Zeolite-Encapsulated Cobalt Salophen Complexes as Efficient Oxygen-Activating Catalysts in Palladium-Catalyzed Aerobic 1,4-Oxidation of 1,3-Dienes

Jens Wöltinger,[a] Jan-E. Bäckvall,*[a] and Ágnes Zsigmond[b]

Abstract: Different cobalt salophen catalysts **1**, **2**, **3**, and **4** were prepared and studied as oxygen-activating agents in the palladium–quinone catalyzed aerobic oxidation of 1,3-dienes. These cobalt salophen catalysts were also encapsulated into the supercage of zeolite Y by the template synthesis method (ship-in-the-bottle technique). The cobalt salophen catalyst **2** from 3,5-di-*tert*-butylsalicylaldehyde and 1,2-diaminobenzene was found to be more active than the unsubstituted parent cobalt salophen and the zeolite-encapsulated variant **2-ZeY** showed remarkably high activity. With this catalyst, palladium-catalyzed aerobic oxidation of 1,3-cyclohexadiene afforded 1,4-diacetoxy-2-cyclohexene in high yield (95%) at room temperature within three hours. It was demonstrated that the zeolite-encapsulated catalyst **2-ZeY** can be isolated and reused several times and still show good conversion in the third run.

Keywords: cobalt · electron transfer · oxidations · palladium · zeolites

Introduction

Mild oxidations are of fundamental importance in organic synthesis.[1, 2] The recent interest in organometallic chemistry and homogeneous catalysis has led to the development of a large number of mild catalytic oxidation reactions of organic substrates.[3–9] In particular, oxidation processes that employ O_2 or H_2O_2 have attracted considerable attention[1b, 1c, 2, 3, 6–9] due to potential industrial applications and environmental concerns. These reactions often proceed at low temperature under mild conditions and water is the only side product. Many aerobic oxidation reactions presently used in industry, however, employ rather high temperatures and/or high pressures.[3]

We have been involved in the development of biomimetic aerobic oxidation reactions of organic substrates with ruthenium and palladium catalysts.[9–13] These reactions are based on a mild multistep electron transfer in which electrons are transferred from the substrate to molecular oxygen in a way that is reminiscent of processes in living organisms. These mild oxidation reactions employ a substrate-selective redox catalyst (Pd^{II}, Ru^{II}) and an oxygen-activating metal macrocyclic catalyst. In most cases it is necessary to use an electron-transfer mediator (usually a quinone) to facilitate the transport of electrons from the substrate-selective redox catalyst to the metal macrocyclic oxygen complex. In one such reaction, 1,3-dienes are oxidized to 1,4-diacetoxy-2-alkenes[9, 10] (Scheme 1; where ML^m is a porphyrin or a salophen/salen complex). In this reaction none of the three catalysts can be omitted without stopping the reaction.

The limiting step of this catalytic system is associated with the metal macrocyclic complex ML^m. First, the electron transfer from the hydroquinone to the oxidized form of the metal macrocycle $(ML^m)_{ox}$ (e.g. a peroxo or oxo complex) is usually slow compared to the other electron transfer steps. Second, the metal macrocyclic complex undergoes oxidative degradation as well as dimerization and this will severely shorten the lifetime of the biomimetic catalytic system. The dimerization may involve formation of dimeric peroxo complexes[14] or μ-oxo dimers.[15] In an effort to improve the electron transfer between hydroquinone (HQ) and the oxidized form of the metal macrocycle, $(ML^m)_{ox}$, the quinone and ML^m were incorporated into the same molecule.[10b] Thus, the use of a cobalt tetraquinoylporphyrin in place of separated quinone and porphyrin increased the efficiency and the rate of the oxidation reaction,[10b] but the system still suffered from deactivation of the macrocycle through oxidative degradation and/or dimerization.

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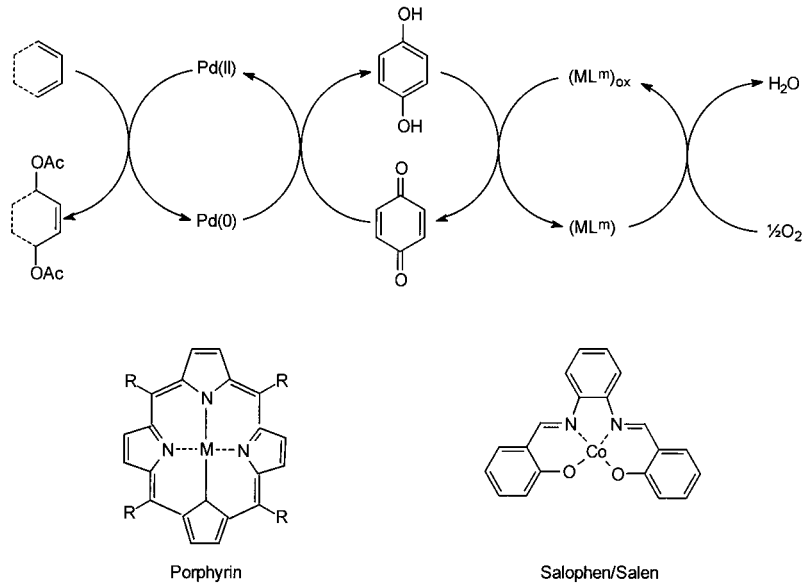


Scheme 1. Triple catalytic system for aerobic oxidation.

