the disorder model to be overly simplified.

**Acknowledgment**. We thank the NIH for support of this research and NRSA Postdoctoral Fellowships (C.M.G., J.J.K.) and K. Houk for the data in ref 33a.

**Supplementary Material Available**: Tables of atomic coordinates and anisotropic thermal parameters for (*RS,SR*)-$3b^+BF_4^-$ and (*RS,SR*)-$3f^+PF_6^-\cdot(CH_2Cl_2)_{0.5}$ and NMR data for **10** (8 pages); table of calculated and observed structure factors for (*RS,SR*)-$3b^+BF_4^-$ (19 pages).[53] Ordering information is given on any current masthead page.

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[53] Calculated and observed structure factors for (*RS,SR*)-$3f^+PF_6^-\cdot(CH_2Cl_2)_{0.5}$ are given in the supplementary material in ref 12.

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# Multistep Electron Transfer in Palladium-Catalyzed Aerobic Oxidations via a Metal Macrocycle–Quinone System

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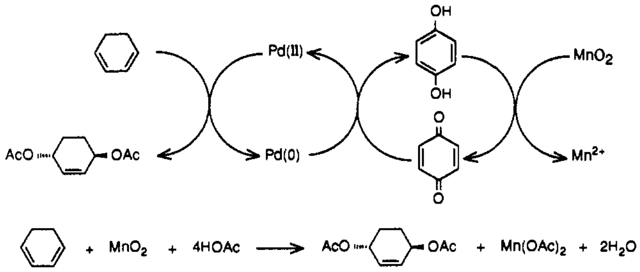
**Abstract**: Selective palladium-catalyzed aerobic conditions of olefins and conjugated dienes with the aid of a metal macrocycle–quinone system have been developed. This involves a multistep electron transfer with three catalysts ($Pd(OAc)_2$, hydroquinone, metal macrocycle). The triple catalytic system was applied to (i) 1,4-oxidation of conjugated dienes (1,4-diacetoxylation and 1,4-dialkoxylation), (ii) oxidation of terminal olefins to ketones, and (iii) allylic oxidation of cyclic olefins to 2-alken-1-yl acetates. The reactions occur under very mild conditions, (i) and (ii) at room temperature and (iii) at 60 °C, and are reminiscent of aerobic processes occurring in living organisms. Thus, there is an electron transfer from the substrate to Pd(II) giving Pd(0), followed by another electron transfer from Pd(0) to benzoquinone. The hydroquinone thus formed transfers electrons to the oxidized form of the metal macrocycle, which is reduced. The latter is reoxidized by electron transfer to molecular oxygen. A number of metal macrocycles such as metal(salen) complexes Co(salophen), Co(TPP), and iron phthalocyanine (Fe(Pc)) were tested as oxygen-activating complexes. In the 1,4-diacetoxylation of 1,3-dienes, and in the allylic oxidation, several of these metal macrocycles gave good results. In the 1,4-dialkoxylation of 1,3-dienes and in the oxidation of terminal olefins to ketones, which occur in the presence of a strong acid, only Fe(Pc) survived the reaction conditions.

Metal-catalyzed oxidation of organic compounds is an expanding area of organic chemistry with many applications in industrial processes.[1,2] Today there is an increasing need for mild aerobic catalytic processes due to energy saving and environmental reasons. Most of the known oxidation processes based on molecular oxygen, however, require elevated temperature and pressure.

Scheme I



Recently, macrocyclic metal complexes, in particular metalloporphyrins, have attracted attenation as catalysts in oxidation reactions.[3-9] Most of the metalloporphyrins used have utilized oxidants such as iodosylbenzene,[4] hypochlorite,[5] persulfate,[6] and peroxide.[7] There are only a few examples[8,9] of the use of molecular oxygen as the ultimate oxidant, and in these systems, except in a few,[8c,9] a reductive activation of oxygen is needed. We have been engaged in palladium-catalyzed oxidation of olefins and conjugated dienes and have developed a number of selective reactions.[9-12] Recently we were able to develop procedures that allow an aerobic oxidation via a multistep electron transfer involving three redox systems Pd(II)/Pd(0)–benzoquinone/hydroquinone–$ML^m_{ox}/ML^m$, where $ML^m$ is an oxygen activating macrocyclic transition metal complex.[9] In this paper we give a full account of this remarkably mild triple catalytic system. It has been applied to three principal types of reactions: (i) oxidation

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[1] (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

[2] Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980.

