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Synthesis and Catalytic Activities of Copper(I) Complexes of Bis(diphenylphosphinomethyl)amino Ligand and its Silica-supported Form

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Cu(I) complexes of free ditertiary aminomethylphosphine ligand, N,N-bis(diphenylphosphinomethyl)aminopropyltriethoxysilane (DIPAPTES) and its silica supported form (SiO₂-DIPAPES), have been synthesized under nitrogen atmosphere using Schlenk method and characterized by atomic absorption, FT-IR, NMR (¹H and ³¹P), and elemental analysis. Acetylacetonate (acac)⁻ complexes of Cr(III) and Mn(III) complexes were prepared according to the literature. All the complexes were used as catalysts for the oxidation of 2-methyl naphthalene (2MN) to 2-methyl-1,4-naphthoquinone (Vitamin K₃, menadione, 2MNQ) using hydrogen peroxide as a clean and cheap oxidant. All the complexes did not show good catalytic activity for the selective oxidation of 2-methyl naphthalene to 2-methyl-1,4-naphthoquinone.

Keywords menadione, oxidation, phosphines, quinones, silicasupported complexes, Vitamin K₃

1. INTRODUCTION

Functionalized phosphine ligands and their transition metal complexes have increasingly become important due to their improved catalytic activity. Due to the fact that phosphines play an efficient role on transportation of oxygen to substrate with a transition metal center, synthesis of novel aminomethylphosphinemetal complexes, and investigation of their oxidative catalytic properties are a part of modern production process researches.^[1–7]

Transition metal complexes of acetylacetonate $(acac)^{-}$ are both a radical initiator and a hydroperoxide decomposition

catalyst. Therefore, they can be sometimes used as catalytic synthesis. $^{[8-10]}$

Vitamins K are biologically active compounds that are kinds of naphthoquinones, and are effective for blood coagulation. Vitamin K_3 is a synthetic member of vitamin K group. However, vitamin K_3 is more active than other vitamin K derivatives for blood coagulation. The human body synthesizes vitamin K in their intestine by microorganisms, but some animals have to get vitamin K from feed.^[2,3]

In the classical process, Vitamin K_3 is produced via stoichiometric oxidation of 2-methyl naphthalene with CrO₃ in sulphuric acid with the yield of 30–60%. After this reaction, 18,000 g. of chromium containing waste is obtained for the synthesis of 1,000 g. menadione. It is too difficult to treat chromium containing waste.^[2,3] Alternatively, vitamin K_3 can be cleanly and modernly synthesized in high yield using hydrogen peroxide as clean oxidant in acetic acid via transportation of oxygen in the presence of a catalyst.^[2,3,11]

2. EXPERIMENTAL

2.1. General

All synthesis reaction steps of the phosphine-complexes were carried out under nitrogen atmosphere using Schlenk method. 3'-Aminopropyltriethoxysilane (3'-APTES) was purchased from Fluka. The phosphonium salt [PPh₂(CH₂OH)₂]Cl, which is a starting compound for the synthesis of phosphines, and [Mn(acac)₃], [Cr(acac)₃] complexes were prepared as described in the literature.^[1-5,12,13] The liquid state NMR spectra were recorded at 25°C in DMSO-d₆ and CDCl₃ using a Varian Mercury 200 MHz NMR spectrometer. ³¹P-NMR spectra were recorded with complete proton decoupling and are reported in ppm using 85% H₃PO₄ as external standard. Solid state NMR spectra were measured using Bruker superconducting FT-NMR spectrometer avance TN 300 MHz WB. FT-IR spectra were

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SCH. 1. Multiple pathways in the oxidation of 2-methyl naphthalene.^[7]

obtained using KBr pellets with Perkin-Elmer RX1 FT-IR system in the range 4000–450 cm⁻¹. Elemental analyses were performed using LECO CHNS 932 instrument. During oxidation experiments, the reaction products were analyzed on a Varian 3800 GC (FID) with Silicone OV-17 packed column and characterized by Perkin Elmer Clarus 500 GC-MS Electron Impact (70 eV) with an Elite 5-MS capillary column. Metal contents were determined by Perkin elmer analyst 400 atomic absorption. All chemicals and reagents were purchased from Merck, Riedel de Haen, Fluka, and Sigma, and all solvents were dried using established procedures and immediately distilled nitrogen atmosphere prior to use. Silica having particule size of 0.150-0.250 mm and density of 170-300 m²/g was used as solid support for heterogeneous catalysts. [Mn(acac)₃] (1) and [Cr(acac)₃] (2) complexes were prepared according to the literature.^[12,13]

