 mL of ethyl ether were stirred at RT for 12 h. The resulting reaction mixture was filtered through Celite, and the solvent was evaporated in a vacuum. The residue was recrystallized from 10 mL of toluene, affording 0.27 g (85%) of nickel compound **20** as a black powder. <sup>1</sup>H NMR ( $CD_2Cl_2$ ):  $\delta$  1.45 (br, 2-allyl-H), 2.10 (s, 6H, CH<sub>3</sub>), 2.40 (br, 2-allyl-H), 4.35 (br, 1H central allyl-H); 6.50-8.00 (m, arom. 26H). Anal. Calcd for C<sub>53</sub>H<sub>43</sub>F<sub>6</sub>N<sub>2</sub>-NiO<sub>4</sub>Sb (M<sub>w</sub> 1066.36): C, 59.70; H, 4.06; N, 2.63. Found: C, 59.83; H, 4.10; N, 2.67. The structure of 20 was proved by X-ray analysis.

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**Supporting Information Available:** The crystallographic information files (CIF) of compounds **4–6**, **9**, **15–17**, and **20** are available free of charge via the Internet at http:// pubs.acs.org.

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