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Vinyl Polymerization of Norbornene by Bis(salicylaldiminate)copper(II)/Methylalumoxane Catalysts

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The polymerization of norbornene in the presence of different bis(salicylaldiminate)copper(II) complexes and methylalumoxane has been investigated. In all cases a high molecular weight vinyl-type polymer was obtained. The presence of electron-withdrawing nitro groups on the chelate ligand markedly increased the activity of the catalyst. The influence on the catalytic performances and polymer characteristics as a function of reaction parameters, such as temperature, duration, and content of free trimethyl aluminum in the commercial MAO, was studied.

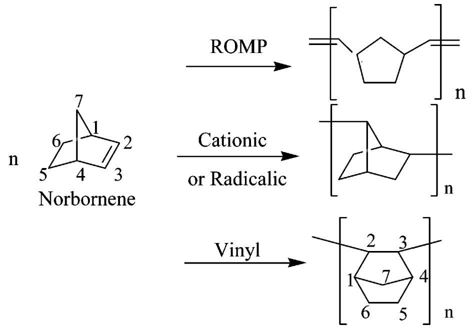
Introduction

It is well established that bicyclo[2.2.1]hept-2-ene, better known as norbornene (NB), can be polymerized by different routes, affording polymeric products that are very different in structure and properties (Scheme 1).[1,2]

Ring-opening metathesis polymerization (ROMP) is by far the most investigated route, giving rise to a polyalkenamer that still contains double bonds in the polymer backbone.[3,4]

On the contrary, both the cationic and radical polymerizations give rise to a low molecular weight polymer with a 2,7-connectivity of the monomeric units.[5] Finally, it is also possible to polymerize NB maintaining the bicyclic structure, i.e., only opening the double bond, in a typical vinyl polymerization.[1,6] This type of poly(norbornene) (PNB) is a special polymer, due to its good mechanical properties, heat resistivity, transparency, high glass transition temperature, and good solubility in polar organic solvents. PNB has been deeply investigated for many optical and microelectronic applications, and its films have excellent optical transparency, heat stability, and good UV resistance; therefore they can be employed as components for condensers or cover layers for liquid-crystal displays.[7−9] Moreover, the high optical transparency in the infrared region of the spectrum makes PNBs very promising materials for data storage and telecommunication waveguides.[10]

Scheme 1



Up to now, catalytic systems based on titanium,[11] zirconium,[12] hafnium,[13] vanadium,[14] cobalt,[15] chromium,[16,17] nickel,[17−20] and palladium[21−23] have been mainly reported for the vinyl polymerization of NB. Recently, rare-earth metals were also used in such a reaction, although with a low activity.[24]

Notwithstanding that many efforts in the past five years have been devoted to late-transition polymerization catalysts,[25,26] no

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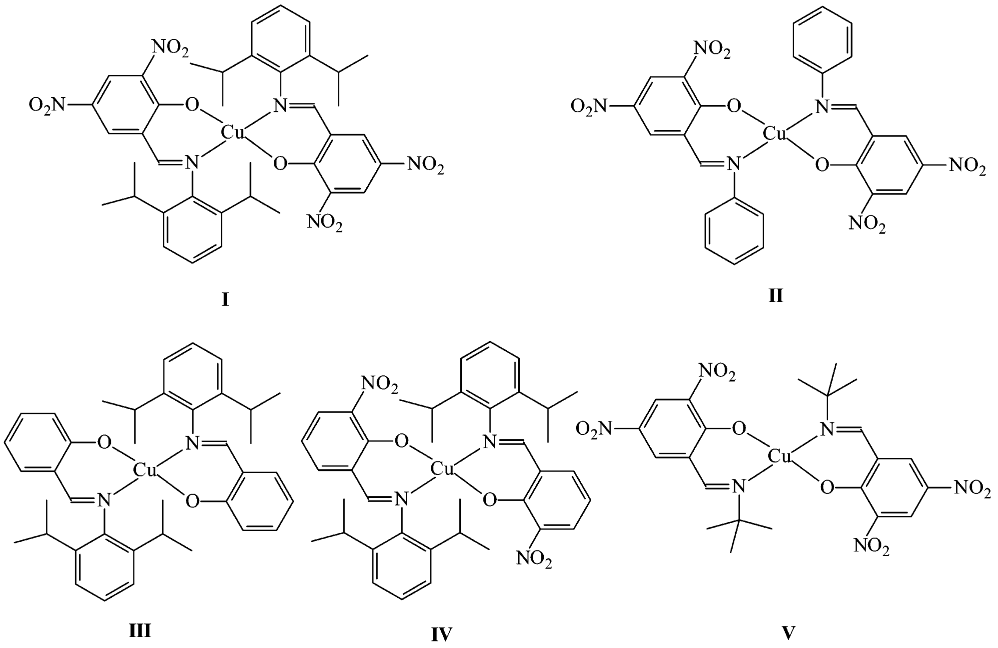
Chart 1