[3] For a review, see: Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, 578.

[4] (a) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (b) Groves, J. T.; Kruper, W. J.; Haushalter, R. S. *Ibid.* **1980**, *102*, 6375. (c) Hill, C. L.; Schardt, J. A. *Ibid.* **1980**, *102*, 6374.

[5] (a) Guilmet, E.; Meunier, B. *Tetrahedron Lett.* **1980**, *21*, 4449. (b) De Carvalo, M. E.; Meunier, B. *Tetrahedron Lett.* **1983**, *24*, 3621.

[6] De Poorter, B.; Ricci, M.; Meunier, B. *Tetrahedron Lett.* **1985**, *26*, 4459.

[7] (a) Renaud, J. P.; Battioni, P.; Bartoli, J. F.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1985**, 888. (b) Mansuy, D.; Bartoli, J. F.; Momenteau, M. *Tetrahedron Lett.* **1982**, *23*, 2781.

[8] (a) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456. (b) Perrée-Fauvet, M.; Gaudemer, A. *J. Chem. Soc., Chem. Commun.* **1981**, 874. (c) Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790. (d) Tabushi, I.; Morimitsu, K. *Ibid.* **1984**, *106*, 6871. (e) Mansuy, D.; Fontecave, M.; Bartoli, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 253.

[9] (a) Bäckvall, J. E.; Awasthi, A. K.; Renko, Z. D. *J. Am. Chem. Soc.* **1987**, *109*, 4750. (b) Bäckvall, J. E.; Hopkins, R. B. *Tetrahedron Lett.* **1988**, *29*, 2885.

[10] (a) Bäckvall, J. E.; Nyström, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 3676. (b) Bäckvall, J. E.; Granberg, K. L.; Hopkins, R. B. *Acta Chem. Scand.* In press.

[11] (a) Bäckvall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619. (b) Bäckvall, J. E.; Vågberg, J.; Nordberg, R. E.; *Tetrahedron Lett.* **1984**, *25*, 2717.

[12] Bäckvall, J. E.; Vågberg, J. O. *J. Org. Chem.* **1988**, *53*, 5695.

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of 1,3-dienes to 1,4-diol derivatives; (ii) oxidation of terminal olfeins to methyl ketones; and (iii) allylic oxidation of cyclic olefins.

## Results and Discussion

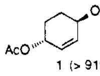
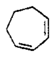
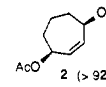
Benzoquinones are well-known oxidants in synthetic organic chemistry[13] and they have found use as oxidants and electron carriers in selective palladium-catalyzed oxidations.[9-12,14-18] One important goal of this research is to find a rapid and mild system for reoxidation of hydroquinone to benzoquinone by molecular oxygen.

**Aerobic 1,4-Oxidation of Conjugated Dienes.** We have developed a number of stereoselective palladium-catalyzed 1,4-oxidations of conjugated dienes.[10-12,19] These reactions proceed through a ($\pi$-allyl)palladium intermediate formed by addition of a nucleophile to the 1-position of the diene. Attack by the second nucleophile, which is induced by coordination of an electron-withdrawing ligand such as *p*-benzoquinone, gives the product. In these reactions the formal oxidant is either *p*-benzoquinone or $MnO_2$/catalytic amounts of *p*-benzoquinone. In the latter case the quinone serves as a catalytic electron carrier and $MnO_2$ is continuously reoxidizing hydroquinone to benzoquinone. Thus an efficient oxidation reaction of conjugated dienes with $MnO_2$ as the oxidant was developed.[11] The principal stoichiometry for this "double-catalysis" is depicted in Scheme I.

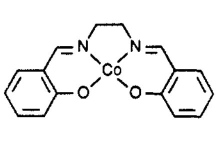
It would be of great interest if one could reoxidize the hydroquinone with oxygen under these reaction conditions, thus replacing $MnO_2$ by $O_2$. Unfortunately, direct oxidation of hydroquinone to benzoquinone by molecular oxygen is too slow at room temperature to match the rate of the other steps of the catalytic reaction. However, it has been reported that metal–salen complexes and related metal–macrocycles catalyze the aerobic oxidation of catechols and hydroquinones to quinones.[20,21] We therefore undertook a study with the aim of replacing $MnO_2$ in Scheme I by catalytic amounts of a macrocyclic metal complex and molecular oxygen.

