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## Iminopyridine Copper Complex based Catalysts for 1,3-Dienes Stereospecific Polymerization

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**KEYWORDS:** copper catalysts, stereospecific polymerization, 1,3-butadiene, isoprene, polybutadiene, polyisoprene.

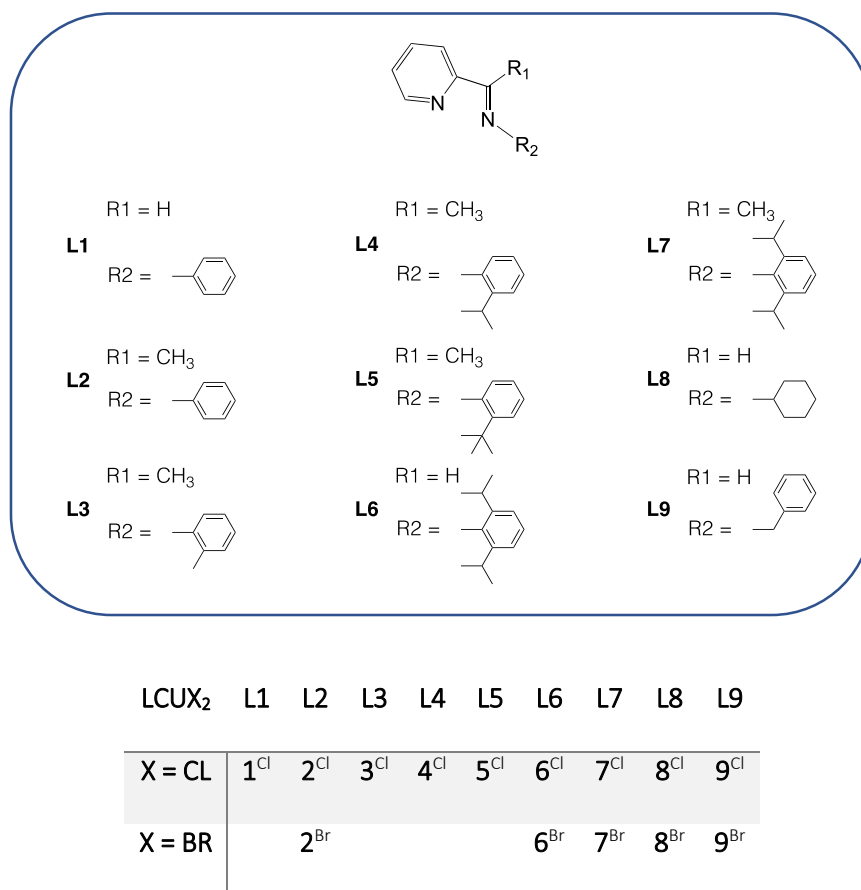
**ABSTRACT:** Some novel copper complexes were synthesized by reacting copper(II) chloride and copper(II) bromide with pyridyl-imine ligands, and spectroscopically characterized. For some of them single crystals were obtained, and their molecular structure was determined by X-ray diffraction. The complexes were combined with methylaluminoxane (MAO) for the polymerization of 1,3-dienes (*i.e.*, butadiene and isoprene) obtaining active and selective copper-based catalysts and, in case of isoprene, polymers with quite unusual structures, *i.e.* predominantly alternating *cis*-1,4-*alt*-3,4 structures containing *cis*-1,4 unit sequences within the polymer chain.

## 1. Introduction

In recent years, the research activity in the field of stereospecific polymerization of conjugated dienes <sup>[1]</sup> has particularly focused on the study of new catalytic systems based on organometallic complexes of transition metals and lanthanides with various types of organic ligands (*e.g.*, phosphines, pyridylimines, bis-imines) and with a well-defined structure.<sup>[2-11]</sup> This because it has been amply demonstrated that the nature of the ligand can exert a considerable influence on the polymerization regio- and stereoselectivity.<sup>[12-21]</sup>

But the regio- and stereo-selectivity are also strongly affected by the conjugated diene structure,<sup>[22]</sup> and in general we can state, without fear of being denied, that obtaining polymers, more or less stereoregular, from conjugated diene monomers depends on the right choice of type of metal, type of ligand and type of monomer, as clearly pointed out by the results obtained in the polymerization of different 1,3-dienes with various transition metal- and lanthanide-based catalysts. As an example we can mention several cases: *i)* the same catalytic system,  $\text{FeCl}_2(\text{bipy})_2/\text{MAO}$  ( $\text{bipy} = 2,2'$ -bipyridine), gives a crystalline highly syndiotactic 1,2 polymer from 3-methyl-1,3-pentadiene and a crystalline highly *cis*-1,4 polymer from 2,3-dimethyl-1,3-butadiene);<sup>[18,23-26]</sup> *ii)* the same diene, 1,3-butadiene, gives a syndiotactic 1,2 polymer with the system  $\text{CrCl}_2(\text{dmpe})_2/\text{MAO}$  ( $\text{dmpe} = 1,2$ -bis(dimethylphosphino)ethane) and an isotactic 1,2 polymer with  $\text{CrCl}_2(\text{dmpm})_2/\text{MAO}$  ( $\text{dmpm} = \text{bis}(\text{dimethylphosphino})\text{methane}$ );<sup>[19,20]</sup> *iii)* the same ligand can provide more or less active and selective catalytic systems depending on the metal to which it is coordinated (see for instance  $\text{dmpe}$ ;  $\text{CrCl}_2(\text{dmpe})_2/\text{MAO}$  is an extremely active and selective catalyst for the polymerization of 1,3-butadiene,<sup>[19]</sup> while  $\text{FeCl}_2(\text{dmpe})_2/\text{MAO}$  is practically inactive<sup>[2]</sup>), and *iv)* the same metal can give rise to active and selective catalysts depending on the type of ligand coordinated (see for instance iron;  $\text{FeCl}_2(\text{dmpe})_2$  is inactive in the polymerization of isoprene,<sup>2</sup>  $\text{FeCl}_2(\text{bipy})_2/\text{MAO}$  is extremely active in the polymerization of isoprene giving a highly syndiotactic 3,4-polymer,<sup>[18,23,27,28]</sup> while pyridyl-imine iron dichloride complexes in combination with MAO are quite active in the polymerization of isoprene, giving poly(isoprene)s with a mixed 1,4/3,4 structure. The 1,4 and 3,4 units are randomly or alternately distributed along the polymer chain depending on the nature of the pyridyl-imine ligand).<sup>[14,15,21,22,29,30]</sup>

In principle indeed, each transition metal or lanthanide could be able to provide active and selective catalytic system for the polymerization of 1,3-dienes once the *right* combination of metal, ligand and diene monomer was chosen. Following this idea, in the framework of our research work dealing with the synthesis and the characterization of transition metal coordination compounds<sup>[31,32]</sup> and the study of their behavior in the polymerization of 1,3-dienes, we have taken into consideration copper. To date only one very recent report on the stereospecific polymerization of 1,3-dienes with copper-based catalysts appeared in the literature.<sup>[33]</sup> In this paper, we are reporting on the synthesis and characterization of some novel copper dichloride and dibromide complexes (Figure 1) with pyridyl-imine ligands, and on the results obtained in the polymerization of some 1,3-dienes (*i.e.*, butadiene and isoprene) with catalyst systems based on the combination of MAO with the above complexes.



