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New *N*,*O*-containing ligands for the biomimetic copper-catalyzed polymerization of 2,6-dimethylphenol

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Abstract

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE), which is widely used in high-performance engineering plastics, is obtained by the copper-catalyzed oxidative coupling of 2,6-dimethylphenol. The oxidative polymerizations have been carried out in acetonitrile with structurally related [copper-(*N*,*O*-containing ligand)] complexes as the catalyst precursor compounds, which appeared to be of great interest for a better understanding of the factors influencing the catalytic activities. Steric effects (influence of a methyl group close to the metal center; ligands **4**–**7**) or electronic effects (imino versus amino group; ligands **4**, **5**, **8** and **6**, **7**, **9**, respectively) on the polymerization rates have been demonstrated. The use of mono- or dinucleating ligands has strengthened the proposed mechanism of the reaction involving dinuclear active species.

Keywords: Copper catalysis; *N*,*O*-ligands; Phenol oxidative coupling; Dinucleating ligands

1. Introduction

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is a high-performance thermoplastic, a polymeric material that can be heated and molded more than once [1,2]. Due to its inherent chemical composition, PPE exhibits unusually low moisture absorption. Therefore, good electrical insulating properties are realized over a wide range of humidities and temperatures. PPE is also very resistant, chemically, to water, most salt solutions, acids and bases and has very good mechanical properties [3,4]. This polymer, therefore, finds many industrial applications, such as computer and television housings, keyboard frames, or interface boxes.

Since 1959 [5], the copper-catalyzed polymerization of 2,6-dimethylphenol (DMP, **1**) has been used to produce the desired PPE (**2**), but the unwanted 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadienone (DPQ, **3**) is always present as a side product, see Scheme 1.

This polymerization has been extensively studied [6–8], but, surprisingly, the mechanism is not yet clarified in detail [9–17].

This paper reports the use of a series of closely related ligands for the copper-catalyzed oxidative coupling of DMP. These slight structural modifications are meant to determine which parameters can affect the catalyst activity.

2. Experimental

2.1. General

Solvents and chemicals were commercially available as either reagent grade (*n*-hexane, dichloromethane, diethyl ether, 1-amino-propan-2-ol (99%), 2-amino-propan-1-ol (98%), 2-pyridine carboxaldehyde, 1,3-dibromopropane, *N*,*N*-diisopropylethylamine (+98%), 2,6-dimethylphenol, sodium methoxide (30% solution in methanol), anhydrous $MgSO_4$), or as analytical grade (methanol, acetonitrile, $NaBH_4$, $Cu(NO_3)_2{\cdot}3H_2O$, Na_2CO_3), and were used as

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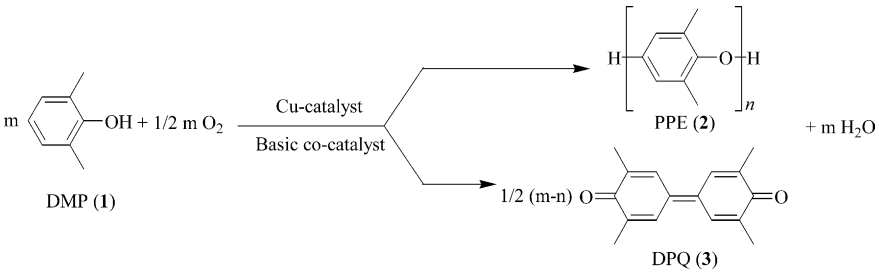
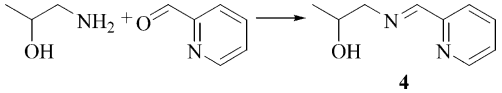


Scheme 1. Copper-catalysed oxidative coupling of DMP.

received unless stated otherwise. 2,6-Dimethylphenol (**1**) was purified by recrystallisation from *n*-hexane.

Infrared spectra were recorded on a Perkin-Elmer Paragon 1000 spectrophotometer and peaks are reported in cm^{-1}. ^1H NMR spectra were recorded on a Brucker DPX 300 (300 MHz) instrument. Chemical shifts are reported in δ (parts per million) relative to an internal standard of tetramethylsilane. *C*,*H*,*N*-analyses were performed on a Perkin-Elmer 2400 series. ESI mass analyses were carried out on a Voyager Elite from PerSeptive Biosystems.

