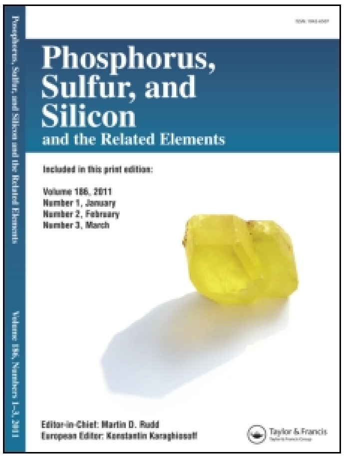

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Catalytic Synthesis of 2-Methyl-1,4-Naphthoquinone (Vitamin K_3) Over Silica-Supported Aminomethyl Phosphine-Ru(II), Pd(II), and Co(II) Complexes

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CATALYTIC SYNTHESIS OF 2-METHYL-1,4-NAPHTHOQUINONE (VITAMIN K_3) OVER SILICA-SUPPORTED AMINOMETHYL PHOSPHINE-Ru(II), Pd(II), AND Co(II) COMPLEXES

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Ru(II), Pd(II), and Co(II) complexes of the free ditertiary aminomethylphosphine ligand, N,N-bis(diphenylphosphinomethyl)aminopropyltriethoxysilane [$(EtO)_3Si(CH_2)_3N(CH_2PPh_2)_2$] (DIPAPTES), and its SiO_2-DIPAPES have been synthesized under a nitrogen atmosphere using Schlenk techniques. All the complexes were used as catalysts for the oxidation of 2-methyl naphthalene (2MN) to give 2-methyl-1,4-naphthoquinone (vitamin K_3, menadione, 2MNQ) in the presence of hydrogen peroxide as a clean and cheap oxidant. The catalytic synthesis of vitamin K_3 was investigated using both homogeneous catalysis with free complexes and heterogeneous catalysis with silica-supported complexes. [(DIPAPTES)$PdCl_2$] and its silica-supported form showed the best catalytic activity for the selective oxidation of 2-methyl naphthalene to 2-methyl-1,4-naphtoquinone compared to the other metal complexes. 2MNQ yield reached 52.26% with the 2MN conversion of 90.52% using complex [(DIPAPTES)$PdCl_2$] and 58.59% with the 2MN conversion of 99.56% using the silica supported [SiO_2(DIPAPES)$PdCl_2$] complex for 1 h. Recycling was investigated for the silica-supported Pd(II) complex and compared with the classical production of vitamin K_3.

Supplemental materials are available for this article. Go to the publisher's online edition of **Phosphorus, Sulfur, and Silicon and the Related Elements** ***to view the free supplemental file.***

Keywords Catalyst design; menadione; oxidation; phosphines; quinones; vitamin K_3

INTRODUCTION

Functionalized phosphine transition metal complexes have been used as catalysts to generate highly enantioselective products in many asymmetric organic processes.[1–5] Chiral nitrogenous phosphine ligands and their transition metal complexes have become

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increasingly important due to their improved catalytic activity.[4] Catalytically efficient chelated palladium phosphine complexes have also been developed for organic synthesis.[1,5]

Due to the fact that phosphines play an efficient role for the transportation of oxygen to substrate via a transition metal center, scientists have focused on the synthesis of novel phosphine–metal complexes and investigation of their oxidative catalytic properties.[5]

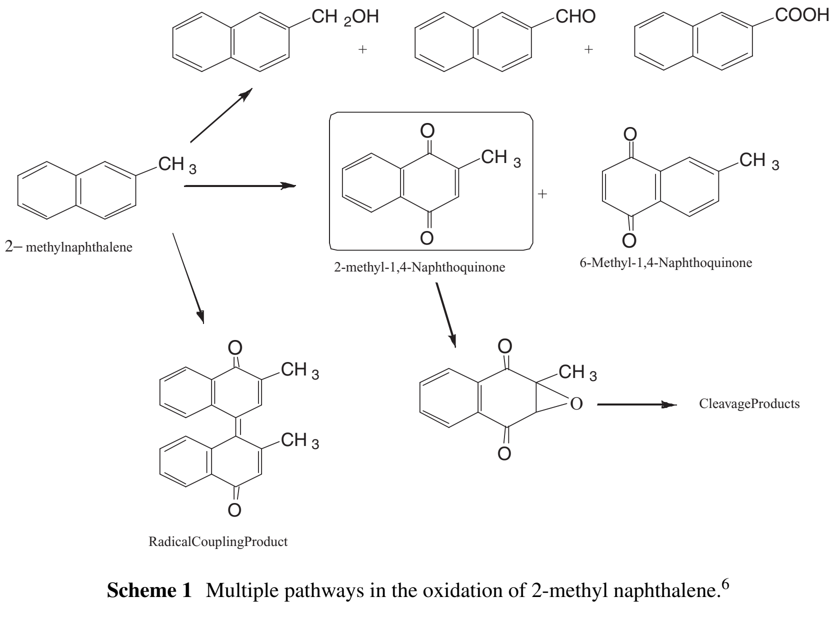
There are several advantages of heterogeneous catalysts compared to homogeneous catalysts, such as reusage in catalytic systems, catalytic selectivity, oxidation efficiency, reaction time, and economy.