**Figure 1.** Copper(II) complexes used in this work.

## 2. Results and Discussion

**2.1. Synthesis and characterization of copper complexes.** The reaction of **L1** – **L9** with  $\text{CuX}_2$  or  $\text{CuX}_2(\text{H}_2\text{O})_2$  ( $\text{X} = \text{Cl}, \text{Br}$ ) ( $\text{L}/\text{Cu}$  molar ratio = 1) to give pure  $\text{Cu}(\text{L})\text{X}_2$  (Chart 1) were initially performed in boiling toluene but we observed that the formation of the complexes occurs smoothly at room temperature when using ethanol as reaction medium. Compounds are the same either starting from anhydrous or from hydrated copper halides. Copper complex **1<sup>Cl</sup>**, **8<sup>Cl</sup>** and **9<sup>Br</sup>** have been already reported in the literature,<sup>[34-36]</sup> while the others are described for the first time.

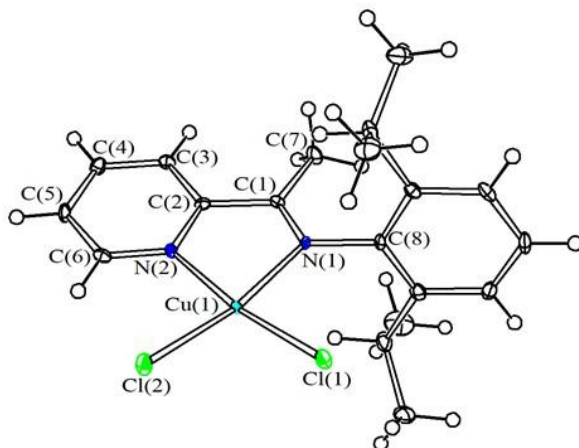
The obtained copper(II) compounds are air stable green ( $\text{X} = \text{Cl}$ ) or red to brown ( $\text{X} = \text{Br}$ ) microcrystalline solids, which were characterized by analytical and infrared data. Infrared spectra are characterized by strong absorptions in the  $1600\text{--}1500\text{ cm}^{-1}$  range due to the  $\text{C}=\text{N}$  stretching vibrations (Figures S1–S14 in the Supporting information) which is ca.  $20\text{ cm}^{-1}$  shifted towards lower wavenumbers with respect to the uncoordinated species. All the copper compounds are soluble in polar solvents such as acetonitrile or dichloromethane and are substantially insoluble in hydrocarbons. **7<sup>Cl</sup>** and **7<sup>Br</sup>** were recrystallized from a  $\text{CH}_2\text{Cl}_2$ /heptane mixture and characterized by X-ray diffraction methods. The molecular structure of **7<sup>Cl</sup>** and **7<sup>Br</sup>** are reported in Figures 1 and 2, respectively, and a selection of bond distances and angles is reported in Table 1.

Compound **7<sup>Cl</sup>** co-crystallized with a  $\text{CH}_2\text{Cl}_2$  molecule in the unit cell and the crystals can be described as **7<sup>Cl</sup>·CH<sub>2</sub>Cl<sub>2</sub>**. Compounds **7<sup>Cl</sup>** and **7<sup>Br</sup>** are mononuclear species. The copper center of **7<sup>Cl</sup>** and **7<sup>Br</sup>** is tetraordinated to two nitrogen atoms of the pyridyl imine ligand and two halides, but the copper atom geometry is different in the two complexes. While the geometry of the copper center in **7<sup>Cl</sup>** can be described as square planar, the coordination mode of **7<sup>Br</sup>** can be described as distorted tetrahedral, or as something in between a planar and tetrahedral geometry. This point can be described using the  $\tau_4$ <sup>[37]</sup> and  $\tau'_4$ <sup>[38,39]</sup> parameters which can be calculated as follow:

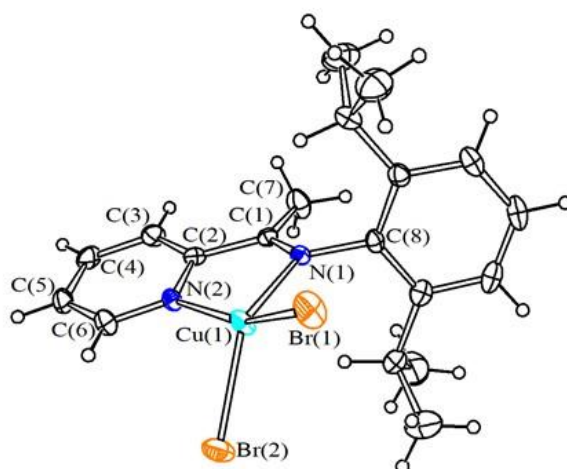
$$\tau_4 = \frac{360 - (\alpha + \beta)}{360 - 2\theta} ; \tau'_4 = \frac{\beta - \alpha}{360 - \theta} + \frac{180 - \beta}{180 - \theta}$$

where  $\alpha$  and  $\beta$  are the two greatest valence angles of coordination center ( $\alpha < \beta$ ), and  $\theta = \cos^{-1}(-1/3) = 109.5^\circ$  is a tetrahedral angle. In the case of a perfect square-planar geometry,  $\tau_4 = \tau'_4 = 0$ , whereas for a perfect

tetrahedron  $\tau_4 = \tau'_4 = 1$ . In the case of **7<sup>Cl</sup>** ( $\alpha = 169.39^\circ$ ,  $\beta = 171.40^\circ$ ), the calculated values of  $\tau_4$  and  $\tau'_4$  are 0.136 and 0.130, respectively, that correspond to an almost perfect square-planar geometry. Conversely, for **7<sup>Br</sup>** ( $\alpha = 135.65^\circ$ ,  $\beta = 157.36^\circ$ ), the calculated values of  $\tau_4$  and  $\tau'_4$  are 0.475 and 0.408, respectively, indicating a geometry in between square-planar and tetrahedral.