2.2. Synthesis of 1-[(pyridin-2-ylmethylene)-amino]-propan-2-ol (*4*)

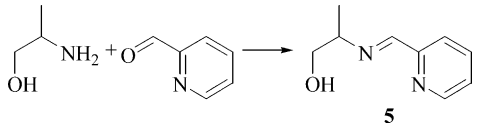


4

Twenty-five gram (33.3 mmol) of 1-amino-2-propanol were dissolved in 25 ml of methanol. A solution of 3.56 g (33.3 mmol) of 2-pyridine carboxaldehyde in 10 ml methanol was added. The resulting reaction mixture was refluxed overnight. The solvent was evaporated under reduced pressure and 5.49 g of compound **4** was obtained as brown oil with a good purity.

Yield: 98%; F.w. = 164.20 g mol^{-1}; IR (neat): 3292, 2969, 2886, 1648, 1588, 1568, 1045, 992, 773 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.25 (d, J = 6.3 Hz, 3H), 3.53 (m, 2H), 3.73 (dd, J = 2.2, 13.6 Hz, 1H), 4.10 (dd, J = 2.4, 7.7 Hz, 1H), 7.25 (m, 1H), 7.41 (dd, J = 7.5, 7.5 Hz, 0.4H), 7.68 (ddd, J = 9.3, 7.6, 1.6 Hz, 1H), 7.92 (d, J = 7.9 Hz, 0.6H), 8.38 (s, 1H), 8.59 (dd, J = 8.9, 5.6 Hz, 1H) ppm; mass (ESI): *m*/*z* ($C_9H_{12}N_2O$, 164.20): 165.4 (M + H^+).

2.3. Synthesis of 2-[(pyridine-2-ylmethylene)-amino]-propan-1-ol (*5*)

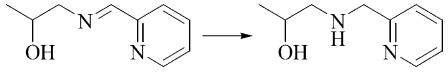


5

2-Amino-1-propanol (1.5 g (20.0 mmol)) was dissolved in 25 ml of methanol. A solution of 2.14 g (20.0 mmol) of 2-pyridine carboxaldehyde in 10 ml methanol was added. The resulting reaction mixture was refluxed overnight. The solvent was evaporated under reduced pressure and 3.43 g of compound **5** was obtained as brown oil with a good purity.

Yield: 98%; F.w. = 164.20 g mol^{-1}; IR (neat): 3270, 2969, 2867, 1647, 1588, 1568, 1046, 994, 774 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.21 (d, J = 6.4 Hz, 3H), 3.38 (dd, J = 4.4, 2.7 Hz, 1H), 3.55 (m, 2H), 3.69 (dd, J = 1.6, 4.8 Hz, 1H), 7.24 (dd, J = 8.2, 4.9 Hz, 1H), 7.40 (dd, J = 7.9, 7.9 Hz, 0.5H), 7.67 (dd, J = 13.1, 6.3 Hz, 1H), 7.89 (d, J = 7.9 Hz, 0.5H), 8.39 (s, 1H), 8.59 (d, J = 4.2 Hz, 1H) ppm; mass (ESI): *m*/*z* ($C_9H_{12}N_2O$, 164.20): 165.4 (M + H^+).

2.4. Synthesis of 1-[(pyridine-2-ylmethyl)-amino]-propan-2-ol (*6*)

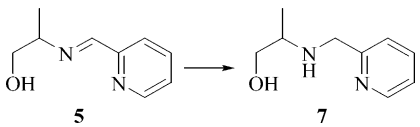


4 **6**

Three grams (18.3 mmol) of **4** were dissolved in 25 ml of methanol. 1.4 g (37.0 mmol) of $NaBH_4$ was added portion wise at room temperature. The reaction mixture was refluxed for 3 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. Distilled water (20 ml) were added and the product was extracted with CH_2Cl_2. Compound **6** (2.53 g) was obtained as a brown oil with a good purity.