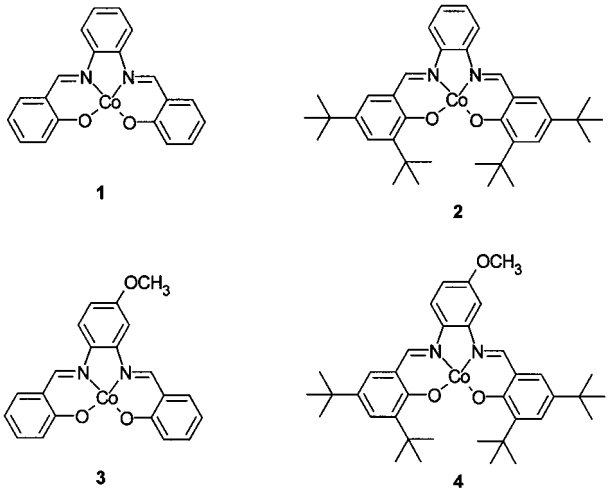
One way to increase the stability of metal macrocyclic complexes in oxidation reactions is to replace the hydrogen atoms of the macrocycle with halogen atoms.[16–18] Thus, perfluorinated porphyrins have shown an interesting stability and also increased activity in aerobic oxidation reactions.[18] An alternative approach to avoid dimerization and degradation of the oxygen-activating catalyst ML^m is to encapsulate it into the supercage of a zeolite. This strategy has previously been used by us[11, 13d] and others[19–25] in oxidation reactions and was found to increase the lifetime of porphyrin and phthalocyanine catalysts, as well as that of the salophen-type catalysts. In preliminary studies, we have shown that iron phthalocyanines and cobalt salophen encapsulated in zeolites are reliable and stable catalysts for aerobic oxidation of hydroquinone to *p*-benzoquinone.[11] These catalysts were employed in the palladium-catalyzed aerobic oxidations of both terminal olefins to ketones and cyclohexene to 2-cyclohexenyl acetate.[11] In this paper we report the preparation of zeolite-encapsulated Co(tetra-*tert*-butyl-salophen) and its efficient application as an oxygen-activating catalyst in the palladium-catalyzed aerobic 1,4-diacetoxylation of 1,3-dienes.

Results and Discussion

Synthesis of cobalt salophen complexes: With the aim of studying the effect of steric hindrance in cobalt salophen complexes, we synthesized four different complexes, **1**–**4**.

The cobalt complexes were prepared by standard methods[9, 14a] from 1,2-diaminobenzene (3-methoxy-1,2-diaminobenzene in the case of complexes **3** and **4**) and salicylaldehyde or 3,5-di-*tert*-butyl-salicyladehyde. The diamine and the aldehyde were refluxed to give the corresponding ligand. When the ligand was refluxed in the presence of cobalt acetate, the cobalt salophen complex was obtained in crystalline form.

Comparison between cobalt salophen catalysts 1–4: The oxygen uptake in the palladium-catalyzed oxidation of 1,3-cyclohexadiene in the presence of the cobalt salophen catalysts **1** and **2** as oxygen-activating complexes was studied. The oxygen uptake was measured by a gas burette. For the cobalt salophen catalyst **1** a linear oxygen uptake was observed (Figure 1). For catalyst **2**, which contains *tert*-butyl groups, the oxygen uptake during the first three hours was faster than for catalyst **1** (Figure 1). The faster initial oxygen uptake for *tert*-butyl-cobalt-salophen **2** may be due to a lower tendency for this catalyst to dimerize. The higher oxygen uptake for catalyst **1** compared to **2** by the end of the reaction is difficult to explain but may be due to oxidative degradation reactions of the former which leads to unproductive oxygen consumption.



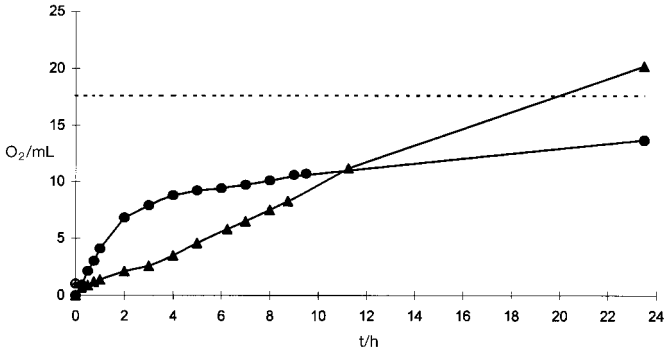


Figure 1. Oxygen uptake for the oxidation of 1,3-cyclohexadiene catalyzed by the triple catalytic system: 1,3-cyclohexadiene (1.19 mmol), $LiOAc_2 \cdot 2H_2O$ (3.31 mmol), hydroquinone (22 mol%), $Pd(OAc)_2$ (4.5 mol%), cobalt catalyst (4.5 mol%). The reactions were carried out in acetic acid (5 mL) at room temperature. ▲: cobalt-salophen **1**, ●: tetra-*tert*-butyl-cobalt-salophen **2**.

In order to evaluate the influence of the different components of the triple catalytic system, oxidation of hydroquinone to benzoquinone was investigated. Figure 2 describes the oxygen uptake for this reaction. The curves in Figure 2 show minor deviations in the activity of the four catalysts. This is in

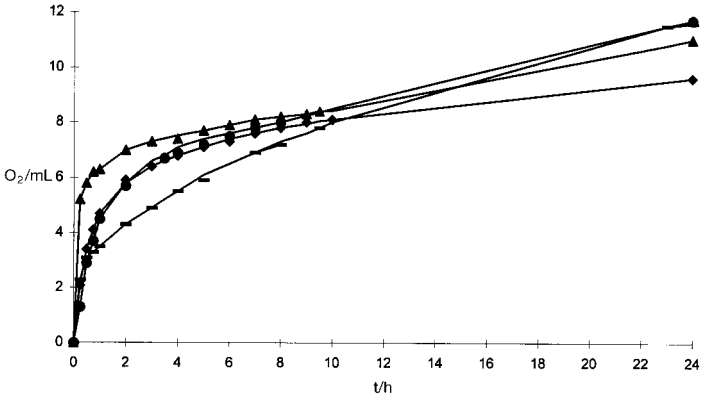


Figure 2. Oxygen uptake for the oxidation of hydroquinone catalyzed by different cobalt salophen complexes: hydroquinone (1.14 mmol), cobalt catalyst (5 mol%). The reactions were carried out in acetic acid (5 mL) at room temperature. -: **1**, ◆: **2**, ●: **3**, ▲: **4**.

contrast to the oxidation of 1,3-cyclohexadiene, shown in Figure 1. One possible explanation for the larger difference between catalyst **1** and **2** in the triple catalytic system is that partial exchange of cobalt for palladium may take place in this case and this metal–metal exchange is expected to be faster for the less sterically hindered catalyst **1**. Stable palladium complexes of Schiff bases obtained from salicylaldehyde are known.[26] If such a metal–metal exchange does occur, the addition of cobalt acetate would, to some extent, inhibit formation of a Pd(salophen) complex by pushing the equilibrium toward Co(salophen). We therefore investigated the effect of cobalt acetate on the oxygen uptake in the presence of palladium(II).