2.2. Preparation of L1 (DIPAPTES) and its silica supported form L2 (SiO₂-DIPAPES)

L1 (DIPAPTES) and its silica supported form **L2** (SiO₂-DIPAPES) were synthesized using $[PPh_2(CH_2OH)_2]Cl$ and 3'-aminopropyltriethoxysilane (3'-APTES) in a solution of NEt₃ according to the literature.^[2-7]

2.3. Preparation of [Cu(L1)₂]Cl (3)

L1 (1.30 g, 2.1 mmol) was added to a stirred solution of CuCl (0.396 g, 4 mmol) in ethyl alcohol (10 mL). The mixture was

stirred at room temperature for 4 h. Addition of diethylether gave the yellow solid which was then filtered off and dried. Yield 2.15 g (75%). $C_{35}H_{45}NO_3P_2SiCuCl$: calcd C 58.65, H 6.32, N 1.95%; anal. C 58.01, H 6.10, N 1.89 %. ¹H-NMR (CDCl₃, 25 °C, δ , ppm): 7.22-7.40 [m, 40H, 8Ph], 3.31 [m, 4H, Si-CH₂CH₂], 2.40 [br, 8H, SiCH₂CH₂CH₂N and P-CH₂-N], 1.32 [m, 4H, SiCH₂CH₂], 3.31 [m, 4H, O-CH₂CH₃], 1.10 [m, 6H, OCH₂CH₃]. ³¹P-NMR (CDCI₃, 25 °C, δ , ppm): 50,91 [s, Cu-PPh₂]. FT-IR (KBr, cm⁻¹): 3070 (m, Ar-H); 2955 (m, R-H); 1634 (m, C=C (Ph); 1455 (m, C-H); 1111 (m, C-N (*ter*-amine)); 802 (s, monosubstitue Ar-H).

2.4. Preparation of [Cu(L2)₂]Cl (4)

L2 (2.0 g) was added to a stirred solution of CuCl (0.396 g; 4 mmol) in ethyl alcohol (10 mL). The mixture was refluxed 6 h to give yellow solid which was then filtered off, rinsed with CH₂Cl₂ and dried under vacuum. Yield 2.10 g. FT-IR (KBr, cm⁻¹) 3077 (m, Ar-H); 2955 (m, R-H), 1640 (w, C=C (Ph)), 1161-1020 (m, C-N (ter-amine)), 803 (s, monosubstitute Ar-H). Cu: 5.1% (AAS). ³¹P-NMR (solid, δ , ppm): 51.05 [s, Pt-PPh₂]. Cu: 5.1% (AAS).

2.5. Catalytic Oxidation of 2-methyl Naphthalene with Complexes 1, 2, 3 and 4

3.15 g 2-methyl naphthalene (0.0222 mol) and 0.1 g catalyst for complex **1**, **2** and **4**, 0.5 g catalyst for complex **3** were used in



SCH. 2. Synthesis of Cu(I) complexes of free aminomethylphosphine ligand and its silica supported form.

Cl



SCH. 3. Possible mechanism of catalytic oxidation of 2MN.^[2]

order to determine optimum oxidation time in the experiments. Various oxidant and catalyst amount parameters were not investigated for the oxidation of 2-methyl naphthalene using the complexes **3** and **4**.

The catalytic reactions were carried out in a glass reactor having a water circulator wrapping around it. Due to the difficulties to keep the reaction temperature constant during the oxidation reaction, the temperature was held around $60 \pm 5^{\circ}$ C. 2-methyl naphthalene and catalyst in glacial acetic acid and hydrogen peroxide containing sulfuric acid were pumped into the reactor with a pump with the flow rate of 10 mL/min, respectively. 2-methyl naphthalene, 2-methyl-1,4-naphthoquinone and 6-methyl-1,4-naphthoquinone (6MNQ, isomer) amounts were calculated from external calibration curves prepared prior to analysis. Catalytic reaction products, as shown in scheme 1, were characterized and verified by GC-MS. All experiments were performed in triplicate.