Members of the vitamin K group, which are naphthoquinones derivatives, are effective for blood coagulation. Vitamin K_3 is a synthetic member of the vitamin K group. However, vitamin K_3 is more active than other vitamin K derivatives for blood coagulation.[6] The human body synthesizes vitamin K in its intestine by microorganisms, but some animals must get vitamin K from nutrients. Vitamin K_3 has five commercial products used for premix in food: menadione sodium bisulfite (MSB), menadione sodium bisulfite stabilized (MSB stab.), menadione sodium bisulfite complex (MSBC), menadione dimethyl pyrimidinol bisulfite (MPB), and menadione nicotinamide bisulfite (MNB). MSB that is soluble in water is the sulfonated form of menadione.[6,7]

In the classical production process, vitamin K_3 is produced via a stoichiometric oxidation reaction of 2-methyl naphthalene by CrO_3 in sulfuric acid with the yield of 30–60%. At the end of this reaction, 18,000 g of waste including chromium that is environmentally hazardous with low selective oxidation efficiency is obtained to yield 1,000 g of product. From an environmental point of view, the treatment of chromium containing waste is quite difficult.[8,9]

Vitamin K_3 can be cleanly synthesized in high yield using hydrogen peroxide as clean oxidant in acetic acid via transportation of oxygen in the presence of a catalyst[6–11] (Scheme 1).

$$CH_3COOH + H_2O_2 \leftrightharpoons CH_3COOOH + H_2O$$



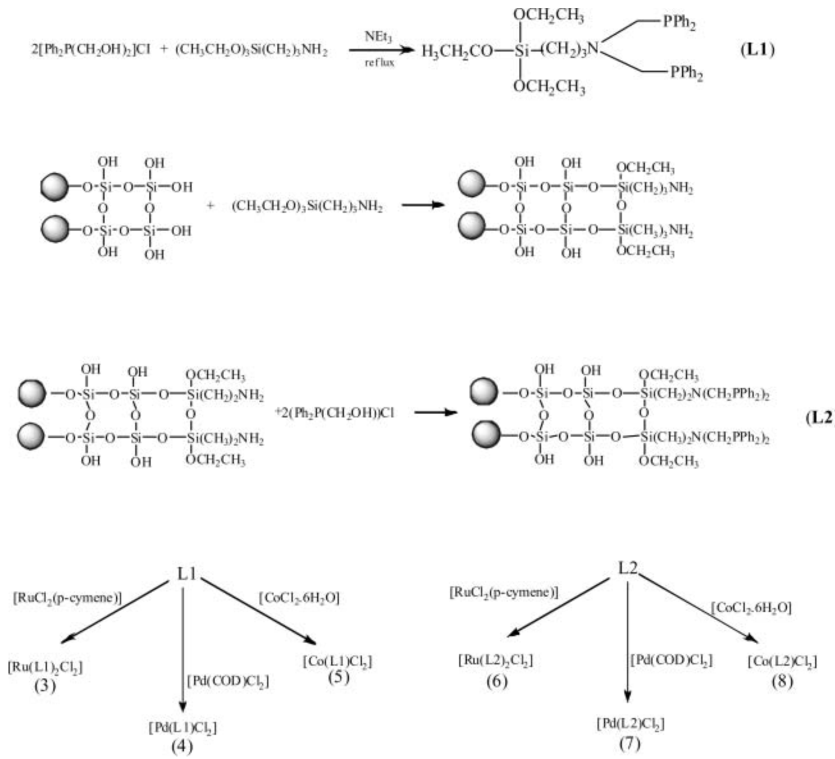
Scheme 1 Multiple pathways in the oxidation of 2-methyl naphthalene.[6]

In this study, transition metal complexes of aminomethylphosphine and its silica-supported form have been synthesized in order to investigate their catalytic activities in vitamin K_3 synthesis reaction.