data have been reported, to the best of our knowledge, on the copper-catalyzed NB vinyl polymerization.[27] However, with the exclusion of the atom transfer radical polymerization (ATRP) systems,[28,29] catalysts based on copper are in general rare and deal with ethylene and acrylate homo- and co-polymerization.[25,30]

Therefore, in the present article the vinyl polymerization of NB catalyzed by different Cu(II) bis(salicylaldiminate) complexes (**I**−**V**) (Chart 1) in combination with MAO will be studied. In fact, these inexpensive, air-stable, and very easy to synthesize copper precursors appear good candidates for this type of reaction.

In particular, the influence of the reaction conditions on their catalytic behavior will be examined and the resulting PNBs will be structurally characterized.

Results and Discussion

It is well known that four-coordinated Cu(II) complexes are usually characterized by a square planar coordination that may be distorted to pseudo-tetrahedral geometry.[31] In particular, for bis(salicylaldiminate)Cu(II) complexes the steric hindrance and the electronic characteristics of the substituents on both the phenol and the imine moieties influence the distortion from planarity.[32−34] However, for many of these substituted complexes, X-ray structural data are not available and the above stereochemical statements are based on spectroscopic studies.

In the case of the complexes **I**−**V**, due to their low solubility, only **IV** was obtained in the crystalline state, and its structure was determined by X-ray diffraction, as shown in Figure 1. The geometrical parameters of the bonding around copper are listed in Table 1. The crystallographic data together with the collection parameters and the refinement parameters are summarized in Table 2. **IV** may be described as distorted square planar. The N and O atoms bonded to the copper are displaced by nearly 0.45 Å over and below the coordination mean plane, respectively. A very similar coordination geometry has been reported for Cu(II) complexes with 2-(2-oxy-5-bromo-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl[35] and 2-(3-nitro-2-oxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl[36] ligands, which share with our ligand the encumbering substitution on the iminic nitrogen and the nitro group in *ortho*-position with respect to the oxygen. A similar structure was also reported for bis(3,5-dibromo-*N*-*o*-tolylsalicylaldiminate)-copper(II).[37]

Preliminary experiments on NB polymerization were carried out in the presence of **I** as copper(II) precursor, characterized by the presence of two electron-withdrawing nitro groups on the salicylaldiminate ligand and of bulky isopropyl substituents on the N-aryl moiety. Indeed, the corresponding nickel(II)

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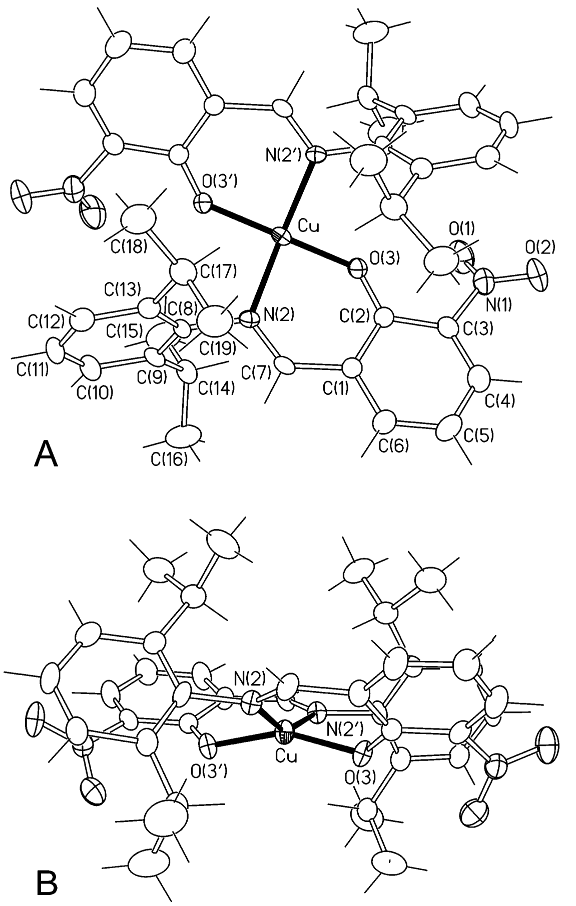