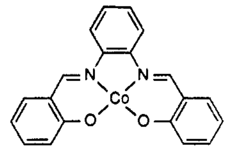
The first examples of macrocyclic complexes studied were the metal(salen) complexes. It was found that Co(salen)/$O_2$ was able to reoxidize hydroquinone (HQ) to benzoquinone (BQ) in the palladium-catalyzed 1,4-diacetoxylation reaction (cf. Scheme I). Thus, reaction of 1,3-cyclohexadiene with $O_2$ (1 atm) at 25 °C in a biphasic system of hexane and acetic acid in the presence of LiOAc and catalytic amounts of $Pd(OAc)_2$ (5 mol %), hydroquinone (15 mol %), and Co(salen) (9 mol %) afforded a 47% yield of *trans*-1,4-diacetoxy-2-cyclohexene (**1**) (trans/cis = 90/10). The rate of the total oxidation was linearly dependent on the concentration of Co(salen) in the range 3–9 mol %, indicating that the rate-limiting step is the reoxidation of hydroquinone. In our preliminary communication[9a] we suggested that the slow reoxidation may be a consequence of a slow electron transfer from hydroquinone to the oxidized form of Co(salen). However, later control experiments have shown that Co(salen)-catalyzed aerobic oxidation of hydroquinone to benzoquinone in acetic acid is much faster than the oxidation in the triple catalytic system (vide infra). A more likely explanation to the low rate of the aerobic oxidation of 1,3-cyclohexadiene is therefore that Co(salen) undergoes degradation, e.g. hydrolysis of the imine function.[22]

**Table I.** Palladium-Catalyzed Aerobic 1,4-Diacetoxylation of Conjugated Dienes with a Triple Catalytic System[a]

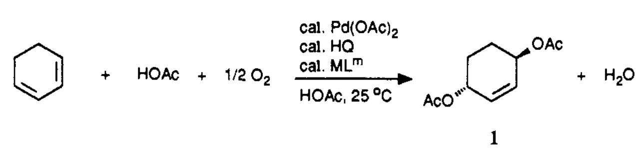
| entry | Starting material | mol%[b] $Pd(OAc)_2$ | mol %[b] HQ | $ML^m$ (mol %)[b] | reaction time | Product | % yield[c] |
|---|---|---|---|---|---|---|---|
| 1 |  | 5 | 15 | Co(salen) (9) | 35[d] |  **1** (> 91% trans) | 47 |
| 2 | | 5 | 15 | Co(salophen (5) | 18 | **1** (> 91% trans) | 79 |
| 3 | | 5 | 7 | Co(salophen (5) | 26[d] | **1** (> 91% trans) | 89 |
| 4 | | 5 | 5 | Co(TTP) (5) | 18[d] | **1** (> 91% trans) | 89 |
| 5 | | 5 | 5 | Mn(TPP) (5) | 48 | **1** (trans/cis = 72/28) | 56 |
| 6 | | 5 | 7 | Fe(Pc) (5) | 12 | **1** (> 91% trans) | 77 |
| 7 |  | 5 | 5 | Co(TPP) (5) | 36[e] |  **2** (> 92% cis) | 65 |
| 8 | | 5 | 10 | Fe(Pc) (5) | 48 | **2** (> 93% cis) | 66 |

[a] Unless otherwise noted all reactions were performed in acetic acid at 25 °C in the presence of LiOAc. [b] mol % toward diene. [c] Isolated yields. [d] A biphasic system with equal amounts of acetic acid and hexane was used. [e] Reaction performed at 40 °C.