Influence of cobalt acetate on the reaction rate: Indeed, for **2**, an increased oxygen uptake was observed for the diacetoxylation reaction in the presence of cobalt acetate, which further supports a metal–metal exchange (Figure 3). When cobalt acetate was used, the desired 1,4-diacetoxy-2-cyclohexene was obtained in 86% yield in five hours. An improvement of the yield in the presence of catalyst **4** was also observed on addition of cobalt acetate (Table 1). The yields and *cis/trans* selectivities are given in Table 1.

However, with catalysts **1** and **3**, the yield and oxygen uptake in the oxidation of 1,3-cyclohexadiene decreased on addition of cobalt acetate (Figure 3, Table 1). The reason for the decreased yield and oxygen uptake with catalysts **1** and **3** is not clear. This phenomenon occurs for the catalysts without *tert*-butyl groups, while the catalysts substituted with *tert*-butyl groups (**2** or **4**) afforded better yields on addition of cobalt acetate. A control experiment showed that cobalt acetate itself in the absence of cobalt salophen catalyst (**1**–**4**) does not catalyze the aerobic oxidation of hydroquinone.

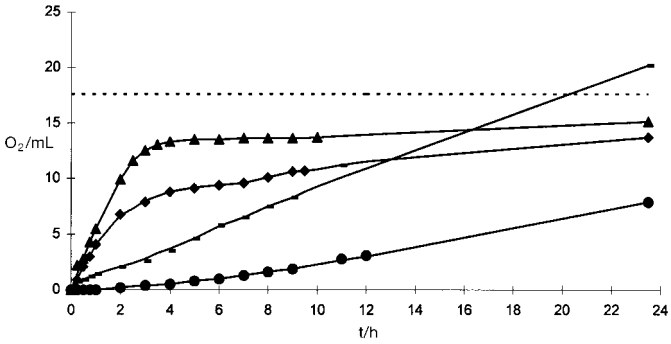


Figure 3. The effect of cobalt acetate on the aerobic oxidation of 1,3-cyclohexadiene catalyzed by the triple catalytic system: 1,3-cyclohexadiene (1.19 mmol), $LiOAc_2 \cdot 2H_2O$ (3.31 mmol), hydroquinone (22 mol%), $Pd(OAc)_2$ (4.5 mol%), cobalt salophen catalyst (4.5 mol%). The reactions were carried out in acetic acid (5 mL) at room temperature. -: **1**, ●: **1**+cobalt acetate, ◆: **2**, ▲: **2**+cobalt acetate.

Table 1. Effect of cobalt acetate on aerobic oxidation of 1,3-cyclohexadiene with complexes **1**–**4**.[a]

Entry	Complex	$Co(OAc)_2 \cdot 4H_2O$[b]	*trans*/*cis*[c]	Time [h]	Yield [%][d]
1	**1**	-	88/12	24	78
2	**1**	2.2 equiv	80/20	24	24
3	**2**	-	90/10	24	74
4	**2**	2.2 equiv	90/10	5	86
5	**3**	-	87/13	24	85
6	**3**	2.2 equiv	80/20	24	61
7	**4**	-	87/13	24	44
8	**4**	2.2 equiv	90/10	24	58

[a] The reactions were carried out employing the reaction conditions of Figure 3. [b] Number of equiv relates to diene. [c] The *trans*/*cis* ratio was determined by ^{1}H NMR spectroscopy. [d] Yield of 1,4-diacetoxy-2-cyclohexene.

Zeolite catalysts for the oxidation of hydroquinone: By the use of catalyst **2** in the presence of cobalt acetate, it was possible to obtain a high yield in the oxidation of 1,3-cyclohexadiene and reduce the reaction time from 24 to five hours (Table 1). To further increase the stability of the metal macrocyclic complex, we decided to study its encapsulation in a zeolite.

For this purpose we prepared catalysts in which complexes **1** and **2** were encapsulated in the supercage of a zeolite (Y type). These new catalysts were prepared by the template method by refluxing a cobalt-exchanged zeolite[11b] with the salicylaldehyde for two hours, followed by addition of 1,2-diaminobenzene. After another two hours reflux, the excess ligand was removed by Soxlet extraction. Drying at 120°C under vacuum afforded the zeolite complexes **1-ZeY** and **2-ZeY** (Figure 4). As shown in Figure 5, the new catalysts obtained by encapsulation of a cobalt salophen complex are more active than the free complex as catalysts for the aerobic oxidation of hydroquinone. The amount of zeolite catalyst employed, 150 mg, contains approximately 0.024 mmol of cobalt salophen catalyst (≈2 mol%).[27]

In both cases the observed oxygen uptake for the catalysts encapsulated in the zeolite is better than for the free catalysts when hydroquinone is the substrate.[28] For the catalyst **2-ZeY**, the activity was dramatically improved and after 30 minutes the oxygen uptake was complete. The high activity of **2-ZeY** is

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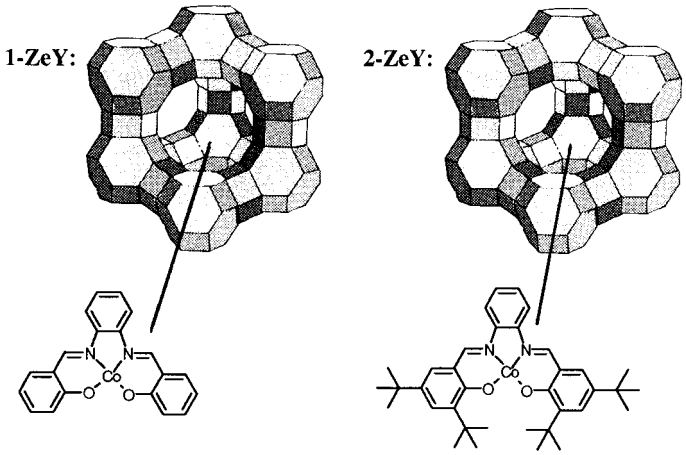