Figure 1. Two views of the molecular structure of **IV** in the 2-fold axis direction (A) and normal to the 2-fold axis (B). The distorted square planar coordination of the copper is evident from B. ′ = −*x*, *y*, 1/2 − *z*. Thermal ellipsoids are at 30% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for IV

Cu−O(3)	1.890(5)	Cu−N(2)	1.976(5)
N(2)−Cu−O(3)	92.5(2)	N(2)−Cu−O(3′)[a]	93.9(2)
N(2)−Cu−N(2′)	148.8(4)	O(3)−Cu−O(3′)	156.3(3)

[a] The slanted prime in the label has the same meaning as in Figure 1.

Table 2. Crystal Data and Structure Refinement for IV

empirical formula	$C_{38}H_{42}CuN_4O_6$
fw	714.30
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a/Å	14.624(4)
b/Å	11.550(3)
c/Å	21.827(4)
β/deg	108.15(2)
U/Å^3	3503.3(15)
Z	4
D_{calc}/Mg·m^{-3}	1.354
μ/mm^{-1}	0.676
no. of measd reflns	4297
no. of unique reflns [R_{int}]	3457 [0.1164]
no. of params	226
R_1, wR_2 [$I > 2\sigma(I)$]	0.0946, 0.1613
goodness of fit on F^2	1.000

complex was recently ascertained to be very active in NB polymerization, when activated by a large excess of MAO as cocatalyst (Al/Ni: 1000−2000 mol/mol).[38] This catalytic behavior has been related to the presence of the nitro groups on the phenol moiety.

Chlorobenzene was chosen as a reaction medium for NB polymerization experiments because it is well known that this polar solvent, where PNB is soluble, improves the catalytic performances in NB vinyl polymerization.[1]

Table 3. Homopolymerization of NB by the I/MAO Catalytic System in Chlorobenzene Solution[a]

run	Al/Cu[b] (mol/mol)	Al/Cu[c] (mol/mol)	T^d (°C)	time (h)	P[e]	M_w[f]	PDI[f,g]
1	100		25	1			
2	1000		25	1			
3	2500		25	1	traces	n.d.	n.d.
4	2500		60	1	60	606 000	2.4
5	2500		80	1	150	432 000	2.6
6	2500		80	24	12	494 000	4.7
7[h]	375		80	1			
8[i]	2125		80	1			
9	2500		100	24	10	386 000	3.9
10	1000		80	1			
11		2500	80	1			

[a] **I**: 1 μmol; NB/Cu: 10 000 mol/mol; chlorobenzene (total volume): 20 mL; n.d. = not determined. [b] Al represents the total amount of aluminum including the free TMA present in MAO-A. [c] Al represents the total amount of aluminum including the free TMA present in MAO-W. [d] Reaction temperature. [e] Productivity expressed as kg of PNB/mol Cu × h. [f] Determined by SEC analysis. [g] Polydispersity index, determined as M_w/M_n. [h] TMA alone was employed; the Al/Cu molar ratio corresponds to that present in MAO-A when an Al/Cu molar ratio equal to 2500 was used (run 5). [i] TMA-depleted MAO was used (see Experimental Section). The Al/Cu molar ratio equal to 2125 corresponds to that of 2500 in run 5, after elimination of TMA in MAO-A.