Co(salen)


Co(salophen)

Other macrocyclic metal complexes with a higher efficiency for catalyzing the aerobic reoxidation of hydroquinone under the conditions for palladium-catalyzed 1,4-oxidation were therefore sought. Mn(salen), Fe(salen), and bis(dimethylglyoximato)cobalt(II) (cobaloxime)[23] were less efficient than Co(salen) and yields of <5% were obtained. For comparison we studied the related salen-type macrocyclic complex Co(salophen). This complex, in which the ethyleneamino bridge of the Co(salen) has been replaced by a phenylenediamino bridge, is expected to be more stable toward hydrolysis. It turned out that Co(salophen) not only gave a fast oxidation of hydroquinone (vide infra) but also survived the reaction conditions of the triple-catalysis. Thus, oxidation of 1,3-cyclohexadiene under the usual reaction conditions with 5 mol % $Pd(OAc)_2$, 7–15 mol% of hydroquinone (HQ), and 5 mol % of Co(salophen) afforded a 79–89% yield of *trans*-1,4-diacetoxy-2-cyclohexene (**1**) (Table I).



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We also investigated metalloporphyrins as possible oxygen-activating complexes. Metalloporphyrins have been reported to catalyze many $O_2$ oxidations, and in particular cobalt and manganese porphyrins are known to catalyze the oxidation of phenols to quinones by molecular oxygen.[21b] It was found that $Co^{II}$(TPP) (TPP = *meso*-tetraphenylporphyrinato)[24] efficiently catalyzed a fast electron transfer from hydroquinone to dioxygen in the

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(13) Becker, H. D. In *The Chemistry of Quinoid Compounds*; Patai, S., Ed.; Wiley: New York, 1974; pp 335–423.

(14) (a) Bäckvall, J. E.; Gogoll, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1236. (b) Bäckvall, J. E.; Gogoll, A. *Tetrahedron Lett.* **1988**, *29*, 2243.

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(17) (a) Heumann, A.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1988**, 1516. (b) Antonsson, T.; Moberg, C.; Tottie, L.; Heumann, A. *J. Org. Chem.* **1989**, *54*, 4902.

(18) (a) Brown, R. G.; Davidson, J. M. *J. Chem. Soc. A* **1971**, 1321. (b) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800.

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(21) Németh, S.; Szeverényi, Z.; Simandi, L. I. *Inorg. Chim. Acta* **1980**, *44*, L 107.

(22) In a control experiment salicylaldehyde was detected when Co(salen) was employed as the macrocyclic complex.

(23) The use of the pyridine complex cobaloxime as catalyst gave no oxidation product in acetic acid. This complex is known to catalyze the oxidation of hydroquinone to *p*-benzoquinone by molecular oxygen in acetone.[21]

(24) (a) Momenteau, M.; Mispelter, J.; Loock, B.; Bisagni, E. *J. Chem. Soc., Perkin Trans 1* **1983**, 189. (b) Lindsey, J. S.; Hsu, H. C.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, *27*, 4969. (c) Alder, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

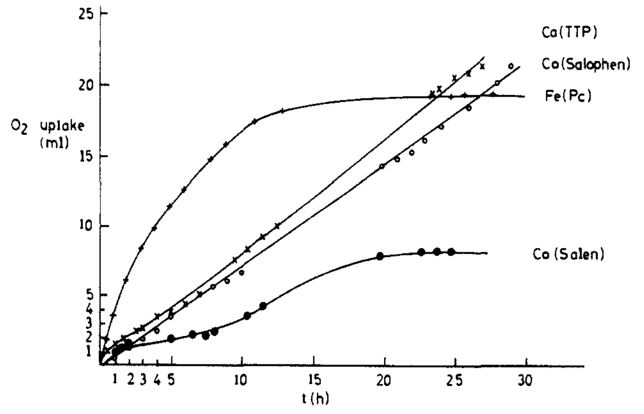
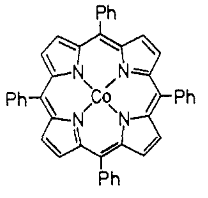
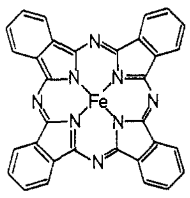


**Figure 1.** Oxygen uptake for the oxidation of 1,3-cyclohexadiene catalyzed by the triple catalytic system Pd(OAc)$_2$–hydroquinone–ML$^m$ with different metal macrocyclic complexes (ML$^m$): (+) Fe(Pc); (×) Co(salophen); (○) Co(TPP); (●) Co(salen). The experiments were performed in acetic acid on a 1.5-mmol scale with 5 mol % each of Pd(OAc)$_2$ and metal macrocycle (see Experimental Section).

palladium–hydroquinone catalyzed oxidation of conjugated dienes. Thus, the oxidation of 1,3-cyclohexadiene under the usual reaction conditions with 5 mol % each of Co(TPP), hydroquinone, and Pd(OAc)$_2$ afforded an 89% isolated yield of **1** at 25 °C. 1,3-Cycloheptadiene was also oxidized with this system and the results are given in Table I.