Yield: 83%; F.w. = 166.22 g mol^{-1}; IR (neat): 3312, 2967, 2923, 1592, 1570, 995, 756 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.12 (d, J = 6.2 Hz, 3H), 2.47 (dd, J = 12.2, 9.4 Hz, 1H), 2.74 (dd, J = 12.2, 3 Hz, 1H), 2.86 (m, 2H), 3.78 (m, 1H), 3.91 (s, 2H), 7.15 (dd, J = 5.1, 6 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.63 (ddd, J = 7.6, 7.6, 1.6 Hz, 1H), 8.53 (d, J = 4.1 Hz, 1H) ppm; mass (ESI): *m*/*z* ($C_9H_{14}N_2O$, 166.22): 167.2 (M + H^+).

2.5. Synthesis of 2-[(pyridine-2-ylmethyl)-amino]-propan-1-ol (*7*)



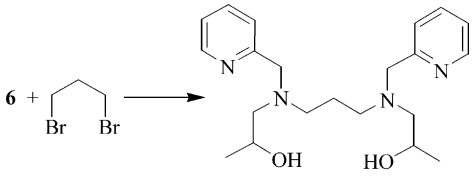
5 **7**

Two grams (12.2 mmol) of **5** were dissolved in 25 ml of methanol. $NaBH_4$ (0.95 g (25.0 mmol)) was added portion wise at room temperature. The reaction mixture was refluxed

for 3 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. Distilled water (20 ml) were added and the product was extracted with CH_2Cl_2. Compound **7** (1.68 g) was obtained as a brown solid with a good purity.

Yield: 82%; F.w. = 166.22 g mol^{-1}; IR (neat): 3301, 3200, 2964, 2814, 1590, 1568, 1055, 988, 756 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.09 (d, J = 6.5 Hz, 3H), 2.71 (m, 2H), 2.86 (m, 1H), 3.34 (dd, J = 6.8, 10.9 Hz, 1H), 3.60 (dd, J = 10.8, 3.8 Hz, 1H), 3.88 (d, J = 14.4 Hz, 1H), 4.01 (d, J = 14.4 Hz, 1H), 7.15 (dd, J = 5.0, 5.0 Hz, 1H), 7.27 (d, J = 6.4 Hz, 1H), 7.63 (ddd, J = 7.6, 7.6, 1.7 Hz, 1H), 8.53 (d, J = 4.2 Hz, 1H) ppm; mass (ESI): m/z ($C_9H_{14}N_2O$, 166.22): 167.2 ($M + H^+$).

2.6. 1-({3-[(2-Hydroxy-propyl)-pyridin-2-ylmethyl-amino]-propyl}-pyridin-2-ylmethyl-amino)-propan-2-ol (**10**)

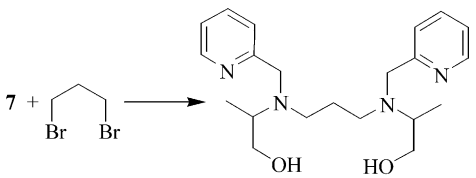


10

Five hundred milligrams (3.0 mmol) of **6** were dissolved in 10 ml of CH_2Cl_2. 1,3-Dibromopropane (300 mg (1.5 mmol)) and 500 mg (3.8 mmol) of *N*,*N*-diisopropylethylamine were added. The reaction mixture was refluxed for 72 h. It was then cooled down to room temperature and 20 ml of distilled water were added to extract the *N*,*N*-diisopropylethylamine hydbromide salt. The organic phase was dried over $MgSO_4$ and CH_2Cl_2 was evaporated under reduced pressure. Compound **10** (276 mg) was obtained as a brown oil with a good purity.

Yield: 49.5%; F.w. = 372.50 g mol^{-1}; IR (neat): 3360, 2966, 2930, 1593, 1570, 998, 754 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86 (t, J = 6.0 Hz, 6H), 1.07 (d, J = 6.1 Hz, 2H), 1.16 (d, J = 6.5 Hz, 2H), 1.23 (d, J = 8.3 Hz, 2H), 1.42 (m, 2H), 2.47 (m, 2H), 2.93 (m, 2H), 3.36 (m, 4H), 3.87 (m, 2H), 7.14 (dd, J = 10.9, 5.1 Hz, 2H), 7.20 (dd, J = 7.6, 3.6 Hz, 2H), 7.59 (ddd, J = 7.6, 7.6, 1.6 Hz, 2H), 8.49 (d, J = 4.4 Hz, 2H); mass (ESI): m/z ($C_{21}H_{32}N_4O_2$, 372.50): 373.1 ($M + H^+$).