RESULTS AND DISCUSSION

Catalyst Preparation

The Pd(II) complexes of aminomethylphosphine ligands $[(EtO)_3Si(CH_2)_3N(CH_2PPh_2)_2]$ (**L1**), and its silica supported form (**L2**), were synthesized according to the literature.[12–17] **L1** and **L2** complexes of Ru(II) were synthesized as reported earlier.[17] The Co(II) complexes of **L1**, **L2** are novel (Scheme 2).



Scheme 2 Synthesis of Ru(II), Pd(II), and Co(II) complexes of free aminomethylphosphine ligand (**L1**) and its silica-supported form (**L2**).

The reaction of the complexes of Ru(II), Pd(II), and Co(II) with **L1** and **L2** gave red, pale yellow, and blue solids, respectively. Pd(II) and Co(II) complexes have four coordination, and Ru(II) complex has six coordination. The complexes are soluble in dichloromethane, ethanol, dimethyl sulfoxide, and glacial acetic acid.

All the complexes were synthesized by reacting ligand **L1** and **L2** with metal compounds in toluene and ethyl alcohol by refluxing for 2–12 h. All products were purified by washing with toluene and acetone, respectively.

The P-aryl bands in ligands were assigned to about 1078 cm^{-1} and 3032 cm^{-1} in the FT-IR spectra. The phosphonyl band and the P-aryl bands of the metal complexes shift to

1096 cm^{-1} and 3051 cm^{-1} for complex **3**, 1088 cm^{-1} and 3145 cm^{-1} for complex **4**, 1083 cm^{-1} and 3053 cm^{-1} for complex **5**, 1099 cm^{-1} and 3344 cm^{-1} for complex **6**, 1093 cm^{-1} and 3344 cm^{-1} for complex **7**, and 1096 cm^{-1} and 3459 cm^{-1} for complex **8**, respectively. Assignment of these results showed that P-aryl wave numbers of the metal complexes shifted to higher values comparing with uncoordinated ligand. The shifted spectra of the ligand incorporated into all the complexes show that the ligand coordinated to metal ions.[15]

The proton signals of the phenyl ring in the phosphine ligand and their metal complexes in ^{1}H NMR spectra were observed as multiplet at around 7.20–7.46 ppm. The multiple peaks of P-C$\underline{H_2}$-N and NC$\underline{H_2}$CH$_2$ protons of phosphine and their complexes were present at around 2.41–2.52 ppm, which is in agreement with reported studies.[15,16] The ^{1}H NMR spectra showed no remarkable differences between the uncoordinated ligands and their metal complexes. The NCH$_2$ 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.[13–15]

^{31}P NMR spectra of all the metal phosphine complexes showed more shielded signals compared with the uncoordinated aminomethylphosphine ligand. The coordination shift values of the complexes (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 I).[13–17] Elemental analysis results of the catalysts show that the L:Ru(II) ratio is 2:1, and the L:Pd (II) and L:Co (II) ratios are both 1:1.

Catalytic Activity

Homogeneous and heterogeneous catalyst experiments were carried out using similiar processes. In the catalytic 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 was control pumped onto the substrate mixture. The temperature was controlled with a water circulator, and the reaction mixture was stirred vigorously. The oxidation reaction temperature was held between 60 ± 10°C, since it was very difficult to control at a constant temperature.

The results of the blank reactions indicated that the 2MNQ yield 3.7% with 30.5% 2MN conversion, 5.3% with 40.2% 2MN conversion, and 15.9% with 68.7% 2MN conversion analyzed at 30 min, 60 Min, and 90 min. Furthermore, when 5, 10, and 15 mL hydrogen peroxide volumes were used in different experiments and studied for 60-min reaction time, 2MNQ yield and 2MN conversions were 3.1% and 22.4%, 5.4% and 40.9%, 10.8% and 69.6%, respectively.