Co(TPP)



Fe(Pc)

The corresponding oxidation with Mn(TPP) in place of Co(TPP) was less efficient and gave a much lower yield even if the reaction time was prolonged. The highest yield in the 1,4-diacetoxylation of 1,3-cyclohexadiene with Mn(TPP) was only 56% with a much lower stereoselectivity (trans/cis = 72/28). A more successful result was obtained with the porphyrin analogue iron phthalocyanine, Fe(Pc).[25] This is a very stable complex, which has a low solubility in most organic solvents. In spite of its low solubility it was very efficient in catalyzing the electron transfer from hydroquinone to oxygen without any sign of degradation. This property has led us to use it in other related oxidations[9b] (see below). It was found to work very well under the conditions for the triple catalysis, and several conjugated dienes were oxidized with the combination Pd(OAc)$_2$–hydroquinone–Fe(Pc), and it also gave a faster oxidation than the other macrocyclic transition-metal complexes tested. A comparison between the oxygen uptake in the oxidation of 1,3-cyclohexadiene with four different macrocyclic complexes is given in Figure 1. The figure shows that the reaction with Co(salen) is slow and dies out after approximately 20 h. On the other hand the Co(salophen)- and Co(TPP)-catalyzed reactions showed an almost linear rate of the oxygen uptake. Finally, the reaction with Fe(Pc) showed a fast uptake of oxygen in the beginning of the reaction, which stops after ca. 12 h, when the theoretical amount of oxygen has been consumed. The rates of oxygen uptake for the triple catalytic reactions did not follow the rate of the oxygen uptake for the isolated oxidation of hydroquinone to benzoquinone. For the latter reaction the order of the rate of oxidation was Co(salophen) > Fe(Pc) > Co(salen) > Co(TPP) (Figure 2).

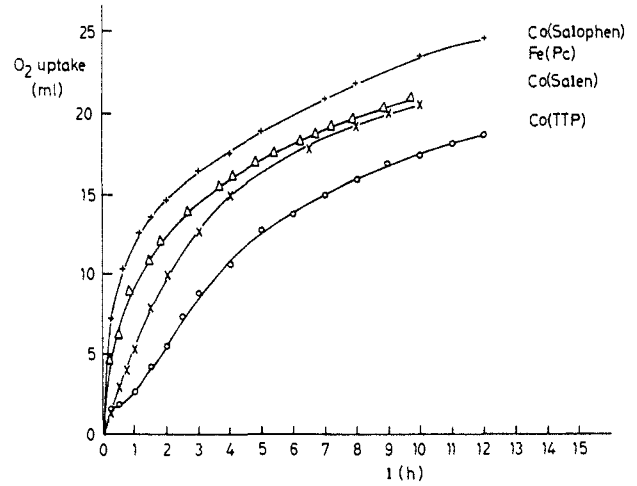
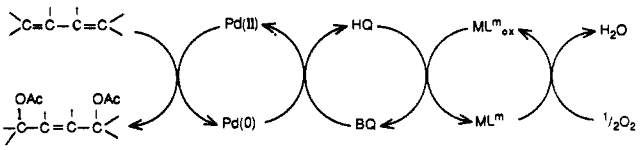


**Figure 2.** Oxygen uptake for the oxidation of hydroquinone catalyzed by different metal macrocyclic complexes: (+) Co(salophen); (△) Fe(Pc); (×) Co(salen); (○) Co(TPP). The experiments were performed in acetic acid (5 mL) with 2.27 mmol of hydroquinone and 0.114 mmol of metal macrocycle (5 mol %).