2.7. 2-({3-[(2-Hydroxy-methyl-ethyl)-pyridin-2-ylmethyl-amino]-propyl}-pyridin-2-ylmethyl-amino)-propan-1-ol (**11**)



11

Three hundred milligrams (1.80 mmol) of **7** were dissolved in 10 ml of CH_2Cl_2. 1,3-Dibromopropane (182 mg (0.9 mmol)) and 325 mg (2.5 mmol) of *N*,*N*-diisopropylethylamine were added. The reaction mixture was refluxed for 72 h. It was then cooled down to room temperature and 20 ml of distilled water were added to extract the *N*,*N*-diisopropylethylamine hydbromide salt. The organic phase was dried over $MgSO_4$ and CH_2Cl_2 was evaporated under reduced pressure. Compound **11** (137 mg) was obtained as a brown oil with a good purity.

Yield: 41%; F.w. = 372.50 g mol^{-1}; IR (neat): 3367, 2964, 2931, 1593, 1570, 1045, 1001, 751 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86 (t, J = 6.0 Hz, 6H), 1.07 (d, J = 6.1 Hz, 2H), 1.16 (d, J = 6.5 Hz, 2H), 1.23 (d, J = 8.3 Hz, 2H), 1.42 (m, 2H), 2.47 (m, 2H), 2.93 (m, 2H), 3.36 (m, 4H), 3.87 (m, 2H), 7.14 (dd, J = 10.9, 5.1 Hz, 2H), 7.20 (dd, J = 7.6, 3.6 Hz, 2H), 7.59 (ddd, J = 7.6, 7.6, 1.6 Hz, 2H), 8.49 (d, J = 4.4 Hz, 2H); mass (ESI): m/z ($C_{21}H_{32}N_4O_2$, 372.50): 373.1 ($M + H^+$).

4-Methyl-2-*N*-(pyridylmethyl)iminophenol (**8**) and 4-methyl-2-*N*-(pyridylmethyl)aminophenol (**9**) were synthesized according to the procedure reported by Wong et al. [18].

2.8. Catalyst and substrate solutions

A typical catalyst solution was prepared by dissolving, in a 10 mL volumetric flask, 24.2 mg (0.1 mmol) of $Cu(NO_3)_2{\cdot}3H_2O$ in 5 mL of acetonitrile, adding 0.1 mmol of ligand and filling up to 10 mL with acetonitrile. This resulted in a 0.01 M Cu(Ligand)$(NO_3)_2$ solution in acetonitrile. The substrate solution was prepared *just before* use by dissolving, in a second 10 mL volumetric flask, 366.5 mg (3.0 mmol) of DMP (**1**) in 5 mL of acetonitrile, adding 20 μL (0.1 mmol) of sodium methoxide (30% solution in methanol), and filling up to 10 mL with acetonitrile, which resulted in a 0.3 M solution of DMP and a 0.01 M solution of NaOMe in acetonitrile.

2.9. Dioxygen-uptake measurements

In a typical quantitative, time-resolved dioxygen-uptake experiment, one compartment of a special two-compartment reaction vessel was filled with 5 mL of the 0.01 M copper(II)/ligand solution, and the other with 10 mL of the substrate solution. Intense shaking in a dioxygen atmosphere combined these solutions and started the reaction. The resulting reaction mixture was 3.33 mM in copper and 0.2 M in DMP (**1**). All polymerization reactions were performed at 25 °C under pure dioxygen at atmospheric pressure. These are the conditions referred to as standard conditions. The catalytic activity has been determined from the initial dioxygen-uptake rate R_0.

2.10. Preparation of the coordination compound $[Cu(NO_3)_2(Pyma\text{-}2\text{-}pol)]$ (**12**)

Pyma-2-pol (50 mg (0.30 mmol)) (**6**) were dissolved in 5 ml of acetonitrile. $Cu(NO_3)_2{\cdot}3H_2O$ (73 mg; 0.30 mmol)