Figure 4. Intrazeolite complexes **1-ZeY** and **2-ZeY** from encapsulation of cobalt salophens into zeolite Y

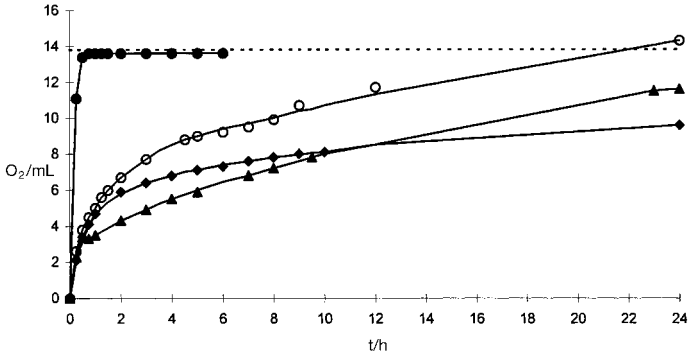

Figure 5. Oxygen uptake for the oxidation of hydroquinone catalyzed by different Co-salophen complexes: hydroquinone (1.14 mmol), cobalt salophen catalyst (5 mol %), or zeolite (150 mg) catalyst. The reactions were carried out in acetic acid (5 mL) at room temperature. ●: **2-ZeY**; ◆: **2**; ○: **1-ZeY**; ▲: **1**.

remarkable and requires some comment. Molecular modeling suggests that **2** would be too large to fit into the ≈13 Å cavity of zeolite Y. However, with a slight distortion of complex **2**, two of the *tert*-butyl groups could protrude from two of the channel windows. Such an explanation was recently proposed to account for the encapsulation of a large metalloporphyrin into zeolite Y.[24]

Zeolite catalysts for the oxidation of 1,3-cyclohexadiene: The next step was to investigate whether the excellent results for catalyst **2-ZeY** could be reproduced in the oxidation of 1,3-cyclohexadiene. The zeolite-encapsulated catalysts **1-ZeY** and **2-ZeY** were compared with the free catalysts **1** and **2** in the aerobic oxidation of 1,3-cycohexadiene (Figure 6). Again, with both zeolite-encapsulated catalysts, the oxygen uptake was much better than with the free cobalt salophen complexes. For the tetra-*tert*-butyl-Co-salophen zeolite catalyst (**2-ZeY**) the oxygen uptake was complete within three hours.

The influence of cobalt acetate on the oxidation of 1,3-cyclohexadiene for the catalysts **1**, **2**, **3** and **4** was discussed above (see Figure 3). For the catalysts which include the *tert*-butyl groups, catalysts **2** and **4**, an increase of the oxygen uptake was detected on addition of cobalt acetate. For **2-ZeY**

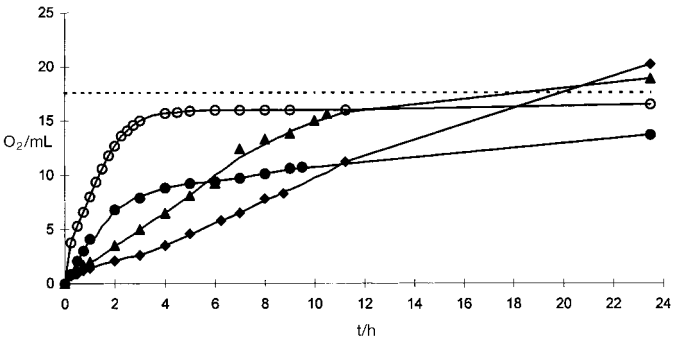

Figure 6. Oxygen uptake for the oxidation of 1,3-cyclohexadiene catalyzed by different cobalt-salophen complexes: 1,3-cyclohexadiene (1.19 mmol), $LiOAc_2 \cdot 2H_2O$ (3.31 mmol), $Pd(OAc)_2$ (5 mol %), hydroquinone (22 mol %), cobalt salophen catalyst (5 mol %), or zeolite catalyst (150 mg). The reactions were carried out in acetic acid (5 mL) at room temperature. ◆: **1**, ▲: **1-ZeY**, ●: **2**, ○: **2-ZeY**.

the oxygen uptake and the yield in the oxidation reaction of 1,3-cyclohexadiene is roughly the same whether cobalt acetate is used or not (Table 2). For the catalyst **1-ZeY** the oxygen uptake was significantly decreased on addition of cobalt acetate. This is in accordance with the results for the non-encapsulated catalyst **1**. The reason for this negative effect by cobalt acetate on the nonsubstituted salophen complexes is unclear at present. The yields and *cis/trans* selectivities for the experiments with zeolite complexes **1-ZeY** and **2-ZeY** are given in Table 2.

Table 2. Effect of cobalt acetate on aerobic oxidation of 1,3-cyclohexadiene with complexes **1-ZeY** and **2-ZeY**.[a]

Entry	Complex	$Co(OAc)_2 \cdot 4H_2O$[b]	*trans*/*cis*[c]	Yield [%][d]
1	**1-ZeY**	-	88/12	72
2	**1-ZeY**	2.2 equiv	85/15	57
3	**2-ZeY**	-	90/10	84
4	**2-ZeY**	2.2 equiv	89/11	85

[a] The reactions were carried out employing the reaction conditions of Figure 6. [a] Number of equiv relates to diene. [c] The *trans*/*cis* ratio was determined by ^{1}H NMR spectroscopy. [d] Yield of 1,4-diacetoxy-2-cyclohexene.

Zeolite catalyst recovery and scale-up: The results with the zeolite catalyst **2-ZeY** show that it is possible to oxidize 1,3-cyclohexadiene to 1,4-diacetoxy-2-cyclohexene in high yield, with good *cis/trans* selectivity and short reaction times.