Table I Coordination shift values of the complexes (Δ) (δ_{L1}: –28.18 ppm, δ_{L2}: –27.00 ppm)

Ligands	^{31}P NMR (ppm)	Complexes	^{31}P-NMR (ppm)	Δ ($\delta_{complex}$- $\delta_{free\ ligand}$) (ppm)
L1	–28.18	3	27.11	55.29
		4	7.60	35.88
		5	29.58	57.76
L2	–27.00	6	26.24	53.24
		7	9.90	36.90
		8	32.90	59.90

Phosphine–M complexes (M: Pd, Pt) are known as oxidative catalysts in the presence of 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. The first step is the rate-determining step because it is slow (Scheme S1, available online in the Supplemental Materials)[5,18,19] and needs to be controlled using a suitable catalyst and oxidant amount in order to increase the 2MNQ selectivity.

Oxidation times were monitored with an interval of 30 min for all complexes. An aliquot of the reaction mixture was taken from the reactor at 30 min, 60 Min, and 90 min and extracted with the appropriate amount of acetone. According to the possible mechanism of the oxidation of 2-methyl naphthalene, when the reaction time is increased over 1 h, further oxidation can form and some other oxidized organic compounds can arise. Based on the experimental results, 1 h reaction time has been found to be adequate for the oxidation of 2-methyl naphthalene (Figure 1).

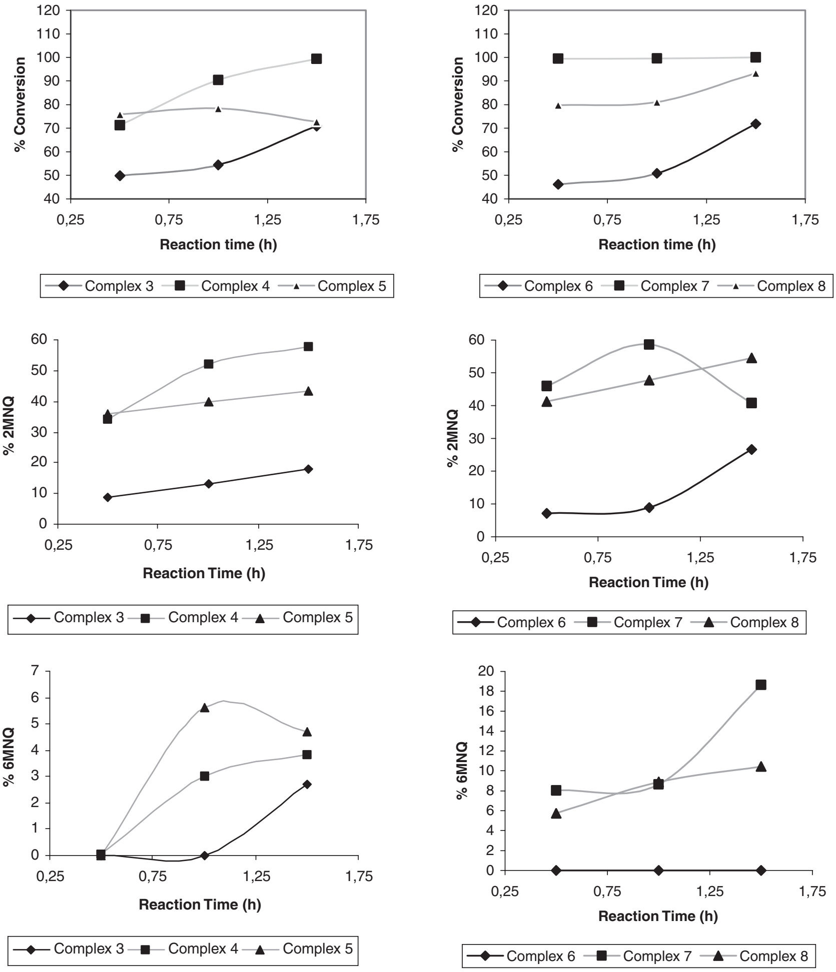
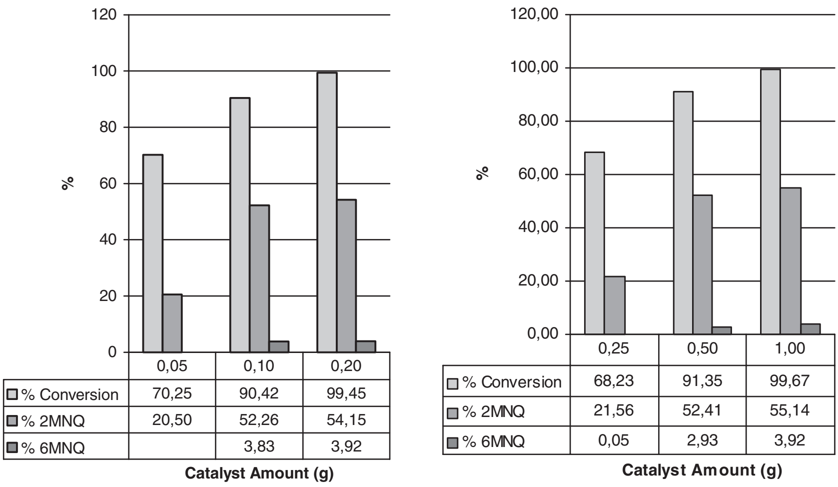