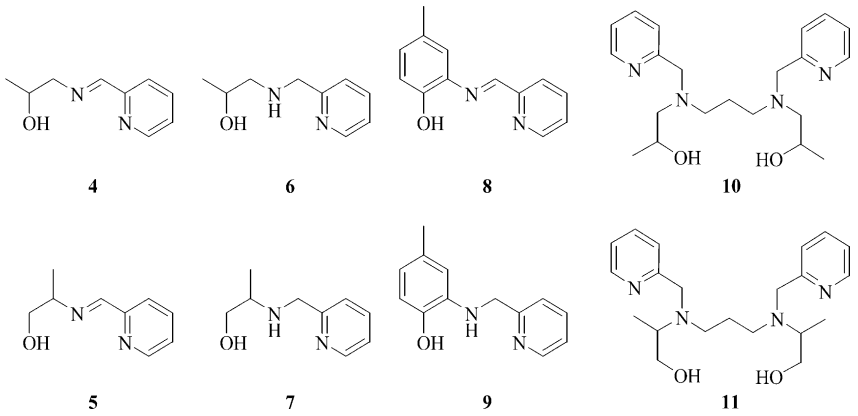


Fig. 1. Ligands used with copper(II) for the catalytic polymerization of **1**.

were dissolved in 5 ml of acetonitrile. The copper solution was added to the ligand one and the resulting solution became dark blue. It was then let evaporate slowly. Crystals appeared after a few days, suitable for X-ray crystal structure determination.

Elemental analysis: analysis and calculation for $C_9H_{14}N_4O_7Cu$: C, 30.55; H, 3.99; N, 15.84. Found: C, 30.47; H, 3.78; N, 15.94; ligand field: 268 nm (LMCT), 320 nm (LMCT), 693 nm (d-d transition); IR (cm^{-1}): 3214, 2982, 1282, 1017, 1009, 768; EPR.: g = 2.0718, 2.2512.

2.11. X-ray data collection and structure refinement

The molecular structure of compound **12** was determined by single crystal X-ray diffraction methods. Intensity data and cell parameters were recorded at room temperature (25 °C) on a Bruker AXS Smart 1000 single-crystal diffractometer (Mo Kα radiation) equipped with a CCD area detector. The data reduction was performed using the SAINT and SADABS programs.[19]. The structure was solved by Direct Methods using the SIR92 program [20] and refined on F_o^2 by full-matrix least-squares procedures, using the SHELXL-97 program [21]. All non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealized geometry (C–H 0.95 Å) and refined ''riding'' on the corresponding parent atoms, with the exception of H10 which was located in the difference Fourier map. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_o^2 + (0.0726P)^2]$ (where $P = (F_o^2 + 2F_c^2)/3$).

Molecular geometry calculations were carried out using the PARST97 program [22]. Drawings were obtained by ORTEP3 in the WinGX suite [23]. All calculations were carried out on a DIGITAL Alpha Station 255 Computer.

Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-218510 and can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

3. Results and discussion

The activity of the catalytic systems formed by copper(II) and the ligands depicted in Fig. 1 has been evaluated during the polymerization of **1**, according to the procedure outlined in the experimental section.

In order to assess the influence of various parameters like steric or electronic effects, mono- or dinucleating ligands, on the catalytic activity, the polydentate ligands **4**–**11** have been tested and the results obtained are reported in Table 1, along with the ligand-to-copper ratios used.

Table 1
Catalytic activity of Cu(II) with various polydentate ligands during the polymerization of **1** in acetonitrile

Entry	Ligand	L/Cu	Conversion (%)	Reaction time (h)[a]	R_0 (10^{-5} mol L^{-1} s^{-1})
1	**4**	1	46	1.4	7
2	**5**	1	81	2.5	10
3	**6**	1	33	0.83	4
4	**7**	1	42	1.5	6
5	**8**	1	30	1.6	5
6	**9**	1	33	1.9	3
7	**10**	0.5	37	0.5	12
8	**11**	0.5	39	0.75	19

[a] Reaction time corresponding to the maximum conversion reached (plateau).

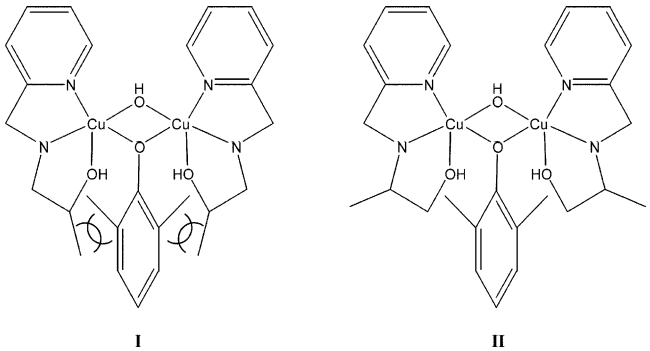


Fig. 2. Steric hindrance: active dinuclear species obtained with ligand **6** (**I**) and with ligand **7** (**II**).