**Scheme II**



It is interesting to note that the Fe(Pc)-catalyzed O$_2$-oxidation of hydroquinone to benzoquinone most likely occurs via heterogeneous catalysis. The Fe(Pc) complex is a finely divided powder in the reaction mixture and can be recovered essentially unchanged after the reaction. In one experiment Celite was added after the reaction was over and the Fe(Pc)–Celite was recovered by filtration and washed. A new aerobic 1,4-diacetoxylation of 1,3-cyclohexadiene with the recovered Fe(Pc)–Celite was performed under the usual conditions (5 mol % Pd(OAc)$_2$, 10 mol % BQ). This reaction was found to proceed at ~80% of the rate of the original reaction.[26]

The mechanism of this biomimetic triple catalysis is given in Scheme II. It is known that benzoquinone coordinates to palladium in the intermediate ($\pi$-allyl)palladium complex formed in the reaction.[11a,14b] The rate of attack by the second nucleophile on the $\pi$-allyl group is dramatically increased by the coordination of the quinone.[14b,27] During this attack a Pd(0)–benzoquinone complex may form, which would rapidly disproportionate to hydroquinone and Pd(II) under the acidic reaction conditions.[28] The hydroquinone is then reoxidized to benzoquinone by the metal–macrocycle/O$_2$ system. The nature of the oxidized form of the macrocyclic transition-metal complexes may be slightly different for the different complexes. However, it is likely that both peroxo- and oxo-metal species are involved.

The mechanism of the aerobic oxidation depicted in Scheme II has similarities with that of biochemical processes, in which an oxidation becomes very mild and selective when several redox couples with falling redox potentials interact. In many biological systems metalloporphyrins and *p*-hydroquinones/*p*-benzoquinones play important roles as electron carriers. The system described here leads to a mild electron transfer at room temperature from the substrate (diene) to oxygen. Under these mild conditions the oxidation stops completely if one of the redox couples is removed. There are four species to be oxidized (diene, Pd(0), HQ, ML$^m$) and four oxidizing species (O$_2$, ML$^m_{ox}$, BQ, Pd(II)). If we consider only the thermodynamically favorable oxidations and omit the

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[25] Byrne, G. T.; Linstead, R. P.; Lowe, A. R. *J. Chem. Soc.* **1934**, 1017.

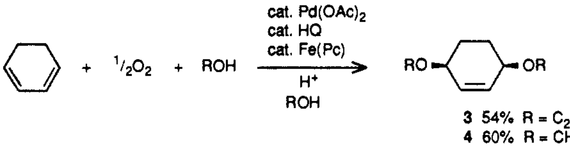
[26] The lower rate is most likely due to the absorption on Celite.

[27] (a) Bäckvall, J. E.; Nordberg, R.; Wilhelm, D. *J. Am. Chem. Soc.* **1985**, *107*, 6892. (b) Goliaszewski, A.; Schwarz, J. *J. Am. Chem. Soc.* **1984**, *106*, 5028.

[28] It is known that the related (cyclooctadiene)Ni$^0$(benzoquinone) complex when treated with hydrochloric acid afforded nickel(II) chloride and hydroquinone: Uhlig, E.; Fischer, R.; Kirmse, R. *J. Organomet. Chem.* **1982**, *239*, 385.

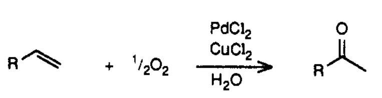
unproductive electron transfer within a redox couple (e.g. quinone oxidizing a molecule of hydroquinone) we would have 10 possible redox reactions that could occur. Apparently the energy barriers for six of these ($O_2$ + diene, $O_2$ + Pd(O), etc.) are too high and only the four redox steps depicted in Scheme II are kinetically favored. This is an example of highly selective kinetic control and does not require the complex structure of naturally occurring enzymes to distinguish between the electron-transfer processes. This kinetic control is possible because several of the selective electron-transfer processes occur via coordination (olefin coordination to Pd, BQ coordination to Pd, and $O_2$ coordination to $ML^m$).