Figure 1 Influence of the reaction time on the oxidation of 2-methyl naphthalene. Temperature: 60 ± 10°C, $H_2O_2 = 10$ mL, 2-methyl naphthalene = 3,15 g.



	0,05	0,10	0,20
□ % Conversion	70,25	90,42	99,45
▨ % 2MNQ	20,50	52,26	54,15
■ % 6MNQ		3,83	3,92

	0,25	0,50	1,00
□ % Conversion	68,23	91,35	99,67
▨ % 2MNQ	21,56	52,41	55,14
■ % 6MNQ	0,05	2,93	3,92

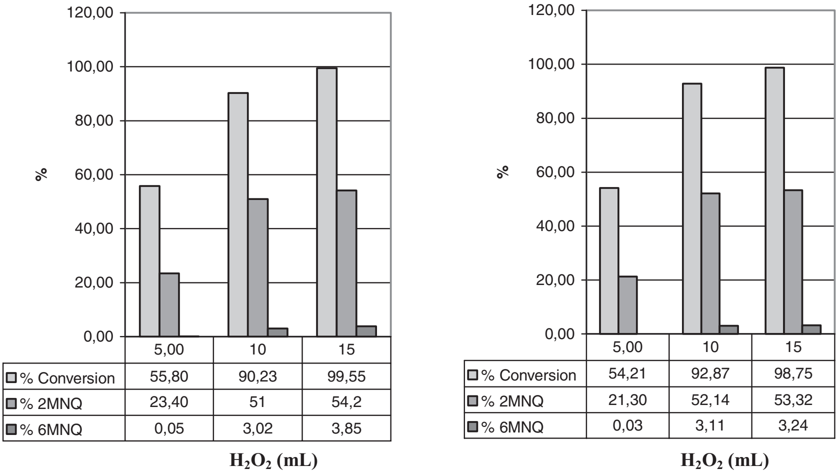
(4) **(7)**

Figure 2 Influence of the amount of the catalysts **4** and **7** on the oxidation of 2-methyl naphthalene. Temperature: 60 ± 10°C, $H_2O_2 = 10$ mL, 2-methyl naphthalene = 3.15 g.

The oxidation of 2-methyl naphthalene was also studied by changing the amount of the catalyst **4** from 0.05 g to 0.20 g and solid supported catalyst complex **7** from 0.25 g to 1.0 g in each reaction, respectively. Because of the very fast oxidation of naphthol derivatives to 2-methyl-1,4-naphthoquinone and 6-methyl-1,4-naphthoquinone (isomer), and also to other organic compounds, 2-methyl-1,4-naphthoquinone selectivity reached its maximum value using 0.1 g of catalyst for complex **4** and 0.5 g for complex **7**, respectively.[9] The amount of 2-methyl-1,4-naphthoquinone increases together with a slight increase in amount of isomer (6-methyl-1,4-naphthoquinone) with increased amount of catalyst (Figure 2).