**Figure 2.** Molecular structure of **7<sup>Cl</sup>**·CH<sub>2</sub>Cl<sub>2</sub> with labelling. Displacement ellipsoids are at the 30% probability level.



**Figure 3.** Molecular structure of **7<sup>Br</sup>** with labelling. Displacement ellipsoids are at the 30% probability level.

**Table 1.** Selection of bond distances (Å) and angles (°) for  $7^{\text{Cl}}\cdot\text{CH}_2\text{Cl}_2$  and  $7^{\text{Br}}$ .

X = Cl or Br	$7^{\text{Cl}}\cdot\text{CH}_2\text{Cl}_2$	$7^{\text{Br}}$
Cu(1)–N(1)	2.041(3)	2.044(3)
Cu(1)–N(2)	2.004(3)	1.973(3)
Cu(1)–X(1)	2.2236(10)	2.3226(7)
Cu(1)–X(2)	2.2680(10)	2.3740(8)
C(1)–N(1)	1.284(4)	1.280(5)
C(1)–C(2)	1.485(5)	1.484(6)
N(1)–Cu(1)–X(2)	169.39(9)	135.65(10)
N(2)–Cu(1)–X(1)	171.40(9)	157.36(11)
N(1)–Cu(1)–N(2)	79.80(12)	80.27(14)
X(1)–Cu(1)–X(2)	92.54(4)	100.29(3)
N(1)–Cu(1)–X(1)	93.47(9)	99.32(10)
N(2)–Cu(1)–X(2)	93.34(9)	95.34(10)
Cu(1)–N(1)–C(1)	115.6(2)	114.0(3)
N(1)–C(1)–C(2)	115.5(3)	116.2(4)
C(1)–C(2)–N(2)	114.3(3)	113.3(4)
C(2)–N(2)–Cu(1)	114.8(2)	115.5(3)

Within the structure of  $7^{\text{Cl}}\cdot\text{CH}_2\text{Cl}_2$ , an inter-molecular contact is present between the copper centre of one molecule and the chloride ligand of a second molecule of  $7^{\text{Cl}}$  [Cu(1)⋯Cl(2)#1 3.02 Å; symmetry operation #1: 1-x, -y, 1-z]. For a comparison, the sum of the covalent and van der Waals radii of Cu and Cl are 2.31 and 3.15 Å, respectively.<sup>[40]</sup> Therefore, this inter-molecular contact is in the limiting region between bonding and non-bonding. The Cu(1)⋯Cl(3) contact [3.686 Å] is well above the van der Waals interaction. Conversely, short inter-molecular contacts are not present within the solid-state structure of  $7^{\text{Br}}$ . Thus, the different geometry of Cu in  $7^{\text{Cl}}\cdot\text{CH}_2\text{Cl}_2$  and  $7^{\text{Br}}$  may be ascribed to the different nature of the halide ligands (Cl vs Br) or to packing effects.

Examples of Cu(ImPy) $X_2$  complexes have been reported in the literature, and the bonding parameters are quite similar to those of  $7^{\text{Cl}}\cdot\text{CH}_2\text{Cl}_2$  and  $7^{\text{Br}}$ . Cu(ImPy) $X_2$  complexes may exist as monomers or dimers depending on the steric requirements of the organic ligand employed.<sup>[41,42]</sup> In the case of mononuclear compounds, they usually display distorted tetrahedral geometry, regardless of the halide present. A distorted square pyramidal coordination at copper atom has been observed in dichlorido{2-[(4-iodophenyl)iminomethyl]pyridine- $\kappa^2\text{N},\text{N}'$ }copper(II).<sup>[41d]</sup> Thus,  $7^{\text{Cl}}\cdot\text{CH}_2\text{Cl}_2$  represents the first example of a nearly perfectly square planar Cu(pyridylimine) $X_2$  complex.



**2.2. Polymerization of 1,3-dienes.** The results obtained in the polymerization of 1,3-butadiene with the catalytic systems obtained by combining the above copper(II) complexes with MAO are shown in Table 2 and can be summarized as follows.

Copper dibromide complexes give no active catalysts, and this could be due to the fact that the Cu-Br bond is weaker than the Cu-Cl one, and therefore the reduction of the copper oxidation state of from +2 to +1 in case of brominated compounds, with formation of a species not able to give rise to an active site, is more likely. Catalysts characterized by a moderate catalytic activity were instead obtained by combining copper dichloride complexes (*i.e.*, **1<sup>Cl</sup>**–**9<sup>Cl</sup>**) with MAO, exhibiting a predominantly 1,2-type selectivity.

Imino-pyridyl copper dichloride complexes in which no substituents (*i.e.*, complexes **1<sup>Cl</sup>** and **2<sup>Cl</sup>**) or only one low hindered substituent (methyl in **3<sup>Cl</sup>** or *iso*-propyl group in **4<sup>Cl</sup>**) are present on the phenyl ring, in combination with MAO, gave predominantly syndiotactic 1,2 poly(1,3-butadiene)s, with a 1,2 content in the range 60 ÷ 70%, and a syndiotactic index ( $[rr]\%$ ) up to 70% (Figure 3). The remaining units are exclusively *cis*-1,4, being *trans*-1,4 units not detectable. The same is true for complexes with a cycloalkyl (**8<sup>Cl</sup>**) or benzyl (**9<sup>Cl</sup>**) type substituent on the imine-nitrogen. The FT-IR spectra, the <sup>1</sup>H and <sup>13</sup>C NMR spectra, the RX spectra of the polybutadienes reported in Table 1 are given as Supplementary Information. The increase in the bulkiness of the substituents on the phenyl ring or in their number had a remarkable effect on the catalytic activity; imino-pyridyl copper dichloride complexes in which only one hindered substituent (*tert*-butyl group in **5<sup>Cl</sup>**) or two *iso*-propyl groups in *ortho*-position (**6<sup>Cl</sup>** and **7<sup>Cl</sup>**) are present on the phenyl ring, in combination with MAO, were found to be inactive in the polymerization of 1,3-butadiene giving no polymer.