No catalytic activity was observed when **I** was adopted in the absence of an organometallic cocatalyst. When 1 μmol of **I** was employed at room temperature in combination with MAO-A (containing about 15 mol % of free TMA and 85 mol % of oligomeric MAO), no catalytic activity was ascertained up to an Al/Cu molar ratio of 2500 (runs 1−3, Table 3), and also in this case only traces of PNB were formed. When the reaction temperature was increased to 60 °C (run 4, Table 3), a higher productivity was observed to give a PNB sample with high molecular weight (M_w = 606 000) and a polydispersity around 2.

No traces of oligomeric products were detected in the reaction mixture. A further increase of the reaction temperature to 80 °C (run 5, Table 3) caused a further enhancement of the productivity up to 150 kg of PNB/mol Cu × h. When the reaction time was prolonged to 24 h (run 6, Table 3), a modest increase of the molecular weight was observed with a significant enhancement of its polydispersity. Taking into account that the employed MAO-A contains about 15 mol % of free TMA, to understand the role of this last component, run 5 was repeated in the presence of TMA alone, adopting an Al/Cu = 375 mol/mol (run 7, Table 3), corresponding to the content of TMA introduced with MAO-A. No catalytic activity was observed, and over-reduction of **I** with metal deposition was also found. An analogous experiment carried out with **I** and TMA-free MAO (Al/Cu = 2125 mol/mol) (run 8, Table 3) again did not show any catalytic activity. However, no metal deposition was observed in this case. These results clearly indicate that both TMA and MAO are necessary for the activation of the catalytic system. Similar results were obtained for ethylene polymerization when bis(salicylaldiminate)nickel(II)/MAO catalysts were employed.[39]

When the reaction temperature was raised to 100 °C, a slight decrease of the catalytic activity was observed (compare run 9 with run 6), thus suggesting that 80 °C is the optimum working temperature.

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Table 4. Homopolymerization of NB by II-V/MAO Catalytic Systems in Chlorobenzene Solution[a]

run	Cu precursor	Al/Cu[b] (mol/mol)	Al/Cu[c] (mol/mol)	T^d (°C)	time (h)	P[e]	M_w[f]	PDI[f,g]
12	**II**	2500		60	1	traces	n.d.	n.d.
13	**II**	2500		80	1	110	344 000	2.2
14	**II**	2500		80	24	11	411 000	2.3
15	**II**		2500	80	1	traces	n.d.	n.d.
16	**III**	2500		80	1	60	116 000	2.9
17	**III**	2500		80	24	5	125 000	3.1
18	**IV**	2500		80	1	70	227 000	2.4
19	**IV**	2500		80	24	4	450 000	3.1
20	**V**	2500		80	1	30	129 000	3.2
21	**V**	2500		80	24	5	180 000	3.3
22[h]	$Cu(OAc)_2$	2500		80	1	0		
23[h]	$Cu(acac)_2$	2500		80	1	0		

[a] Cu precursor: 1 μmol; NB/Cu: 10 000 mol/mol; chlorobenzene (total volume): 20 mL; n.d. = not determined. [b] Al represents the total amount of aluminum including the free TMA present in MAO-A. [c] Al represents the total amount of aluminum including the free TMA present in MAO-W. [d] Reaction temperature. [e] Productivity expressed as kg of PNB/mol Cu × h. [f] Determined by SEC analysis. [g] Polydispersity index, determined as M_w/M_n. [h] Metal deposition was observed.

When run 5 was replicated in the presence of a lower amount of MAO-A (Al/Cu = 1000, run 10), only traces of PNB were formed.

With the aim of verifying the effect on catalytic activity when different relative amounts of TMA and oligomeric MAO were employed, run 5 was repeated by using MAO-W (containing about 28 mol % of TMA), and hence the TMA concentration almost doubled (run 11, Table 3). The complete deactivation of the catalytic system was observed, an analogous detrimental effect being previously observed with the corresponding nickel-based catalysts.[40]

When **I** was replaced by **II**, not containing the bulky isopropyl groups on the N-aryl moiety but still bearing the nitro groups on the phenol moiety of the ligand, once again no appreciable catalytic activity was observed at 60 °C (run 12, Table 4).

When the temperature was raised to 80 °C (runs 13−15), the catalytic performances, in terms of productivity and PNB characteristics, were substantially similar to those observed in the corresponding experiments carried out in the presence of **I**. These results suggest that for these bis(salicylaldiminate) Cu(II)/MAO systems the catalytic behavior is not significantly affected by the presence or absence of bulky substituents on the N-aryl moiety.