An important test of the new zeolite-encapsulated catalyst **2-ZeY** was to recover and reuse it after an aerobic 1,4-diacetoxylation reaction. Thus, after three hours, once oxygen uptake was complete, the zeolite catalyst **2-ZeY** was filtered off and used in a second run. This procedure was repeated a third time. Small amounts of the zeolite catalyst were lost during work-up, so the next reaction was run on smaller scale. The results given in Table 3 show that the catalyst can be reused and that efficiency is maintained in the second run and is only slightly lower in the third run. The yields of the reactions were 85 % (1st run), 80 % (2nd run) and 78 % (3rd run). When the reaction was run at 40 °C, the reaction time drops to 1.5 h with the same yield and *cis*/*trans* selectivity as for the reaction carried out at room temperature.

Table 3. Aerobic oxidation of 1,3-cyclohexadiene with recovery and reuse of **2-ZeY**.[a]

Entry	Run	1,3-Cyclohexadiene [mmol]	Time [h]	Yield [%][b]
1	1	1.19	3	85
2	2	1.02	4	80
3	3	1.02	6	78

[a] All reactions were carried out as in Table 2, entry 3. [b] Yield of *trans*-1,4-diacetoxy-2-cyclohexene > 90 % *trans*).

We next studied the scale-up of the reaction. Therefore, the concentration of starting material in acetic acid and the amount of zeolite catalyst were increased. Table 4 shows that a concentration of 10.5 mmol 1,3-cyclohexadiene in 25 mL acetic acid leads to a 95 % isolated yield after three hours at room temperature (entry 2). Attempts to run the reaction at even higher concentration resulted in poor yields and with 105 mmol in 25 mL the yield was less than 15 % (entry 3). A likely explanation of this phenomenon is that the Diels–Alder reaction between benzoquinone and 1,3-cyclohexadiene predominates at this high concentration.[29, 30]

Table 4. Effect of the concentration in aerobic oxidation of 1,3-cyclohexadiene.[a]

Entry	1,3-Cyclohexadiene [mmol]	HOAc [mL]	**2-ZeY** [g]	Yield [%][b]
1	1.19	5	0.15	85
2	10.5	25	1.0	95
3	105	25	2.5	15

[a] The reactions were carried out under 1 atm of O_2 at room temperature employing 4.5 mol % of $Pd(OAc)_2$ and 22 mol % hydroquinone. The reactions were run for 3 h. [b] Yield of *trans*-1,4-diacetoxy-2-cyclohexene > 90 % *trans*).

In the attempt to scale-up the reaction, it was evident that there is a limit for the concentration of the diene (Table 4). To utilize the catalytic system in a more efficient way, continuous addition of 1,3-cyclohexadiene was explored to maintain a moderate concentration throughout the reaction. Therefore, the same reaction conditions from the best batch reaction were employed but now the diene was added continuously with a syringe pump. Figure 7 shows the oxygen uptake for continuous addition of 1,3-cyclohexadiene (15.8 mmol) over seven hours. The straight line shows the theoretical maximum O_2 uptake if conversion occurs at the same rate as addition. After two hours, the oxygen uptake is lower and the efficiency of the catalytic system decreases. The gap between the theoretical uptake and the measured uptake becomes larger with time. This is most likely due to the formation of a Diels–Alder adduct between the 1,3-cyclohexadiene and 1,4-benzoquinone, which results in decreased activity.[29, 30]

The efficiency of the system could be increased by decreasing the rate of addition and therefore the steady-state concentration of diene (Figure 8). As can be seen from Figure 8, there is no difference between the observed and the maximum O_2 uptake during the first 3.5 hours. The turnover number (TON) on palladium after 3.5 h is 97. After this time the oxygen uptake curve deviates from the straight line and the efficiency of the system slowly decreases. After nine hours the TON is 190 with respect to the palladium catalyst.

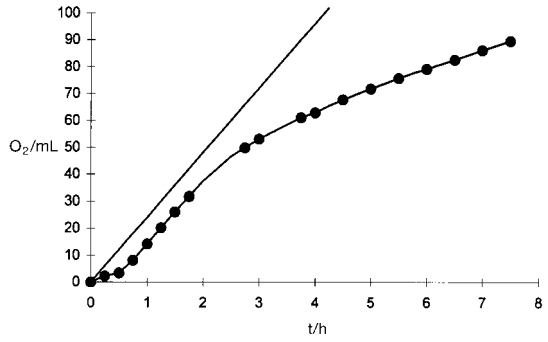

Figure 7. 1,3-Cyclohexadiene (1.5 mL, 15.8 mmol) was added by a syringe pump over 7 h. The line gives the theoretical oxygen uptake (6 mL/15 min). The curve gives the experimental oxygen uptake. The reaction was carried out at 40 °C, with $Pd(OAc)_2$ (12 mg, 0.053 mmol), hydroquinone (28 mg, 0.26 mmol), 150 mg catalyst **2-ZeY**, $Co(OAc)_2 \cdot 4H_2O$ (654 mg, 2.63 mmol), and $LiOAc_2 \cdot 2H_2O$ (3.38 mg, 3.31 mmol) in acetic acid (5 mL).

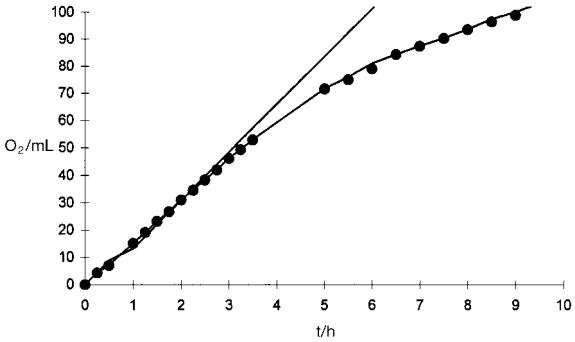

Figure 8. 1,3-Cyclohexadiene (1.2 mL, 12.6 mmol) was added by a syringe pump over 8 h. The line gives the theoretical oxygen uptake (4.42 mL/15 min). The curve gives the experimental oxygen uptake. The reaction was carried out at 40 °C, with $Pd(OAc)_2$ (12 mg, 0.053 mmol), hydroquinone (28 mg, 0.26 mmol), 150 mg catalyst **2-ZeY**, $Co(OAc)_2 \cdot 4H_2O$ (653 mg) and $LiOAc_2 \cdot 2H_2O$ (3.38 mg, 3.31 mmol) in acetic acid (5 mL). The turnover number (TON) is 97 after 3.5 hours and 190 after 9 hours. The corresponding estimated TONs on **2-ZeY** were 214 and 420.