RESULTS AND DISCUSSION

Catalyst Preparation

L1 (DIPAPTES) and its silica supported form **L2** (SiO₂-DIPAPES) were synthesized according to the reported studies.^[2-4] The novel [Cu(L1)₂]Cl (**3**) and [Cu(L2)₂]Cl (**4**) complexes were synthesized using CuCl, as shown in Scheme 2. Mn(III) and Cr(III) complexes of [CH₃COCHCOCH₃]⁻ (acac⁻) (**L3**) were prepared according to the literature.^[11,12]

The colors of synthesized $[Cu(L1)_2]Cl(3)$ and $[Cu(L2)_2]Cl(4)$ complexes were yellow, prepared $[Mn(acac)_3](1)$ and $[Cr(acac)_3](2)$ complexes were maroon and dark, respectively.

	r-ININ			
Ligands	δ_P (ppm)	Complexes	δ_P (ppm)	$\Delta\delta(\text{ppm})^{\prime\prime}$
L1	-28.2	$[Cu(L1)_2]Cl$	50.91	79.11
L2	-27.0	$[Cu(L2)_2]Cl$	51.05	78.05

TABLE 1 ³¹P-NMR data of the complexes

^aCoordination shift values of the complexes $\Delta \delta = \delta_{\rm P}$ (complex)- $\delta_{\rm P}$ (free ligand).^[9,10]

All the complexes except 4 are soluble in glacial acetic acid.

The phosphonyl band and the P-aryl bands of the complexes of **3** and **4** shifted to 1111 cm^{-1} and 3070 cm^{-1} , 1161 cm^{-1} and 3077 cm^{-1} , respectively. Assignment of these results showed that P-aryl wave numbers of the metal complexes shifted to higher values comparing with uncoordinated ligand if compared to the free ligands in the literature.^[1-7,14-16] The shifted spectra of the ligand incorporated into the complexes indicated that the ligand coordinated to metal ions.

The phosphine ligand and its silica-supported form and their Cu(I) complexes were characterized using ¹H-NMR, ³¹P-NMR, elemental analysis, and FT-IR. The proton signals of the phenyl ring in the free phosphine ligand and their metal complexes in ¹H-NMR spectra were observed in the range of 7.3–6.9 ppm.

The multiplet peaks of P-C<u>H</u>₂-N and NC<u>H</u>₂CH₂ protons of phosphine ligand **L1** and its Cu(I) complex **3** was present around 2.4–2.5 ppm, which is in agreement with reported studies.^[1–9] The ¹H-NMR spectra showed no remarkable differences between the free ligands and their metal complexes. The NCH₂ resonances of the complexes are only slightly shifted to low field compared to the free ligands, indicating that the N atom is not coordinated, as also reported in the literature.^[1,4–7,14,15]

³¹P-NMR spectra of the Cu-phosphine complexes showed more shielded signals compared with the uncoordinated aminomethylphosphine ligand. The coordination shift values of the complexes **3** and **4** (Δ), as varied depending on the metal centers and the chemical structures of the ligands showed that the ligands were bound to metal centers via a P-P bidentate to give chelated complexes rather than M-N interaction (Table 1).^[14,15]

Catalytic Activity

Phosphine-M complexes (Especially M: Pd, Pt) are known as oxidative catalysts by peroxides. In the first step of the catalytic process, 2MN is oxidized to 2-methyl-1-naphthol and then to 2-methyl-1,4-naphthalenediol. Oxidation rate can be described as $\gamma = k[cat][H_2O_2]$ formula. If the catalyst amount is a constant, reaction rate is first-order with equation $\gamma = k[H_2O_2]$.^[2] According to the equation, hydrogen peroxide concentration