The catalyst activity was found to increase with increasing the Al/Cu molar ratio (entry 3 vs 4 and entry 5 vs 6, Table 2) and this could be due, as we have tried to explain below in the discussion paragraph, to the formation of a larger number of active centers at higher Al/Cu molar ratio. Some of the polymers obtained were practically insoluble in the most common organic solvents, making impossible to determine the molecular weight via SEC, even at high temperature. Only a few polymers dissolved in *o*-DCB and we were able to determine the polymer molecular weight, which resulted to be very high (around  $2 \times 10^6$  g mol<sup>-1</sup>), with a rather narrow molecular weight distribution ( $1.3 < M_w/M_n < 2.5$ ), suggesting a single site nature of the active sites.

Figure 3. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the polybutadiene of Table 2, run 8 (exp\_435)

Table 2. Polymerization of 1,3-butadiene with Copper Based Catalysts<sup>a</sup>.

entry	Cu	Al/Cu (molar ratio)	time (h)	yield (g)	conv (%)	<i>cis</i> -1,4 <sup>b</sup> (%)	1,2 <sup>b</sup> (%)	[ <i>rr</i> ] <sup>c</sup> (%)	<i>M<sub>w</sub></i> <sup>d</sup> (g/mol)	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>d</sup>	<i>T<sub>m</sub></i> <sup>e</sup> (°C)
1	CuCl <sub>2</sub>	1000	24	—	—						
2	1 <sup>d</sup>	1000	1	0.44	32	38.4	61.6	55.1			
3	1 <sup>d</sup>	1000	3	0.88	64.9	38.8	61.2	54.5			
4	1 <sup>d</sup>	100	4	0.32	23	38.5	61.5	56.2			
5	2 <sup>d</sup>	1000	3	0.65	47.8	29.1	70.9	69.7	2100000	2.3	105
6	2 <sup>d</sup>	100	3	0.16	11	32.7	67.3	68.9	2300000	2.5	101
7	3 <sup>d</sup>	1000	2	0.25	18	32.5	67.5	70.7	2000000	2.4	108
8	4 <sup>d</sup>	1000	2	0.41	29	32.2	67.8	73.5	1800000	2.0	121
9	5 <sup>d</sup>	1000	24	—							
10	6 <sup>d</sup>	1000	24	—							
11	7 <sup>d</sup>	1000	24	—							
12	8 <sup>d</sup>	1000	1	0.41	29	31.3	68.7	63.4	1700000	1.5	
13	9 <sup>d</sup>	1000	1	0.28	50	38.1	60.9	53.2	1900000	1.3	

<sup>a</sup> polymerization conditions: butadiene, 2 mL; toluene, total volume 16 ml; MAO; Cu, 1×10<sup>-5</sup> mol; <sup>b</sup> determined by <sup>1</sup>H NMR; <sup>c</sup> percentage of syndiotactic triads determined by <sup>13</sup>C NMR; <sup>d</sup> molecular weight (*M<sub>w</sub>*) and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) determined by SEC; <sup>e</sup> melting point, determined by DSC.

Most of the above copper dichloride complexes were also used, in combination with MAO, for the polymerization isoprene, and the results obtained are shown in Table 3.

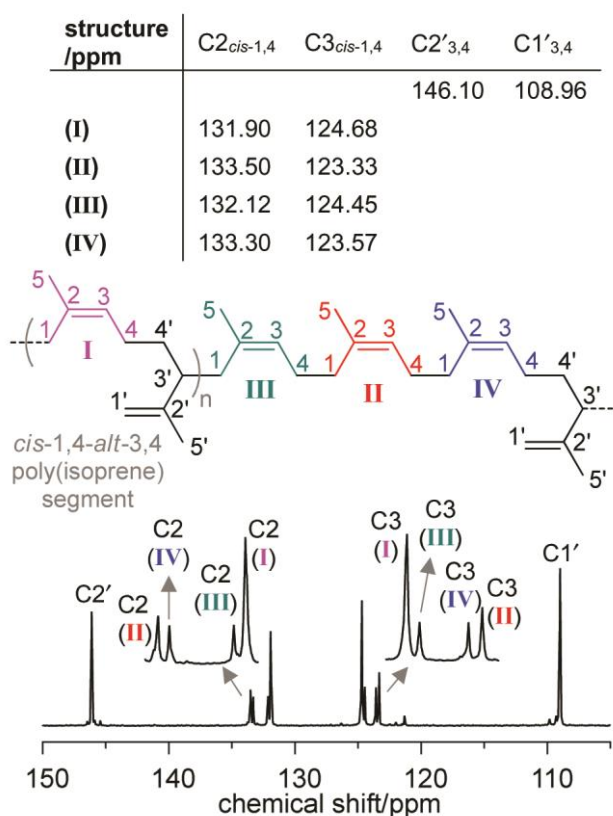
Table 3. Polymerization of Isoprene with Copper Based Catalysts<sup>a</sup>.

entry	Cu	time (h)	yield (g)	conv (%)	<i>cis</i> -1,4 <sup>b</sup> (%)	3,4 <sup>b</sup> (%)	<i>M<sub>w</sub></i> <sup>c</sup> (g/mol)	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>c</sup>	<i>T<sub>g</sub></i> <sup>d</sup> (°C)
14	CuCl <sub>2</sub>	24	—						
15	1 <sup>d</sup>	2	0.44	32.4	42.3	57.7	421000	2.0	-17
16	2 <sup>d</sup>	1.5	0.80	58.8	49.9	50.1	638000	1.8	-20
17	3 <sup>d</sup>	3	0.44	32.4	60.1	39.9	195000	2.0	-31.5
18	4 <sup>d</sup>	2	0.71	52.2	59.1	40.9	310000	1.6	-29.1
19	4 <sup>d</sup>	3	1.36	100	59.8	40.2	575000	1.7	-30.1
20	5 <sup>d</sup>	24	—						
21	6 <sup>d</sup>	24	—						
22	7 <sup>d</sup>	24	—						

<b>23</b>	<b>8<sup>Cl</sup></b>	1	0.66	24.3	45.0	55.0	350000	2.1	-22
<b>24</b>	<b>9<sup>Cl</sup></b>	1	0.22	16.2	40.2	59.8	404000	2.2	-19

<sup>a</sup> polymerization conditions: monomer, 2 mL; toluene, total volume 16 ml; MAO/Cu = 1000; Cu, Cu, 1×10<sup>-5</sup> mol; 22°C. <sup>b</sup> determined by <sup>1</sup>H NMR. <sup>c</sup> molecular weight (*M<sub>w</sub>*) and molecular weight distribution (*M<sub>w</sub>*/*M<sub>n</sub>*) determined by SEC. <sup>d</sup> transition glass temperature, determined by DSC.