After a yield of 85–95 % of 1,4-diacetoxy-2-cyclohexene was obtained in the aerobic oxidation of 1,3-cyclohexadiene at 20–40 °C with reaction times of 1.5–3 h, we also applied our triple catalytic system to the 1,4-diacetoxylation reaction of 1,3-cycloheptadiene. The preparative results for the two dienes are summarized in Table 5. The *trans*-diacetate from 1,3-cyclohexadiene was obtained on a multi-gram scale in 95 % yield after three hours at room temperature (entry 3). Reaction of 1,3-cycloheptadiene at room temperature gave only 40 % yield after 24 hours. When the reaction time was prolonged to 48 hours, the yield increased to 57 % (entry 6). When the reaction was run at 40 °C, the yield improved to 72 % but at the expense of the selectivity for the *cis* product (entry 7). Finally, an increase of the LiOAc concentration resulted in a yield of 69 % of the diacetate (entry 8) with a good *cis* selectivity (> 95 % *cis*).

Conclusion

This paper provides an example of the successful combination of homogeneous and heterogeneous catalysis. The homoge-

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Table 5. Pd-catalyzed aerobic 1,4-diacetoxylation with **2-ZeY** as oxygen-activating catalyst.[a]

Entry	Starting material	Product	Time	Temperature	Yield [%][b]	*trans*/*cis*[c]
1			3h	RT	85	90:10
2			1.5 h	40 °C	85	90:10
3			3 h	RT	95[d]	> 91 % *trans*
4			24 h	RT	40	6:94
5			40 h	RT	52	9:91
6			48 h	RT	57	9:91
7			24 h	40 °C	72	18:82
8			24 h	RT	69[e]	> 95 % *cis*

[a] Unless otherwise noted the reactions were carried out with 1.19 mmol of diene employing 3.31 mmol of $LiOAc_2 \cdot 2H_2O$, 4.5 mol % of $Pd(OAc)_2$, 22 mol % of hydroquinone, and 150 mg of **2-ZeY** in acetic acid (5 mL). [b] Yield of isolated product. [c] The *trans*/*cis* ratio was determined by ^1H NMR spectroscopy. [d] 10.5 mmol of diene and 1.0 g of **2-ZeY**. [e] 16.6 mmol $LiOAc_2 \cdot 2H_2O$ and 25 mol % of hydroquinone.

neous part controls the selectivity of the organic transformation; the heterogeneous part contains the oxygen-activating catalyst protected by a zeolite framework. Zeolite-encapsulated tetra-*tert*-butyl-Co-salophen **2-ZeY** was found to be an efficient oxygen-activating catalyst in the palladium-catalyzed aerobic 1,4-diacetoxylation of 1,3-dienes. The unexpectedly high activity of this catalyst, as observed in the aerobic re-oxidation of hydroquinone to benzoquinone, can be explained by distortion of the complex **2** in zeolite Y.

Experimental Section

NMR spectra were recorded with a Varian XL-300 spectrometer. All NMR spectra were recorded in $CDCl_3$ or [D_6]DMSO solutions with tetramethylsilane as the internal standard for ^1H NMR and $CDCl_3$ for ^{13}C NMR. Analytical gas chromatography was performed with a Varian 3400 GC with FID detector connected to a Varian 4270 computing integrator. A 30 m DB-5 J&M fused silica column was used. The IR spectra were recorded with a Perkin-Elmer 1600 Series FTIR spectrometer. The oxygen uptake was measured by a gas burette.

Co(salophen) (**1**): For the preparation and spectroscopic data see ref. [9].

Tetra-*tert*-butyl-salophen (*N*,*N*′-bis-(3,5-di-*tert*-butylsalicylidene)-1,2-phenylenediamine): 3,5-Di-*tert*-butylsalicylaldehyde (500 mg, 2.14 mmol) and 1,2-diaminobenzene (108 mg, 1 mmol) were refluxed in ethanol (4 mL; 95 %) for 3 h. The solution was allowed to cool to room temperature and left for 44 h. The precipitate was filtered off and washed with ethanol. The product was dried under high vacuum to yield 453 mg (84 %) as yellow crystals. M.p. 193 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 13.54$ (s, 2H), 8.66 (s, 2H), 7.44 (d, $J = 2$, 2H), 7.34 – 7.27 (m, 4H), 7.27 – 7.34 (m, 4H), 1.44 (s, 18H), 1.32 (s, 18H); ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta = 164.53$, 158.41, 142.61, 140.16, 137.05, 128.05, 127.19, 126.65, 119.69, 118.24, 35.16, 34.21, 31.51, 29.47; IR ($CDCl_3$): $\tilde{\nu} = 3904$, 3870, 3854, 3838, 3821, 3802, 3751, 3735, 3712, 3690, 3676, 3649, 3629, 3567, 2963, 2253, 1793, 1734, 1718, 1700, 1684, 1654, 1616, 1576, 1508, 1466, 1438, 1393, 1363, 1272, 1250, 1200, 1171, 1106, 908, 734 651 cm^{-1}.