On the contrary, when **III**, not bearing nitro groups on the phenol moiety, was employed in the place of **I**, a significant reduction of both the catalytic activity and the molecular weight was observed (runs 16, 17, Table 4). On the other hand, an intermediate result was achieved when **IV**, containing only one nitro group in the *ortho*-position of the phenol moiety, was employed (runs 18, 19, Table 4), thus suggesting that the presence of the electron-withdrawing nitro groups on the above copper precursors plays an important role in the activation of the catalysts.

Finally, when **V**, characterized by the presence of an N-alkyl moiety, was employed as copper precursor, a further reduction of the activity was observed (runs 20, 21, Table 4). In all cases when the reaction time was prolonged to 24 h, a broadening of the molecular weight polydispersity was observed, probably related to the increase of the number of different active species.

To verify if commercial Cu(II) precursors in the presence of MAO can be employed for NB polymerization, run 5 was replicated employing Cu(II) acetate as precursor (run 22, Table 4). No catalytic activity was observed, and at the end of the experiment metal deposition was ascertained. A complete deactivation was also observed when Cu(II) acetylacetonate was tested (run 23, Table 4); also in this case under the adopted reaction conditions over-reduction to metal was detected, never ascertained in the case of the corresponding catalytic experiments performed with precursors **I**−**V**.

FT-IR and ^{1}H and ^{13}C NMR spectra of all the PNB samples are typical of a nonstereoregular vinyl-type structure. In fact, in the FT-IR spectra no signals related to double bonds were observed in the 1680−1620 cm^{-1} region.[18,41] Moreover, ^{1}H NMR analysis showed signals in the 0.9−2.6 ppm range, whereas no resonances were observed in the 5−6.5 ppm region, typical of vinylic hydrogen atoms.[42]

^{13}C NMR spectra confirmed the above statements. In fact, they showed the resonances of methylenes and methines at 29.5−33.5 ppm for C5 and C6 (see Scheme 1), at 35.5 and 38.5 ppm for C7, at 38.5−42.5 ppm for C1 and C4, and in the 46.6−54 ppm region for C2 and C3, according to what was previously reported for vinyl-type addition PNBs.[40,43]

TGA analysis showed that all the PNB samples were stable up to 450 °C. Our attempts to determine the glass transition temperature (T_g) of PNB samples failed, DSC spectra not evidencing well-defined endothermic signals upon heating to the decomposition temperature, as previously observed for vinyl-type PNBs obtained with other catalytic systems.[18,44]

The observed vinyl-type structure of the resulting PNB samples represents an indirect indication that a nonradical reaction mechanism is working with the above copper(II)/MAO catalytic systems. However, to gain a better insight into the oxidation state of the active species, ESR studies were carried out on the **I**/MAO-A catalytic system. The initial strong ESR signal (Figure 2A) of the copper(II) precursor **I** at 293 K (g_{iso} = 2.108, A_{iso} = 78.6 G) was progressively reduced by the addition of MAO-A, a complete disappearance of the Cu(II) ESR signal (Figure 1C) being observed for an Al/Cu molar ratio equal to 150. Moreover, no appearance of any other radical species was ascertained, at least up to an Al/Cu molar ratio equal to 2500. Taking into account that NB itself, due to its high concentration, may behave as a stabilizing agent for the active species, the above-described ESR experiments were repeated in the presence of NB (NB/Cu = 10 000 mol/mol). No