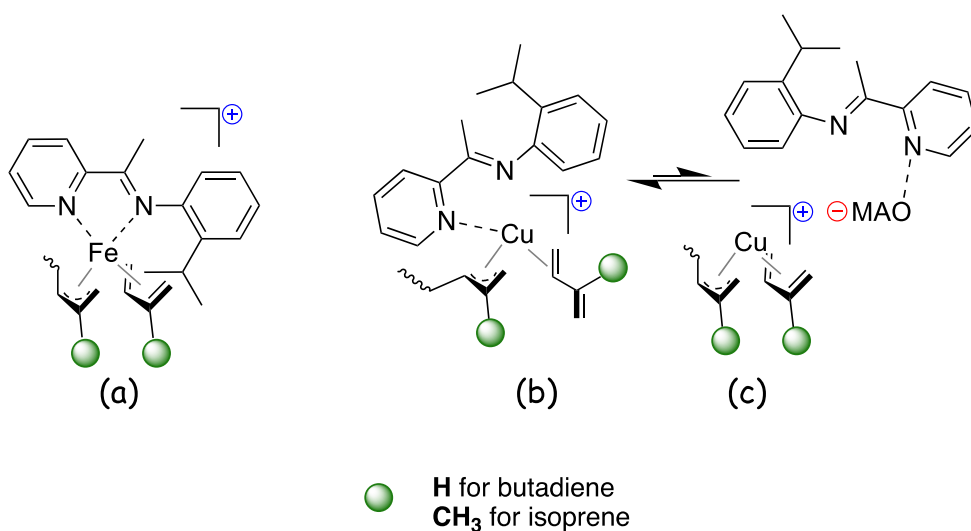
Pyridyl-imine copper complexes- based catalysts gave from isoprene polymers with a mixed 1,4/3,4 structure. The 1,4 units were essentially of *cis*-type, while the 3,4 content vary in the range 40÷60% depending on the nature of the ligand (see <sup>1</sup>H and <sup>13</sup>C NMR spectra, and FT-IR spectra in the Supporting Information). In particular, the polymers obtained with the systems **3<sup>Cl</sup>**/MAO and **4<sup>Cl</sup>**/MAO (runs 17-19 in Table 3) exhibited an alternating *cis*-1,4/3,4 structure in which however short *cis*-1,4 sequences (three units) can be detected along the polymer chain, as clearly indicated by the <sup>13</sup>C NMR spectrum shown Figure 4. It is worth to note that such a microstructure is identical to that exhibited by the polyisoprene obtained with the analogues iron-based catalyst, so that for the polymer NMR characterization you can refer to the corresponding paper.<sup>[22]</sup>



**Figure 4.** <sup>13</sup>C NMR spectrum (olefin region) of the polyisoprene obtained with **4<sup>Cl</sup>**/MAO (Table 3, entry 18\_exp 434\_ZG837)

The polyisoprenes obtained have a rather high molecular weight, in the range 200000÷800000 g×mol<sup>-1</sup>, depending on the nature of the ligand on the copper atom, and a narrow polymer molecular weight distribution (in the range 1,5÷2). The glass transition temperature T<sub>g</sub> varies from -24 to -30°C, decreasing with increasing the *cis* content.

**2.3. Some mechanistic considerations.** The results obtained in the polymerization of butadiene and isoprene with the catalytic systems based on the copper complex **4<sup>Cl</sup>** are quite similar to those obtained with the analogues iron-based complex. [22,43] At first glance, one could therefore think that the structure of the catalytic center hypothesized in case of iron catalysts (Figure 4a) [18,22,23] is also valid for copper catalysts: the monomer *cis*- $\eta^4$  coordinated, the growing chain bonded to the copper atom through an anti  $\eta^3$ -allyl group, and the bidentate ligand on the copper atom.



**Figure 4.** Possible active site structures

However, from a deeper examination of the structure, it emerges that such a structure is not possible in case of copper, as this disposition would have 3 more electrons than allowed on the basis of the rare gas rule (*18 electrons*). This means that we have to think of a different structure of the catalytic center. We can think of a *trans- $\eta^2$*  coordination of the conjugated diene, of a growing chain bonded to the copper atom through a *syn- $\eta^3$ -allyl* group (a *trans- $\eta^2$*  coordination of the monomer leads to a *syn-allyl* group, while a *cis- $\eta^4$*  coordination to an *anti-allyl*-group) and of a coordination of the bidentate ligand with only one donor atom (Figure 4b), as also hypothesized in the case of catalytic systems based on cobalt complexes with bi- and tridentate ligands.<sup>[2,11]</sup> However, this is not yet sufficient to explain the results obtained: we have in fact observed that the not 1,2 units in the case of polybutadiene or 3,4 in the case of polyisoprene, have a *cis-1,4* structure, and such units, as it is well known,<sup>[1,12]</sup> originate only from *anti* allyl units, which, in turn, are formed through a *cis- $\eta^4$*  coordination of the conjugated diene.

We can therefore hypothesize that the bidentate ligand may occasionally completely migrate onto methylaluminoxane, thanks to the affinity between the nitrogen donor atoms and aluminum, thus allowing the *cis- $\eta^4$*  coordination of the diene, and the formation of an *anti-allyl* unit leading to a *cis-1,4* unit (Figure 4c). Such a migration should be favored at high MAO/Cu ratio, and in fact, as a support of this hypothesis, we have observed that the copper-based systems activity increases with increasing the MAO/Cu molar ratio. A sort of

equilibrium can be hypothesized between the form (b), with the monomer *trans*- $\eta^2$  coordinated, and the ligand coordinated with only one nitrogen atom, and the form (c), with the monomer *cis*- $\eta^4$  coordinated and the ligand onto MAO, with formation of 1,2 (3,4) units rather than *cis*-1,4 depending on whether the equilibrium is more shifted towards form (b) or form (c), respectively. The occurrence of such complete migration and the frequency with which it occurs may be a function of the type of ligand coordinated to the copper atom but also of the type of monomer, and may determine the length of the *cis* units sequences.