Tetra-*tert*-butyl-Co-salophen (**2**): Tetra-*tert*-butylsalophen ligand (756 mg) was suspended in 95 % ethanol (36 mL) under reflux. Potassium hydroxide (133 mg) was dissolved in ethanol (4.7 mL) and added to the solution. The mixture was refluxed until all of the salophen **5** was dissolved. $Co(OAc)_2 \cdot 4H_2O$ (756 mg, 3.04 mmol) was dissolved in water (2.3 mL) and added to the reaction mixture. After 1 h of reflux, the mixture was cooled down to room temperature and stirred for another hour. $LiOAc \cdot 2H_2O$ (344 mg, 3.37 mmol) in water (1.1 mL) was added. The mixture was stirred for another 3 h. The reaction mixture was filtered through a short celite pad and washed with ethanol. The solution was evaporated to a volume of approximately 10 mL and water (37 mL) was added. After the solution was left to stand overnight, the precipitated brown crystals were filtered off and washed with water. The crystals were dissolved in dichloromethane and the solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent and drying under high vacuum (0.05 mbar) at 100 °C for 7 h afforded 404 mg (46 %) of **2**. IR ($CDCl_3$): $\tilde{\nu} = 3852$, 3820, 3749, 3733, 3710, 3688, 3674, 3445, 3258, 3208, 2492, 1684, 1653, 1616, 1507, 1457, 1416, 1108, 1069, 1022, 895, 836, 720, 615 cm^{-1}.

Methoxy-salophen ligand (*N*,*N*′-bis(salicylidene)-4-methoxy-1,2-phenylenediamine): 3-Methoxy-1,2-diaminobenzene (461 mg, 3.34 mmol) and salicylaldehyde **2** (0.78 mL, 7.35 mmol)) were dissolved in 95 % ethanol (3 mL) under reflux for 3 h. After the mixture was cooled to room temperature, a black oil was formed which was used without further purification for the Co-complex formation.

Methoxy-Co-salophen (**3**): The crude product of methoxy-salophen ligand (from methoxy-*o*-phenylendiamine (461 mg, 3.34 mmol) and salicylaldehyde (0.78 mL, 7.35 mmol) was dissolved in 95 % ethanol (33 mL) under reflux. Potassium hydroxide (206 mg, 3.68 mmol) was dissolved in ethanol (15 mL) and added to the solution. The mixture was refluxed until all the salophen ligand had dissolved. $Co(OAc)_2 \cdot 4H_2O$ (2.56 g, 10.3 mmol) was dissolved in water (7.4 mL) and the resulting solution was added to the reaction mixture. After 1 h of reflux, the mixture was cooled down to room temperature and stirred for another hour. $LiOAc \cdot 2H_2O$ (1.12 g; 11.0 mmol) in water (3.6 mL) was added. The mixture was stirred for another 3 h. The reaction mixture was filtered through a short celite pad and washed with ethanol. The solution was evaporated to approximately 15 mL and water (180 mL) was added. After the mixture was left to stand overnight, the brown crystals were filtered off and washed with water. The crystals were dissolved in dichloromethane and the solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent and drying under high vacuum (0.05 mbar) at 100 °C for 7 h afforded 152 mg (11 % over two steps) of **3**.

Methoxy-tetra-*tert*-butylsalophen ligand (*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-4-methoxy-1,2-phenylenediamine): 3-Methoxy-1,2-diaminobenzene (438 mg, 3.17 mmol) and 3,5-di-*tert*-butyl-salicylaldehyde (1.632g, 6.97 mmol) were dissolved in 95 % ethanol (3 mL) and refluxed for 1 h. The precipitate was filtered off. Recrystallization from ethanol (95 %) and drying under high vacuum afforded 767 mg (43 %). M.p. 204 °C. ^1H NMR ($CDCl_3$): $\delta = 13.66$ (s, 1H), 13.44 (s, 1H), 8.65 (s, 2H), 7.45 – 7.44 (d, $J = 2$, 1H), 7.42 – 7.41 (d, $J = 2$, 1H), 7.25 – 7.19 (m, 3H), 6.87 – 6.86 (d, $J = 3$, 1H), 6.83 – 6.84 (d, $J = 1$, 1H), 6.76 – 6.75 (d, $J = 3$, 1H), 3.87 (s, 3H), 1,45 (s, 9H), 1.42 (s, 9H), 1.32 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 164.95$, 162.67, 160.74, 158.91, 158.46, 158.22, 143.84, 140.24, 140.08, 137.10, 136.95, 135.67, 120.21, 127.62, 126.76, 126.43, 120.10, 118.43, 118.18, 112.56, 105.42, 55.73, 35.20, 35.17, 34.23, 31.56, 29,51; IR ($CDCl_3$): $\tilde{\nu} = 3854$, 3838, 3751, 3735, 3690, 3676, 3649, 3629, 2962, 2253, 1793, 1654, 1616, 1498, 1466, 1438, 1363, 1274, 1249, 1198, 1170, 1101, 1039, 908, 734, 650 cm^{-1}.

Methoxy-tetra-*tert*-butyl-Co-salophen (**4**)**:** Methoxy-tetra-*tert*-butyl-salophen (750 mg, 1.315 mmol) was dissolved in 95 % ethanol (36 mL) under reflux. A solution of potassium hydroxide (142 mg) in ethanol (5 mL) was added and the mixture was refluxed until all the methoxy-tetra-*tert*-butyl-salophen ligand had been dissolved. $Co(OAc)_2 \cdot 4H_2O$ (805 mg, 3.23 mmol) was dissolved in water (2.5 mL) and added to the reaction mixture. After 1 h under reflux, the mixture was cooled to room temperature and stirred for another hour. $LiOAc \cdot 2H_2O$ (366 mg, 3.59 mmol) in water (1.2 mL) was added and the mixture was stirred for another 3 h and then filtered through a short celite pad. The solution was concentrated in vacuum to approximately 15 mL and then diluted with water (40 mL). After the mixture was left to stand overnight, the precipitated brown crystals were filtered off and washed with water. The crystals were dissolved in dichloromethane and the solution was washed with water and dried ($MgSO_4$). Evaporation of the solvent and drying under high vacuum (0.05 mbar) at 100 °C afforded 202 mg (25 %) of **4**.

Cobalt-exchanged zeolite (CoY zeolite): NaY zeolite was dried at 500 °C for at least 12 h. The dried zeolite (1 g) was stirred and refluxed for 72 h with an aqueous solution of $Co(OAc)_2 \cdot 4H_2O$ (0.1M, 25 mL). The pink solid

was filtered off and dried under vacuum (120 °C, 0.05 mbar) until it turned violet (5 h).