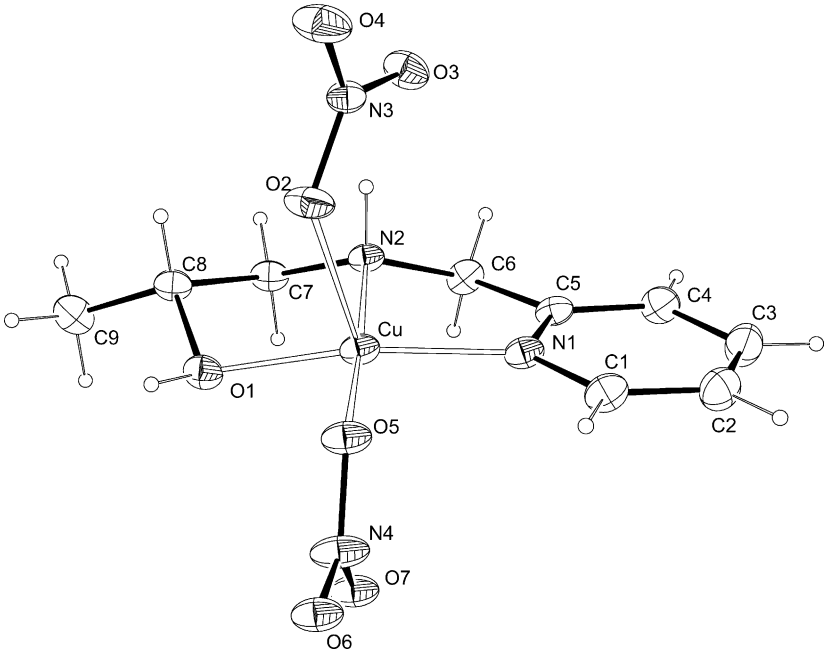


Fig. 3. Molecular structure of $[Cu(NO_3)_2(Pyma\text{-}2\text{-}pol)]$ (**12**). Selected bond lengths (Å) and angles (deg): Cu–O(1) 1.990(2), Cu–O(2) 2.281(2), Cu–O(5) 1.951(2), Cu–N(1) 1.969(3), Cu–N(2) 1.986(2); O(1)–Cu–O(2) 93.17(9), O(1)–Cu–O(5) 96.38(9), O(1)–Cu–N(1) 154.79(9), O(1)–Cu–N(2) 82.91(9), O(2)–Cu–O(5) 78.12(8), O(2)–Cu–N(1) 109.36(9), O(2)–Cu–N(2) 97.05(8), O(5)–Cu–N(1) 99.16(10), O(5)–Cu–N(2) 175.08(9), N(1)–Cu–N(2) 83.21(10).

The complexes obtained from an imine-containing ligand (**4**, **5** and **8**) led to higher catalytic activities compared with the ones obtained from their respective amino ligand (**6**, **7** and **9**). For example, the use of **5** (entry 2) gave an R_0 of 10×10^{-5} mol L^{-1} s^{-1} and 81% conversion in 2.5 h while **7** (entry 4) led to an R_0 of 6×10^{-5} mol L^{-1} s^{-1} with only 42% conversion. This beneficial effect of the imine group can be explained by the rigidity of the ligand through the conjugation of the imine function with the aromatic ring. Furthermore, this delocalization of the electrons induces the modification of the electronic and hence catalitic properties of the copper complex.

The results obtained with a series of very similar ligands (ligands **4**–**7**, entries 1–4) show that the position of the methyl group has a big influence on the activity of the catalysts. For instance, when ligand **4** was used (entry 1), 46% conversion of **1** was achieved in 1.4 h with an R_0 of 7×10^{-5} mol L^{-1} s^{-1}. With ligand **5** (entry 2), 81% conversion could be reached revealing a much more stable copper catalyst. This may be due to the steric hindrance of the methyl group of the ligand, which prevents the substrate to coordinate to the copper(II) ions and form the proposed dinuclear active species of the polymerization [24–26]. This steric effect is stronger in the case of ligand **6** (species **I**) than with ligand **7** (species **II**) (Fig. 2).