$\gamma = k\,[\text{cat}][H_2O_2]$ formula can be simplified if the catalyst amount is a constant; reaction rate is first-order with equation $\gamma = k'[H_2O_2]$. According to the equation, hydrogen peroxide concentration directly affects the reaction.[20–22] In Figure 3, conversion of 2-methyl naphthalene and 2-methyl-1,4-naphthoquinone vs. three different volumes of hydrogen peroxide are displayed using metal complexes **4** and **7** in the oxidation reaction. The increase in the concentration of hydrogen peroxide increased 2MNQ selectivity and 2MN conversion. H_2O_2 amount certainly depends on participation of the catalyst, because, in the oxidation mechanism, H_2O_2 is activated by formation of metal-peroxo pre-complexes, which are a prerequisite for oxygenation activity.[9]

Although complex **5** and its silica-supported form complex **8** showed medium oxidative catalytic activity, complex **3** and complex **6** did not exhibit any catalytic effect. Complex **4**, which is a free complex, has been found as the best catalyst for the selective oxidation of 2-methyl naphthalene to 2-methyl-1,4-naphthoquinone in comparison with the other complexes. The selective catalytic activity of the silica-supported forms of these complexes were similar to free forms of them (Table S1, Supplemental Materials). Due



	5,00	10	15
□ % Conversion	55,80	90,23	99,55
▨ % 2MNQ	23,40	51	54,2
■ % 6MNQ	0,05	3,02	3,85

	5,00	10	15
□ % Conversion	54,21	92,87	98,75
▨ % 2MNQ	21,30	52,14	53,32
■ % 6MNQ	0,03	3,11	3,24

(4) (7)

Figure 3 Influence of the concentration of H_2O_2 on the oxidation of 2-methyl naphthalene. Temperature: 60 ± 10°C, $H_2O_2 = 10$ mL, 2-methyl naphthalene = 3.15 g, 0.1 g complex **4** and 0.5 g complex **7**.

to the fact that the complex **7** heterogeneous catalyst system has some advantages (easily recyclable, and clean, cheap oxidant with high 2MNQ yield), it was worthwhile to investigate catalytic recycling for complex **7**. Thus, three recycling oxidation experiments were carried out using complex **7**.

The results of the recycling process showed that complex **7** had almost the same selective catalytic activity in the oxidation of 2-methyl naphthalene in first two recycle. In the third recycle, catalytic activity slightly decreased. Despite the decrease in activity in the last period, the average results of three catalytic recycles have indicated that selective catalytic synthesis of vitamin K_3 using silica supported Pd(II)-phosphine, complex **7**, is efficient in comparison to the classical process of synthesizing vitamin K_3 (Table S2, Supplemental Materials).

Acetic acid and sulfuric acid join in the oxidation mechanism together with the catalysts by transporting oxygen to the aromatic ring. In comparison with classical production, modern synthesis of vitamin K_3 will be applicable and cheaper in the near future.

EXPERIMENTAL

All synthesis reactions were carried out under nitrogen atmosphere using the Schlenk method. The ^{1}H NMR and ^{31}P NMR spectra were recorded at 25°C in DMSO-d_6 and $CDCl_3$ using a Varian Mercury 200 MHz NMR spectrometer. Solid NMR spectra were measured using solid NMR Bruker Superconducting FT-NMR Spectrometer Avance TN 300 MHz WB. The infrared spectra were recorded with a Perkin Elmer Spectrum RXI/FT-IR System. Elemental analyses were performed using a LECO CHNS 932 instrument. During oxidation experiments, the products were analyzed on a Varian 3800 GC-FID with Silicone OV-17 packed column and characterized by Perkin Elmer Clarus 500 GC-MS with 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 under nitrogen atmosphere prior to use. $[(EtO)_3Si(CH_2)_3N(CH_2PPh_2)_2]$ (**L1**) and its silica supported form (**L2**) ligands and their metal complexes $[Ru(L1)_2Cl_2]$ (**3**), $[Pd(L1)Cl_2]$ (**4**), $[Ru(L2)Cl_2]$ (**6**), and $[Pd(L2)Cl_2]$ (**7**) were synthesized according to the literature.[12–17] 0.150–0.250 mm, 170–300 m^2/g silica was used as solid support for heterogeneous catalysts.