The above reported obviously represents only a working hypothesis, with the aim of stimulating the discussion and the formulation of further mechanistic hypotheses suitable for interpreting the experimental results obtained. Further work is therefore necessary to reach more satisfactory and reliable mechanistic interpretations, and for this purpose also modeling and computational studies could be of great help. Nevertheless, the presence of a sort of equilibrium through which the ligand may transfer from the metal atom to methylaluminoxane, or migrate from one metal atom to another one appears quite plausible, since it has already been postulated in the case of polymerization of butadiene with some cobalt-based catalytic systems.<sup>[44]</sup>

### 3. Conclusions

A series of novel copper(II) complexes was synthesized and characterized and, for the first time in the field of stereospecific polymerization, it was reported on copper-based catalysts able to selectively polymerize 1,3-butadiene and isoprene, exhibiting at the same time a fair activity. In particular, polymers with a rather unusual structure have been obtained from isoprene, exhibiting some peculiarities (molecular weight and glass transition temperatures) such as to make them of potential interest for applications in the elastomeric field.

Given the large availability of copper, as well as its low environmental impact, and the ability of these new copper-based catalysts to give crystalline syndiotactic 1,2 polybutadiene and amorphous polyisoprene, the results obtained could be interesting and noteworthy both from a scientific and application point of view.

## 4. Experimental Section/Methods

**4.1. General procedures and materials.** Anhydrous copper dichloride and dibromide (Aldrich, 99,9% pure), and copper chloride dihydrate (Aldrich, reagent grade) were used as received. Aniline (Aldrich, 99%) and 2,6-diisopropylaniline (Aldrich, 97%) were distilled at reduced pressure and stored in an inert atmosphere. 2-pyridinecarboxaldehyde (Aldrich, 99%), 2-acetylpyridine (Aldrich, 99%), methanol (Aldrich, 99,8%) and p-toluenesulfonic acid (Aldrich  $\geq 98.5\%$ ) were used as received. Pyridylimines (**L1–L9**, Chart 1) were prepared by condensation of equimolar amounts of amine and 2-acetyl-pyridine or 2-pyridine-carboxyldehyde according to literature procedures.<sup>[32]</sup> Ethyl Alcohol (Aldrich, 96% pure) was degassed under vacuum, then by bubbling dry dinitrogen and kept over molecular sieves; pentane (Aldrich, 99% pure) was refluxed over Na/K alloy for ca. 8 h, then distilled and stored over molecular sieves under dry dinitrogen; toluene (Aldrich, 99,8% pure) was refluxed over Na for ca 8 h, then distilled and stored over molecular sieves under dry dinitrogen; dichloromethane (Aldrich  $\geq 98.8\%$ ) was refluxed over calcium hydride for ca. 8h, then distilled and stored over molecular sieve under dry dinitrogen; diethylether (Aldrich  $\geq 98.7$ ) was refluxed over Na/K alloy for ca. 8 h, then distilled and stored over molecular sieves under dry dinitrogen. 1,3-Butadiene (Aldrich  $\geq 99\%$ ) was evaporated from the container prior to each run, dried by passing through a column packed with molecular sieves and condensed into the reactor which had been precooled to  $-20\text{ }^{\circ}\text{C}$ . Isoprene (Aldrich,  $\geq 99.5\%$ ) was refluxed over calcium hydride for 3 h, then distilled trap-to-trap and stored under dry nitrogen. MAO (Aldrich, 10 wt% solution in toluene), and deuterated solvent for NMR measurements ( $\text{C}_2\text{D}_2\text{Cl}_4$ ) (Aldrich,  $>99.5\%$  atom D) were used as received.

**4.2. Synthesis of pyridyl-imine copper complexes.** Compounds **1<sup>d</sup>**, **5<sup>d</sup>** and **7<sup>d</sup>** were prepared according to literature procedures.<sup>[32]</sup> In the following only the preparation of **6<sup>d</sup>** is described in detail, the other complexes being performed under similar experimental conditions.

**Cu(C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>)Cl<sub>2</sub> (6<sup>d</sup>).** To a solution of copper chloride dihydrate (0.300 g, 1.76 mmol) in ethanol (15 ml) was added an ethanol solution (5 ml) of L6 (0.468 g, 1.76 mmol) and the resulting solution was stirred for 30 min. During the stirring a huge amount of solid precipitated from the solution. The mixture was stirred at room temperature for additional 5 h. The green colored precipitate was recovered by filtration, washed with ethanol

and diethyl ether, and dried in vacuo at room temperature affording 0.670 g (95% yield) of  $\text{Cu}(\text{C}_{18}\text{H}_{22}\text{N}_2)\text{Cl}_2$  as a green microcrystalline solid. Elemental analysis (%): Calc. for  $\text{C}_{18}\text{H}_{22}\text{Cl}_2\text{CuN}_2$ : C, 53.93; H, 5.53; Cl, 17.69; N, 6.99; Cu, 15.85. Found: C, 53.23; H, 5.33; Cl, 17.23; N, 6.65; Cu, 15.32. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3079w, 2968mw, 2869w, 1628m, 1596s, 1450m, 1304m, 1028ms, 913w, 812ms, 782vs, 767vs, 651m.

**$\text{Cu}(\text{C}_{12}\text{H}_{10}\text{N}_2)\text{Cl}_2$  ( $1^{\text{Cl}}$ )**. Green, 81% yield. Elemental analysis (%): Calc. for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{CuN}_2$ : C, 45.51; H, 3.18; N, 8.85; Cl, 22.39; Cu, 20.07. Found: C, 45.65; H, 3.21; N, 8.60; Cl, 21.92; Cu, 19.81. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3049w, 2936w, 1596m, 1490s, 1361m, 1310m, 1230m, 1102m, 1020ms, 780vs, 694vs.

**$\text{Cu}(\text{C}_{13}\text{H}_{12}\text{N}_2)\text{Cl}_2$  ( $2^{\text{Cl}}$ )**. Green, 78% yield. Elemental analysis (%): Calc. for  $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{CuN}_2$ : C, 47.21; H, 3.66; N, 8.47; Cl, 21.44; Cu, 19.21. Found: C, 47.65; H, 3.41; N, 8.20; Cl, 21.90; Cu, 19.70. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3082w, 3021w, 2936w, 1591m, 1486s, 1361m, 1310m, 1240m, 1094ms, 1016ms, 831vs, 779vs.