The comparison between the results obtained with an alcohol-containing ligand (ligands **4**–**7**, entries 1–4) or a phenol-containing ligand (ligands **8** and **9**, entries 5 and 6) shows that the phenolic group leads to lower catalytic activity. Thus, 46% conversion of **1** was observed with ligand **4** (entry 1) whereas only 30% of **1** were polymerized (entry 5) in a comparable reaction time with ligand **8**. A plausible explanation may be the steric interactions between the substrate and the phenolic fragment of the ligand, similarly to the influence of the methyl group of the ligand (see Fig. 2). The delocalization of the electrons from the oxygen atom of the phenolate to the ring may also play a role by changing the electronic properties of the copper complex. A phenol is more acidic than an aliphatic alcohol and this results in an easier deprotonation of the phenolic moiety. This is also supported by the crystal structure[1] of compound **12** (obtained from $Cu(NO_3)_2{\cdot}3H_2O$ and ligand **6** in acetonitrile) which reveals that the alcohol function of the ligand is still protonated (see Fig. 3). On the other hand, in the Cambridge Crystallographic Database, many examples of complexes where the ligands, similar to **8** or **9**, underwent phenol deprotonation upon coordination are listed [27,28]. In spite of this electronic effect, the phenol-containing ligands here described present a lower catalytic effect. Compound **12** consists of a pentacoordinated Cu(II) ion in a square-pyramidal environment. The basal plane is formed by the nitrogen and oxygen donor atoms of the ligand (Cu-N1 1.969, Cu-N2 1.986, Cu-O1 1.990 Å) and one nitrate anion (Cu-O5 1.951 Å). A second nitrate anion occupies the apical position displaying a copper–oxygen bond distance longer then the one of the basal coordinated anion (Cu-O2 2.281).

[1] Crystal data for **12**: $C_9H_{14}CuN_4O_7$, M = 353.78, blue needle 0.15 mm × 0.17 mm × 0.30 mm, triclinic, P, a = 8.720(5), b = 9.018(5), c = 9.955(5) Å, α = 101.83(5), β = 99.96(5), γ = 104,64(5)°, V = 720.1(7) Å^3, Z = 2, $\mu(Mo_{K\alpha})$ = 1.554 mm^{-1}, 7495 reflections collected, 3046 unique (R_{int} = 0.0253), 2401 observed ($I > 2\sigma(I)$), 201 parameters, R_1 = 0.0371, wR_2 = 0.0977 [($I > 2\sigma(I)$)], R_1 = 0.0498, wR_2 = 0.0977 (all data).

Finally, ligands **10** and **11** were prepared, respectively, from **6** and **7** with the aim to compare the catalytic activities of mononuclear and dinuclear copper(II) complexes in the oxidative phenol coupling. In all cases, the activities reached with the dinuclear ligands (entries 7 and 8) are three times higher than the ones observed with the monucleating ligands (entries 3 and 4). Thus, an R_0 of 19×10^{-5} mol L^{-1} s^{-1} was attained with **11** (entry 8) while only an R_0 of 6×10^{-5} mol L^{-1} s^{-1} was achieved when using **7** (entry 4). As expected, this is in perfect accordance with the mechanism previously proposed in our group for the polymerization of DMP [24–26].

4. Conclusions

The use of several ligands containing N_2O chromophores has provided more insight into the understanding of the different factors that may alter the catalytic activity of the copper-catalyzed oxidative coupling of 2,6-dimethylphenol. In all cases, imine ligands led to more active catalysts in comparison with amine ones, probably because of a more rigid and/or electron-rich ligand. The steric hindrance near the binding site of the substrate appeared also important, most likely owing to an easier formation or not at all of the active dinuclear copper species. The results obtained with dinuclear copper complexes tend to confirm the proposed mechanism which involves dinuclear active species to catalyze the polymerization through a nucleophilic pathway.

The preparation of *N*,*O*-containing ligands combining all beneficial effects determined during the course of the present study is currently under investigation.

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