We have also applied our triple catalytic system to the 1,4-dialkoxylation of conjugated dienes. Palladium-catalyzed 1,4-dialkoxylation of conjugated dienes has previously been realized with use of the alcohol as the solvent and benzoquinone as the oxidant.[12] The reaction requires catalytic amounts (~15 mol %) of a strong acid (methanesulfonic acid). Attempts to replace the benzoquinone with catalytic amounts of hydroquinone and Co(salophen)/$O_2$ or Co(TPP)/$O_2$ gave very poor results. Presumably the macrocyclic complexes do not survive the presence of the strong acid. The use of Fe(Pc) as the macrocycle in an attempted Pd(II)–hydroquinone catalyzed aerobic oxidation of 1,3-cyclohexadiene to 1,4-diethoxy-2-cyclohexene led to a fast oxygen uptake. However, the major part of this oxygen uptake resulted in undesired oxidation reactions of which one was aromatization. It turned out that lowering the amount of methanesulfonic acid to 6 mol % with Fe(Pc) as the macrocycle led to an improved yield. Under these reaction conditions the dialkoxylation gave 54–60% yields of the corresponding dialkoxy compound (eq 1).



(eq. 1)

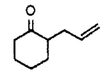
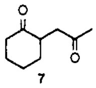
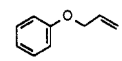
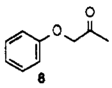
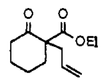
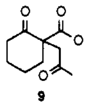
**Aerobic Oxidation of Terminal Olefins to Ketones.** A number of processes for metal-catalyzed oxidations of olefins to ketones by molecular oxygen are known in the literature.[29-34] Most of these reactions proceed at only a moderate rate at room temperature and require elevated temperature and oxygen pressure for good results. It is known that Pd(II) catalyzes the aerobic oxidation of terminal olefins to methyl ketones, and these oxidations form the basis of the Wacker process (eq 2).[30] In this oxidation the Pd(0) formed in each cycle is reoxidized by $CuCl_2$ and the CuCl formed is reoxidized to $CuCl_2$ by oxygen.



(eq. 2)

This double catalysis is also an example of kinetic control (vide supra) in an oxidation reaction (e.g. $O_2$-oxidation of Pd(0) or olefin is slower than $O_2$-oxidation of CuCl). A drawback with the presence of cupric chloride and chloride ions is that the reaction proceeds at a moderate rate,[35] and furthermore, chlorinated side products are often formed.[36] A chloride-free Wacker-oxidation would therefore be highly desirable.

Table II. Aerobic Oxidation of Terminal Olefins via the Triple Catalytic System Pd(II)–Hydroquinone–Fe(Pc)[a]

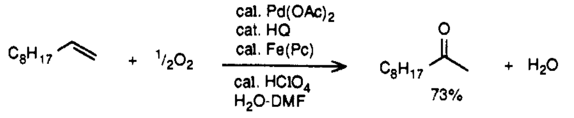
| entry | olefin | reaction time (h) | product[b] | % yield[c] |
|---|---|---|---|---|
| 1 | $CH_3(CH_2)_7CH=CH_2$ | 3 | $CH_3(CH_2)_7COCH_3$<br>**5** | 73 |
| 2 | $CH_3(CH_2)_9CH=CH_2$ | 8 | $CH_3(CH_2)_9COCH_3$<br>**6** | 67 |
| 3 |  | 2 | <br>**7** | 85 |
| 4 |  | 5 | <br>**8** | 47[d] |
| 5 |  | 8 | <br>**9** | 82 |

[a] All reactions were performed in aqueous DMF (DMF:$H_2O$ = 89:11) at 20 °C under an atmospheric pressure of oxygen using 5 mol % of $Pd(OAc)_2$, 5 mol % of Fe(Pc), and 15 mol % of hydroquinone. The olefin was added in portions during 1–2 h. [b] The products were characterized by $^1H$ and $^{13}C$ NMR spectroscopy. The only oxidized products detected were the ketones shown (>98% selectivity). [c] Isolated yields after flash chromatography. [d] Decomposition of the starting material to phenol occurred in this case.

The palladium-catalyzed oxidation of terminal olefins with a stoichiometric amount of *p*-benzoquinone as the oxidant has previously been described.[31a] In the preparative procedure described, $PdCl_2$ is used as the catalyst. With the aim of developing a chloride-free Wacker-oxidation we studied this reaction using $Pd(OAc)_2$ in place of $PdCl_2$. Initial attempts to use $Pd(OAc)_2$ as catalyst failed due to almost immediate precipitation of metallic palladium from the reaction mixture. However, we found that addition of a small amount (5–15 mol %) of a strong acid prevents the precipitation of Pd(0). A likely explanation for this phenomenon is that Pd(0) is protonated by the strong acid to give a palladium hydride species, which stays in solution long enough to be oxidized by the quinone.