**$\text{Cu}(\text{C}_{14}\text{H}_{14}\text{N}_2)\text{Cl}_2$  ( $3^{\text{Cl}}$ )**. Green, 73% yield. Elemental analysis (%): Calc. for  $\text{C}_{14}\text{H}_{14}\text{Cl}_2\text{CuN}_2$ : C, 48.78; H, 4.09; N, 8.13; Cl, 20.57; Cu, 18.43. Found: C, 48.63; H, 3.95; N, 8.21; Cl, 20.90; Cu, 18.69. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3104w, 3032w, 1617w, 1592s, 1486mw, 1441m, 1371m, 1330m, 1261m, 1020m, 807m, 778vs, 754vs, 715m.

**$\text{Cu}(\text{C}_{16}\text{H}_{18}\text{N}_2)\text{Cl}_2$  ( $4^{\text{Cl}}$ )**. Green, 86 % yield. Elemental analysis (%): Calc. for  $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{CuN}_2$ : C, 51.55; H, 4.87; N, 8.47; Cl, 19.02; Cu, 17.05. Found: C, 51.65; H, 4.51; N, 8.21; Cl, 19.60; Cu, 17.71. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3027w, 2974w, 1623mw, 1594s, 1486m, 1445m, 1372ms, 1262ms, 1027m, 853m, 805s, 791vs, 773vs.

**$\text{Cu}(\text{C}_{17}\text{H}_{20}\text{N}_2)\text{Cl}_2$  ( $5^{\text{Cl}}$ )**. Green, 80% yield. Elemental analysis (%): Calc. for  $\text{C}_{17}\text{H}_{20}\text{Cl}_2\text{CuN}_2$ : C, 52.79; H, 5.21; N, 7.24; Cl, 18.33; Cu, 16.43. Found: C, 52.64; H, 5.45; N, 7.50; Cl, 18.95; Cu, 16.78. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3058w, 2954w, 1624mw, 1593m, 1481m, 1453m, 1377m, 1324m, 1260m, 1052m, 831m, 790vs, 773vs.

**$\text{Cu}(\text{C}_{19}\text{H}_{24}\text{N}_2)\text{Cl}_2$  ( $7^{\text{Cl}}$ )**. Green, 83% yield. Elemental analysis (%): Calc. for  $\text{C}_{19}\text{H}_{24}\text{Cl}_2\text{CuN}_2$ : C, 55.01; H, 5.83; N, 6.75; Cl, 17.09; Cu, 15.32. Found: C, 55.35; H, 5.65; N, 6.24; Cl, 16.89; Cu, 17.59. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3024w, 2968m, 2867w, 1594mm, 1440mw, 1373m, 1325m, 1263m, 1019m, 792s, 772vs.

**$\text{Cu}(\text{C}_{12}\text{H}_{16}\text{N}_2)\text{Cl}_2$  ( $8^{\text{Cl}}$ )**. Green, 62 % yield. Elemental analysis (%): Calc. for  $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{CuN}_2$ : C, 44.66; H, 5.00; N, 8.68; Cl, 21.97; Cu, 19.69. Found: C, 43.24; H, 5.39; N, 8.45; Cl, 21.99; Cu, 19.12. Selected IR data (solid state,  $\text{cm}^{-1}$ ): 3023w, 2923ms, 2850m, 1647w, 1599m, 1450m, 1318m, 1232m, 1020s, 892m, 787vs.



**Cu(C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>)Cl<sub>2</sub> (9<sup>Cl</sup>).** Pale green, 80 % yield. Elemental analysis (%): Calc. for C<sub>13</sub>H<sub>12</sub>Cl<sub>2</sub>CuN<sub>2</sub>: C, 47.21; H, 3.66; N, 8.47; Cl, 21.44; Cu, 19.21. Found: C, 47.65; H, 3.41; N, 8.20; Cl, 21.90; Cu, 19.70. Selected IR data (solid state, cm<sup>-1</sup>): 3013w, 1602m, 1428w, 1321w, 1157w, 1007w, 784s, 752s, 697vs.

**Cu(C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>)Br<sub>2</sub> (2<sup>Br</sup>).** Brown, 75 % yield. Elemental analysis (%): Calc. for C<sub>13</sub>H<sub>12</sub>Br<sub>2</sub>CuN<sub>2</sub>: C, 37.21; H, 2.88; N, 6.68; Br, 38.08; Cu, 15.14. Found: C, 37.11; H, 2.60; N, 6.41; Br, 37.89; Cu, 15.55. Selected IR data (solid state, cm<sup>-1</sup>): 3026w, 2906ms, 1633m, 1597s, 1485m, 1435mw, 1374m, 1028m, 787s, 741vs, 698vs.

**Cu(C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>)Br<sub>2</sub> (6<sup>Br</sup>).** Red, 58 % yield. Elemental analysis (%): Calc. for C<sub>18</sub>H<sub>22</sub>Br<sub>2</sub>CuN<sub>2</sub>: C, 44.14; H, 4.53; N, 5.72; Br, 32.63; Cu, 12.97. Found: C, 44.46; H, 4.86; N, 5.49; Br, 32.85; Cu, 12.60. Selected IR data (solid state, cm<sup>-1</sup>): 3073w, 2964w, 2867w, 1595ms, 1460m, 1303m, 1207m, 812s, 778vs, 771vs, 651s.

**Cu(C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>)Br<sub>2</sub> (7<sup>Br</sup>).** Brown, 74 % yield. Elemental analysis (%): Calc. for C<sub>19</sub>H<sub>24</sub>Br<sub>2</sub>CuN<sub>2</sub>: C, 45.29; H, 4.80; N, 5.56; Br, 31.72; Cu, 12.61. Found: C, 45.01; H, 4.61; N, 5.49; Br, 31.52; Cu, 12.23. Selected IR data (solid state, cm<sup>-1</sup>): 3078w, 2962ms, 2868m, 1621w, 1595m, 1446m, 1372m, 1325m, 1266m, 1026m, 801m, 776vs, 651m.

**Cu(C<sub>12</sub>H<sub>16</sub>N<sub>2</sub>)Br<sub>2</sub> (8<sup>Br</sup>).** Brown, 60 % yield. Elemental analysis (%): Calc. for C<sub>12</sub>H<sub>16</sub>Br<sub>2</sub>CuN<sub>2</sub>: C, 35.01; H, 3.92; N, 6.80; Br, 38.82; Cu, 15.44. Found: C, 34.56; H, 3.71; N, 6.29; Br, 38.55; Cu, 15.20. Selected IR data (solid state, cm<sup>-1</sup>): 3027w, 2933ms, 2840m, 1640w, 1578m, 1440m, 1307m, 1212m, 1025s, 899m, 781vs.