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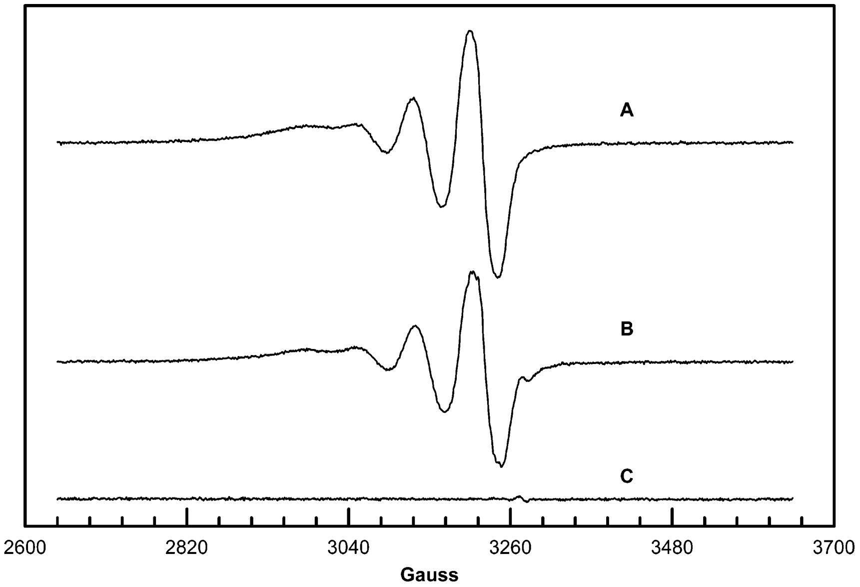

Figure 2. X-band ESR spectra at $T = 293$ K of the catalytic system **I**/MAO-A (A, copper(II) precursor alone; B, Al/Cu molar ratio equal to 15; C, Al/Cu molar ratio equal to 150).

significant spectral changes were observed, thus assigning the stabilizing role to the oligomeric MAO alone.

The formation of an ESR-silent Cu(I) active species was confirmed by the color change of the reaction mixture, which turned from dark green, typical of copper(II), to dark red on the progressive addition of MAO-A. This last result supports a Cu(I)-mediated polymerization mechanism, analogously to what was recently observed in the case of methyl methacrylate polymerization by Cu(II) amidinate/MAO catalysts.[45] When the experiment was repeated by using TMA alone, the ESR spectrum of **I** completely disappeared at a TMA/Cu molar ratio equal to 30, but in this case a rapid decomposition to metal was observed. On the contrary, when TMA-depleted MAO was used up to an Al/Cu molar ratio equal to 2500, the Cu(II) signal remained unchanged. These last results confirm that the active species are formed and stabilized by a synergism between TMA and the oligomeric MAO, the first component having a reducing role and the second one a stabilizing effect, as in general reported for this cocatalyst.[46] However, the required very high excess of MAO-A prevents the isolation and makes very difficult the spectroscopic characterization of the active species. Work is in progress on this interesting point, although at least one residual N,O ligand on the active species should be present, the performances of **I**−**V** being very different from those observed in the presence of acetate or acetylacetonate precursors.

Conclusions

In this work the catalytic activity of bis(salicylaldiminate)copper(II)/MAO catalysts in the vinyl polymerization of norbornene is reported for the first time. The N,O chelate ligand on the metal center appears necessary for the stability of the resulting catalytic system. The presence of electron-withdrawing nitro groups on these precursors enhances the catalytic performances. The obtained polymers are characterized by high molecular weight and a nonstereoregular vinyl-type structure, typical aspects of a nonradical mechanism. Accordingly, the ESR study on the copper species formed under polymerization conditions supports the formation of Cu(I) active species.

Experimental Section

Materials. Manipulations of sensitive materials were carried out under a dry argon atmosphere using Schlenk techniques. Chlorobenzene (Aldrich) and methylene chloride were refluxed on CaH_2 for 8 h, distilled, and stored under dry argon. Methanol (Aldrich) was dried by distillation under dry argon after refluxing for 6 h on magnesium methoxide according to the Lund and Bjerrum method.[47] Methylalumoxane was purchased from Witco as a 5 wt % solution in toluene (free TMA content equal to 28 mol %) (MAO-W) and from Azko Nobel as a 7 wt % in toluene solution (free TMA content equal to 15 mol %) (MAO-A). Both were used as received and stored in the refrigerator. TMA-depleted MAO was obtained from MAO-A as a solid residue by high-vacuum distillation as previously reported.[46,48]TMA (Aldrich) was used as received and stored under dry argon. Norbornene (NB) (Aldrich) was refluxed for 2 h on Na, distilled, and stored under dry argon. NB was employed as a 20 wt % solution in chlorobenzene. Cu(II) acetate [$Cu(OAc)_2$] and Cu(II) acetylacetonate [$Cu(acac)_2$] (both from Aldrich) were used as received. Bis[*N*-(2,6-diisopropylphenyl)salicylaldiminate]copper(II) (**III**) and bis[5-nitro-*N*-(*tert*-butyl)salicylaldiminate]copper(II) (**V**) were prepared according to procedures reported in the literature.[49−51] New complexes such as bis[3,5-dinitro-*N*-(2,6-diisopropylphenyl)-salicylaldiminate]copper(II) (**I**), bis[3,5-dinitro-*N*-(phenyl)salicylaldiminate]copper(II) (**II**), and bis[3-nitro-*N*-(2,6-diisopropylphenyl)-salicylaldiminate]copper(II) (**IV**) were prepared as follows.