Preparation of $[Co(L1)Cl_2]$ (5)

L1 (1.3 g, 2.1 mmol) was added to a stirred solution of $[CoCl_2.6H_2O]$ (0.5 g; 2 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred and refluxed for a further 2 h. The addition of diethyl ether gave a blue solid, which was then filtered off and dried. Yield 1.226 g (82%). Elemental analysis calculation for $[C_{35}H_{45}NO_3P_2Cl_2SiCo]$: C, 56.20, H,6.10, N, 1.87; Found: C, 56.81, H, 5.92, N, 1.80%. ^1H NMR ($CDCl_3$, 25°C): δ 7.30 [m, 20H, 4Ph], 3.73 [m, 2H, $SiC\underline{H_2}$], 1.36 [m, 2H, $SiCH_2C\underline{H_2}$], 2.41 [br, 6H, $SiCH_2CH_2C\underline{H_2}N$ and $P{-}C\underline{H_2}{-}N$], 3.73 [m, 2H, $OC\underline{H_2}$], 1.20 [m, 3H, $OCH_2C\underline{H_3}$] ppm. ^{31}P-NMR ($CDCl_3$, 25°C): δ 29.58. $[Co{-}\underline{P}Ph_2]$ ppm. FT-IR (KBr, cm^{-1}) 3054 (m, Ar—H); 2984 (m, R—H), 1646 (w, C=C (Ph)), 1437 (s, C=C (Ph)), 1126–1083 (m, C—N (ter-amine)), 722–695 (s, monosubstitute Ar—H).

Preparation of $[Co(L2)Cl_2]$ (8)

L2 (2 g) was added to a stirred solution of $[CoCl_2.6H_2O]$ (0.5 g, 2.1 mmol) in ethyl alcohol (5 mL). The mixture was stirred and refluxed for a further 4 h, and a blue solid separated, which was then filtered, washed with CH_2Cl_2, and dried under vacuum. Yield 2.2 g (81%). FT-IR (KBr, cm^{-1}) 3458 (m, Ar—H), 2955 (m, R—H), 1651 (w, C=C (Ph)), 1095 (m, C—N (ter-amine)), 802 (s, monosubstitute Ar—H). ^{31}P-NMR ($CDCl_3$, 25°C): δ 32.90 ppm, Co: 3.8% (AAS).

Catalytic Oxidation of 2-Methyl Naphthalene by Complexes 3, 4, and 5, and Silica-Supported Complexes 6, 7, and 8

To determine the optimum oxidation time in the experiments, 3.15 g 2-methyl naphthalene (0.022 mol), 40 mL glacial acetic acid, 10 mL hydrogen peroxide (30%), 0.6 mL sulfuric acid (98%), and 0.1 g catalyst (for complexes **3**, **4**, and **5**) and 0.5 g catalyst (for the complexes **6**, **7**, and **8**) were used, respectively. Additionally, various oxidant and catalyst amounts were also investigated for the selective oxidation of 2-methyl naphthalene to 2-methyl-1,4-naphthoquinone using complexes **4** and **7**, respectively.

The catalytic reactions were carried out in a glass reactor having a water circulator wrapped around it to control the reaction temperature between 60–80°C. 2-Methyl naphthalene and the catalyst in glacial acetic acid was added into the reactor, and hydrogen peroxide containing sulfuric acid was pumped into the reactor with a pump by the flow rate of 10 mL/min. While the reaction was going on, for each at 30, 60, and 90 min, 5 mL reaction mixture was taken and extracted with acetone and injected to GC. 2-Methyl naphthalene, 2-methyl-1,4-naphthoquinone, and 6-methyl-1,4-naphthoquinone (isomer) amounts were calculated from external calibration curves that were prepared before analysis. Catalytic reaction yields were characterized and verified by GC-MS. All experiments were performed in triplicate.

CONCLUSIONS

Bidentate tertiary aminomethylphosphine complexes of Ru(II), Pd(II), and Co(II) with N,N-bis(diphenylphosphinomethyl)aminopropyltrietoxysilane and its silica-supported form have been synthesized using Schlenk techniques. 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, some catalysts were tested in glacial acetic acid containing sulfuric acid, which accelerates the oxidation reaction. Based on the experimental data, complex **4** has been found an efficient free catalyst, whereas complex **7** is the best recyclable solid-supported catalyst compared with other complexes in the selective oxidation of 2-methyl naphthalene to 2-methyl-1,4-naphthoquinone. For 1 h, 2-methyl-1,4-naphthoquinone yield reached to 52.26% with 2MN conversion 90.42% using complex **4** and reached to 58.58% 2MNQ yield with conversion of 99.56% using complex **7**. According to the results of the recycling tests, solid-supported complex **7** could be an applicable heterogeneous catalyst compared to the classical production based on the recycling numbers, conversion, and 2MNQ selectivity.

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