**Cu(C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>)Br<sub>2</sub> (9<sup>Br</sup>).** Orange-brown, 80 % yield. Elemental analysis (%): Calc. for C<sub>13</sub>H<sub>12</sub>Br<sub>2</sub>CuN<sub>2</sub>: C, 37.21; H, 2.88; N, 6.67; Br, 38.06; Cu, 15.14. Found: C, 37.62; H, 2.61; N, 6.40; Br, 38.50; Cu, 15.71. Selected IR data (solid state, cm<sup>-1</sup>): 3063w, 3026w, 2984w, 2920vw, 1601s, 1452ms, 1381m, 1303w, 1330mw, 1227mw, 1020mw, 778vs, 760s, 744s, 711s, 700s, 653ms.

**4.3. X-ray Structure Determination.** Crystal data and collection details for 7<sup>Cl</sup>-CH<sub>2</sub>Cl<sub>2</sub> and 7<sup>Br</sup> are reported in Table X. Data were recorded on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo-K $\alpha$  radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS). [ref: G. M. Sheldrick, SADABS-2008/1 - Bruker AXS Area Detector Scaling and Absorption Correction, Bruker AXS: Madison, Wisconsin, USA, 2008] The structures were solved by direct methods and refined by full-matrix least-squares based on all data using  $F^2$ . [ref: G. M. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr. 2015, 71c, 3-8] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

**Table 2.** Crystal data and measurement details for 7<sup>Cl</sup>·CH<sub>2</sub>Cl<sub>2</sub> and 7<sup>Br</sup>.

	7 <sup>Cl</sup> ·CH <sub>2</sub> Cl <sub>2</sub>	7 <sup>Br</sup>
Formula	C <sub>20</sub> H <sub>26</sub> Cl <sub>4</sub> CuN <sub>2</sub>	C <sub>19</sub> H <sub>24</sub> Br <sub>2</sub> CuN <sub>2</sub>
FW	499.77	503.76
T, K	100(2)	291(2)
$\lambda$ , Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
$a$ , Å	8.9405(12)	14.4418(8)
$b$ , Å	10.2786(14)	9.9967(6)
$c$ , Å	13.3266(17)	14.5486(9)
$\alpha$ , °	68.555(4)	90
$\beta$ , °	89.970(4)	109.147(2)
$\gamma$ , °	80.757(4)	90
Cell Volume, Å <sup>3</sup>	1122.8(3)	1984.2(2)
Z	2	4
$D_c$ , g·cm <sup>-3</sup>	1.478	1.686
$\mu$ , mm <sup>-1</sup>	1.457	5.131
F(000)	514	1004
Crystal size, mm	0.18×0.13×0.11	0.16×0.13×0.11
$\theta$ limits, °	1.645-27.999	1.724-25.997
Reflections collected	16192	24461
Independent reflections	5356 [ $R_{int} =$ 0.0623]	2909 [ $R_{int} =$ 0.0446]
Data/restraints/parameters	5356 / 0 / 249	3909 / 0 / 222
Goodness of fit on $F^2$	1.086	1.136
$R_1$ ( $I > 2\sigma(I)$ )	0.0658	0.0471
$wR_2$ (all data)	0.1233	0.1025
Largest diff. peak and hole, e Å <sup>-3</sup>	1.570 / -1.115	0.963 / -1.007

**4.4. Polymerization of 1,3-dienes.** Polymerizations were carried out in a 25 mL round-bottom Schlenk flask. A standard procedure is reported. Prior to starting polymerization, the reactor was heated to 110°C under vacuum for 1 h and backfilled with nitrogen. 1,3-Butadiene was condensed into the Schlenk flask kept at -20°C, then toluene was added, and the solution was brought to the desired polymerization temperature. MAO and

a toluene solution (2 mg/mL) of the copper complex were then added in that order. Polymerization was stopped with methanol containing a small amount of hydrochloric acid. The polymer obtained was then coagulated by adding 40 ml of a methanol solution containing 4% of Irganox® 1076 antioxidant and HCl, repeatedly washed with fresh methanol and finally dried in vacuum at room temperature to constant weight. The polymerizations with isoprene were carried out in the same way.

**4.5. Polymer Characterization.** Attenuated total reflectance (ATR)-Fourier transform infrared spectroscopy (FTIR) spectra were recorded at room temperature in the 4000–600  $\text{cm}^{-1}$  range with a resolution of 4  $\text{cm}^{-1}$  using a Perkin Elmer Spectrum Two spectrometer. NMR spectra were recorded on a Bruker NMR advance 400 Spectrometer operating at 400 MHz ( $^1\text{H}$ ) and 100.58 MHz ( $^{13}\text{C}$ ) working in the PFT mode at 103°C. NMR samples were prepared dissolving from 60 to 80 mg of polymer in about 3 mL of  $\text{C}_2\text{D}_2\text{Cl}_4$  in 10mm probes and referred to hexamethyldisilane (HMDS), as internal standard. The relaxation delay was 16 s. The molecular weight average ( $M_w$ ) and the molecular weight distribution ( $M_w/M_n$ ) were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system equipped with a refractometer detector. The experimental conditions consisted of three PL Gel Olexis columns, *ortho*-dichlorobenzene (DCB) as the mobile phase, 0.8 mL/min flow rate, and 145 °C temperature. The calibration of the SEC system was constructed using eighteen narrow  $M_w/M_n$  PS standards with molar weights ranging from 162 to  $5.6 \times 10^6$  g/mol. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of DCB with 0.05% of BHT as antioxidant. The microstructure of the resultant polymers [i.e., *cis*-1,4 unit content (%) and 1,2 (3,4 in the case of isoprene) unit content (%); syndiotactic index (rrrr%) of the 1,2 poly(1,3-butadiene)s and of 3,4 poly(isoprene)s] was determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, according to the literature. [27,45–49]

[CCDC 2115435, 2,115,436, and 2,115,437 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +441,223 336,033].

## Supporting Information.

The supporting information is available free of charge via the Internet at <http://pubs.acs.org/>

FT-IR Spectra of the copper complexes; FT-IR Spectra of the polymers;  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the polymers.

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