Synthesis of I. 3,5-Dinitro-*N*-(2,6-diisopropylphenyl)salicylaldimine (0.881 g, 2.37 mmol) was dissolved in 30 mL of methanol, and the resulting solution was dropwise added at room temperature to a solution of 0.181 g (1.00 mmol) of $Cu(OAc)_2$ in 20 mL of methanol. The reaction mixture was refluxed for 2 h, then it was allowed to stand overnight at room temperature to precipitate a green solid, which was filtered, washed with methanol, and vacuum-dried to give 0.76 g (0.797 mmol) of **I** (yield 79.7%).

Anal. Found: C 57.43, H 4.91, N 10.78. Calcd for $C_{38}H_{38}N_6O_{10}Cu$: C 56.89, H 4.77, N 10.47. FT-IR: ν_{CH} (aromatic) 3091; ν_{CH} (aliphatic) 2966, 2869; $\nu_{C=N}$ 1622, 1511; $\nu_{as\ NO2}$ 1530; $\nu_{s\ NO2}$ 1311; δ_{CH} (isopropyl) 1387, 1375 cm^{-1}.

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Synthesis of II. 3,5-Dinitro-*N*-(phenyl)salicylaldimine (0.656 g, 2.3 mmol) was dissolved in 30 mL of methanol, and the resulting solution was dropwise added at room temperature to a solution of 0.218 g (1.2 mmol) of $Cu(OAc)_2$ in 20 mL of methanol. The reaction mixture was refluxed for 2 h, then it was allowed to stand overnight at room temperature to precipitate a brown solid, which was filtered, washed with methanol, and vacuum-dried to give 0.48 g (0.79 mmol) of **II** (yield 66.1%).

Anal. Found: C 48.52, H 2.91, N 12.78. Calcd for $C_{26}H_{16}N_6O_{10}Cu$: C 49.10, H 2.54, N 13.21. FT-IR: ν_{CH} (aromatic) 3093; ν_{CH} (aliphatic) 2967, 2866; cm^{-1},$\nu_{C=N}$ 1622; $\nu_{as\ NO2}$ 1531; $\nu_{s\ NO2}$ 1313 cm^{-1}

I and **II** were obtained as amorphous powdery solids. Many crystallization attempts failed, thus preventing the determination of their crystal structures.

Synthesis of IV. 3-Nitro-*N*-(2,6-diisopropylphenyl)salicylaldimine (0.536 g, 1.71 mmol) was dissolved in 30 mL of methanol, and the resulting solution was dropwise added at room temperature to a solution of 0.149 g (0.82 mmol) of $Cu(OAc)_2$ in 20 mL of methanol. The reaction mixture was refluxed for 2 h, then it was allowed to stand overnight at room temperature to precipitate a brown solid, which was filtered, washed with methanol, vacuum-dried, and then recrystallized from methylene chloride/methanol to give 0.24 g (0.34 mmol) of **IV** (yield 41%).

Mp > 300 °C. Anal. Found: C 63.41, H 6.01, N 7.79. Calcd for $C_{38}H_{42}N_4O_6Cu$: C 63.90, H 5.93, N 7.84. ^1H NMR analysis failed due the paramagnetic character of **IV**. FT-IR: ν_{CH} (aromatic) 3093; ν_{CH} (aliphatic) 2962, 2875; $\nu_{C=N}$ 1615; $\nu_{as\ NO2}$ 1515; $\nu_{s\ NO2}$ 1302; δ_{CH} (isopropyl) 1384, 1360 cm^{-1}.