Conversion

50.84

68.25

69.44

43.28

75.24

54.00

80.41

51.25

70.08

71.23

45.80

77.85

55.75

81.01

48.01

67.24

79.91

49.22

67.09

79.91

Yields (%)^a

2MNO

10.50

12.38

13.56

10,44

14.26

11.65

17.24

10.10

14.18

14.85

11.40

15.80

12.10

19.75

9.20

14.55

20.71

8.56

11.04

16.54

6MNO

0.98

2.55

2.75

0.58

2.67

0.82

2.89

1.25

2.12

2.78

0.65

2.85

0.91

2.76

1.04

1.11

2.30

0.62

0.69

1.41

TABLE 2 Catalytic activity of the complexes

Catalyst	Amount of catalyst (g)	H_2O_2 (mL)	Time (h)
	0.05	10	1.0
	0.10	10	1.0
	0.20	10	1.0
1	0.1	5	1.0
		15	1.0
			0.5
	0.10	10	1.5
	0.25	10	1.0
	0.50	10	1.0
	1.00	10	1.0
2	0.50	5	1.0
		15	1.0
			0.5
	0.50	10	1.5
			0.5

0.50

0.50

^aReaction conditions: 3.15 g (0.0222 mol) 2MN, 40 mL glacial acetic acid and 0.6 mL sulfuric acid (98 %), Temperature: 60°C.

1.0

1.5

0.5

1.0

1.5

10

10

3

4



FIG. 1. Influence of the reaction time on the catalytic oxidation of 2MN. Temperature: $60 \degree C$, $H_2O_2 = 10 \mbox{ mL}$, $2MN = 3,15 \mbox{ g} (0.0222 \mbox{ mol})$.

directly affects the reaction. The first step is the rate determining step because it is slow and needs to be controlled in order to increase the 2MNQ selectivity.^[2,3,18–23] The predicted catalytic oxidation mechanism is shown in Scheme 3.^[2]

Homogeneous and heterogeneous catalysts experiments were carried out using a similiar process. 2MN and catalyst dissolved in glacial acetic acid were pumped into the reactor, oxidation reaction was started when hydrogen peroxide and sulfuric acid solution were pumped onto the substrate mixture. The temperature was held around $60 \pm 5^{\circ}$ C. 2MN is oxidized by using Na₂Cr₂O₇ / H₂SO₄ solution in a reactor having cooling water in order to keep the temperature 55–65°C according to the classic industrial synthesis of 2MNQ. After the classical industrial synthesis of 2MNQ, 30–60% of 2MNQ yield is obtained.^[2,3,11,18–23]

The results of the blank reactions were indicated that 2MNQ yield, 3.7%, 5.3% and 15.9% with 30.5%, 40.2% and 68.7% 2MN conversion analyzed on the 30. min., 60. min. and



FIG. 2. Influence of the amount of the complex 3 and 4 on the catalytic oxidation of 2MN. Temperature: 60° C, $H_2O_2 = 10$ mL, 2MN = 3.15 g (0.0222 mol).





FIG. 3. Influence of the concentration of H_2O_2 on the catalytic oxidation of 2MN. Temperature: $60^{\circ}C$, $H_2O_2 = 10$ mL, 2MN = 3.15 g (0.0222 mol), 0.1 g complex 3 and 0.5 g complex 4.

90. min. Furthermore; different oxidant volumes (5, 10 and 15 mL) and different catalyst amounts (0.05, 0.1 and 0.2 g) were tested in order to determine optimum reaction conditions, respectively (Figures 1, 2, and 3).

Complexes $[Mn(L3)_3](1)$, $[Cr(L3)_3](2)$, $[Cu(L1)_2]Cl(3)$ and $[Cu(L2)_2]Cl(4)$ did not show a good catalytic effect if compared to our previous studies.^[2,3] Due to the fact that further oxidation products and undetermined products arised using complexes 1, 2, 3 and 4 with a medium conversion, the low 2MNQ yield percentage were obtained.

4. CONCLUSIONS

Bidentate tertiary phosphine complexes of Cu(II) with N, Nbis(diphenylphosphinomethyl)aminopropyltriethoxysilane and its silica supported form have been synthesized using Schlenk method. Catalytic experiments were carried out in a glass reactor having a cooling water circulating in its jacket. The coordination of the ligand to metal ions gave shielded chemical shifts in NMR spectra in comparison with the free ligand. As a clean and more efficient production of 2-methyl-1,4-naphthoquinone, synthesized complexes were tested in glacial acetic acid containing sulfuric acid. Complexes are not efficient, selective catalysts compared to classical synthesis of 2-methyl naphthalene. Because of obtaining the low yield after the results of the optimum reaction parameter tests, the silica-supported complex [Cu(L2)₂]Cl (4) were not applicable for the recycling experiments and synthesis of industrial size.

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