Co-salophen zeolite 1-ZeY: CoY zeolite (1 g) from above was dried under high vacuum for 2 h at 100 °C. Dry ethanol (10 mL) and *o*-phenylendiamine (0.5 g) were added. The reaction mixture was stirred for 1 h under reflux. Salicylaldehyde (1.1 g) was added and the reflux was continued for another 2 h. The mixture was filtered and the solid residue was extracted in a Soxleth extractor until the eluate became colorless (8 h). Noncomplexed cobalt ions were replaced by sodium ions by gentle reflux with saturated NaOAc (75 mL). The solid catalyst, **1-ZeY**, was filtered off, washed with water (50 mL) and dried at 110 °C under high vacuum (0.05 mbar) for 7 h.

Co-salophen zeolite 2-ZeY: CoY zeolite (1 g) from above was dried under high vacuum for 2 h at 100 °C. Dry ethanol (10 mL) and 3,5-di-*tert*-butylsalicylaldehyde (1.079 g) were added. The reaction mixture was stirred for 2 h under reflux. *o*-Phenylendiamine (235 mg) was added and the reflux was continued for another 2 h. Work-up as described for **1-ZeY**.

General Procedure for the catalytic aerobic oxidation of hydroquinone to benzoquinone with different cobalt salophen complexes (1, 2, 3, or 4): Hydroquinone (125 mg, 1.14 mmol) and the appropriate Co-salophen complex (0,057 mmol, 5 mol %) were added to acetic acid (2.5 mL). The reaction mixture was stirred at room temperature under 1 atm oxygen for 24 h. The oxygen uptake was measured.

General procedure for palladium(II)-catalyzed aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene with different cobalt salophen complexes (1, 2, 3, or 4): The appropriate Co-salophen complex (4.5 mol %) was added to a solution of 1,3-cyclohexadiene (113 μL, 1.19 mmol), $LiOAc \cdot 2H_2O$ (338 mg, 3.31 mmol), $Pd(OAc)_2$ (12 mg, 4.5 mol %), and hydroquinone (29 mg, 22 mol %) in acetic acid (5 mL). The resulting slurry was stirred at room temperature and the oxygen uptake was measured under 1 atm of oxygen. After 24 h, the reaction mixture was diluted with brine (10 mL) and extracted with pentane (10 mL). The aqueous layer was extracted again with pentane:ether 4:1 (20 mL). The combined organic layers were washed twice with 2 M NaOH (10 mL) and brine (10 mL). The organic layer was dried ($MgSO_4$) and the solvents were evaporated. The product was characterized according to ref. [30a] and the *cis*/*trans* ratio was determined by ^1H NMR.

General procedure for palladium(II)-catalyzed aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene with different cobalt salophen complexes in the presence of cobalt acetate hydrate: The same procedure and the same amounts of compounds as described above for the palladium(II)-catalyzed aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene was used. In addition, $Co(OAc)_2 \cdot 4H_2O$ (654 mg, 2.63 mmol) were used.

General procedure for the catalytic aerobic oxidation of hydroquinone to benzoquinone with different cobalt salophen zeolite complexes (1-ZeY or 2-ZeY): Hydroquinone (125 mg; 1.14 mmol) and the appropriate Co-salophen zeolite complex (150 mg) were added to acetic acid (2.5 mL). The reaction mixture was stirred at room temperature under 1 atm of oxygen for 24 h. The oxygen uptake was measured.

General procedure for palladium(II)-catalyzed aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene with different cobalt salophen zeolite complexes (1-ZeY or 2-ZeY): The appropriate Co-salopen zeolite catalyst (150 mg) was added to a solution of 1,3-cyclohexadiene (113 μL, 1.19 mmol), $LiOAc \cdot 2H_2O$ (338 mg, 3.31 mmol), $Pd(OAc)_2$ (12 mg, 4.5 mol %), and hydroquinone (29 mg, 22 mol %) in acetic acid (5 mL). The resulting slurry was stirred at room temperature and the oxygen uptake was measured under 1 atm of oxygen. After the appropriate reaction time (24 h for **1-ZeY**; 3 h for **2-ZeY**) the reaction mixture was diluted with saturated NaOAc (10 mL) and worked up as described above. The use of **1-ZeY** and **2-ZeY** gave 72 % and 85 % yield, respectively.

Recovery and reuse of 2-ZeY for 1,4-diacetoxylation of 1,3-cyclohexadiene. The zeolite catalyst **2-ZeY** from the above experiment was collected by filtration and washed with water (50 mL), EtOH (50 mL) and ether (50 mL). Drying under vacuum (0.05 mbar) at 100 °C afforded 125 mg of the recovered zeolite catalyst. This catalyst was reused in a second 1,4-diacetoxylation following the procedure described above (4 h) to give 80 % yield of 1,4-diacetoxy-2-cyclohexene (>90 % *trans*). Recovery of **2-ZeY** with the same procedure and reuse in a third 1,4-diacetoxylation (6 h) afforded 78 % yield of 1,4-diacetoxy-2-cyclohexene (>90 % *trans*).

General procedure for palladium(II)-catalyzed aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene with different cobalt salophen complexes (1-ZeY or 2-ZeY) in the presence of $Co(OAc)_2 \cdot 2H_2O$: The same procedure and the same amounts of compounds as described for the palladium(II)-catalyzed aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene with cobalt salophen zeolite complexes were used. $Co(OAc)_2 \cdot 4H_2O$ (654 mg; 2.63 mmol) was employed.

1,4-Diacetoxy-2-cyloheptene: **2-ZeY** (150 mg) was added to a solution of 1,3-cycloheptadiene (129 μL, 1.19 mmol), $LiOAc \cdot 2H_2O$ (1.69 g; 16.5 mmol), $Pd(OAc)_2$ (12 mg; 4.5 mol %), and hydroquinone (29 mg, 22 mol %) in acetic acid (5 mL). The resulting slurry was stirred at room temperature and the oxygen uptake was measured under 1 atm of oxygen. After 24 h the reaction mixture was diluted with saturated NaCl (10 mL) and worked up as described above. The product was characterized according to ref. [30a] and the *cis*/*trans* ratio was determined by ^1H NMR spectroscopy.

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