Polymerization Procedures. NB homopolymerization experiments were carried out in a 50 mL Carius vessel under magnetic stirring and dry argon atmosphere. In a general procedure the copper precursor was dissolved in chlorobenzene and then the proper amount of the solution was transferred into the Carius vessel. Then NB was added as a 20 wt % solution in chlorobenzene. Finally, the chosen amount of MAO (MAO-W or MAO-A) was added in order to reach the proper Al/Cu molar ratio. When the polymerization experiment was carried out at a temperature > 25 °C, the Carius vessel was immersed in a thermostatic oil bath at the chosen temperature. The polymerization was stopped by adding a large excess of methanol acidified with 5% aqueous HCl to purify the polymer from catalyst residues. The precipitated polymer was washed by fresh methanol, then filtered, dried under vacuum, weighed, and structurally characterized.

Physicochemical Measurements. IR spectra were performed with a FT-IR Perkin-Elmer Spectrum One spectrophotometer equipped with an attenuated total reflectance (ATR) apparatus. Data elaboration was performed by a Spectrum V 3.2 Perkin-Elmer program. The NMR spectra of PNB samples were performed in chlorobenzene and 1,1,2,2-d$_2$-tetrachloroethane on a Varian Gemini 200 spectrometer operating at 200 (^1H) and 50 (^{13}C) MHz. Size exclusion chromatography (SEC) measurements were carried out with a HPLC pump equipped with a 50 μm Rheodyne loop, a Waters 515 oven at 35 °C, and a Waters 2410 refractive index detector. A PL 5 μm gel MIXED-C column was used. Chlorobenzene and 1 mL/min were adopted as the eluent and the elution rate, respectively. Monodispersed polystyrene samples (M_w = 1940, 10 050, 96 000, 483 000, 1 730 000, and 3 065 000) were used for the calibration curve.

Differential scanning calorimetry (DSC) measurements of the PNB samples were performed on a Mettler TA 4000 instrument equipped with a DSC 30 flow calorimeter and assisted by TA72 GraphWare software.

Thermogravimetric analysis (TGA) of the PNB samples was performed on a Mettler TG50 thermobalance and Mettler TC11 processor, using a dry nitrogen purge and a scan rate of 10 °C/min.

X-band ESR spectra of the catalytic systems based on **I** and the aluminum cocatalysts in chlorobenzene solution and in the presence or absence of NB were recorded on a Varian E112 spectrometer equipped with a Varian E257 unit for temperature control. A Varian NMR gaussmeter ER 035M and a XL microwave frequence counter for *g* measurements were employed. The spectrometer was interfaced to an IPC 610/P566C industrial grade Avantech computer by means of a data acquisition system[52] and a software package[53] specially designed for ESR experiments.

X-ray diffractometric analysis was carried out as follows.

A tiny crystal of **IV**, 0.20 × 0.20 × 0.16 mm wide, sealed in a Lindeman capillary, was used for the diffractometric sudy. The measurements were carried out by using a Bruker AXS P4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters listed in Table 2 were calculated from the setting angles of 33 strong reflections.

All data were collected in the $\omega/2\theta$ scan mode, and three standard reflections were monitored every 97 measurements for checking crystal decay and equipment stability. Data reduction was done by the XSCANS program.[54] A set of 4297 intensity data were collected between $1.96° \leq \theta \leq 26.05°$ and corrected for Lorentz polarization and absorption effects (y-scan method). After merging of equivalent reflections ($R_{int} = [\sum|F_o^2 - F_o^2(\text{mean})|/\sum(F_o^2)] = 0.1164$) 3457 independent reflections were obtained. The poor internal *R* factor, 11.6%, must be ascribed to the poor quality of the crystal, which limited to 1461 the intensities greater that $2\sigma(I)$.

The structure solution was obtained by standard direct methods in the *C*2/*c* space group. The hydrogen atoms were placed in calculated positions and in the refinement were let "ride" on the connected carbon atoms. The final reliability factors (anisotropic thermal parameters for all heavy atoms) are listed in Table 2.

The calculations were done by using the SHELXTL program[55] and some routines contained in the WINGX suite.[56]

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