The selection of an oxygen-activating complex for the recycling of hydroquinone in an aerobic catalytic process demanded particular attention. The presence of strong acid along with water limits the use of Schiff's base complexes, such as Co(salophen) or Co(salen). When either of these were used the reaction did not proceed to any great extent. Attempts to employ Co(TPP) also led to poor results. The reaction, as monitored by the oxygen uptake, was initially rapid, but it ceased before complete conversion of the olefin. Analysis of the resulting mixture revealed decomposition of the porphyrin.

In our search for an oxygen-activating complex the best results were obtained with Fe(Pc). As mentioned above, this metal–macrocycle is stable toward strong acids, and it seems to be resistant toward degradation under the reaction conditions employed. Oxidation of 1-decene in aqueous DMF with catalytic amounts of $Pd(OAc)_2$ (5 mol %), hydroquinone (15 mol %), and Fe(Pc) (5 mol %) in the presence of 5 mol % of $HClO_4$ afforded 2-decanone in an isolated yield of 73% after 3 h at room temperature (eq 3). This is approximately 16 times faster than the



(eq. 3)

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(29) Tsuji, J. *Synthesis* **1984**, 369.

(30) (a) Smidt, J.; Hafner, W.; Jira, R.; Sedlmeier, J.; Sieber, R.; Rüttinger, R.; Kojer, H. *Angew. Chem.* **1959**, *71*, 176. (b) Henry, P. M. *Palladium-Catalyzed Oxidation of Hydrocarbons*; D. Reidel Publishing Co.: Dordrecht, 1980. (c) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

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(32) Tsuji, J.; Nagashima, H.; Nemeto, H. *Org. Synth.* **1984**, *62*, 9.

(33) (a) Mimoun, H.; Perez Machirant, M. M.; Sérée de Roch, I. *J. Am. Chem. Soc.* **1978**, *100*, 5437. (b) Roussell, M.; Mimoun, H. *J. Org. Chem.* **1980**, *45*, 5387.

(34) Nyberg, E. D.; Pribich, D. C.; Drago, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 3538.

(35) The rate of the oxidation has an inverse square dependence on chloride ion concentration: Henry, P. M. *J. Am. Chem. Soc.* **1964**, *86*, 3246; **1966**, *88*, 1595.

(36) Stangl, H.; Jira, R. *Tetrahedron Lett.* **1970**, 3589.

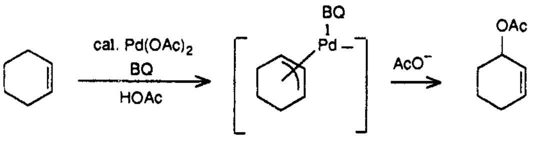
corresponding chloride-based Wacker-type oxidation, which afforded 2-decanone from 1-decene in the same yield after 24 h with twice the amount of palladium.[32] In the oxidation with the Pd$(OAc)_2$–hydroquinone–Fe(Pc) system, the rate increase is mainly due to the absence of chloride.[35] After 3 h there was no 1-decene left, but the presence of some isomerized decenes was evident from GLC and $^1H$ NMR spectroscopic analysis. These isomers are less reactive and will not lead to oxidized products.[37]

Several other terminal olefins were tested and oxidized to their corresponding methyl ketones by this method. The results are summarized in Table II. Increasing the concentration of acid had no major effect on the rate of the oxidation, but it did increase the amount of olefin isomerization. With no acid, palladium metal rapidly precipitated from the reaction mixture. The rate, as monitored by $O_2$ uptake, increased significantly with the amount of hydroquinone. Even in the absence of the hydroquinone there was a slow conversion, giving 19% of 2-decanone from 1-decene after the $O_2$ uptake had ceased. Apparently there is a slow electron transfer from Pd(0) to the oxidized form of Fe(Pc), which is in contrast to the 1,4-diacetoxylation discussed above, for which removal of hydroquinone stopped the reaction.

The mechanism of our chloride-free Wacker-type oxidation proceeds via a multistep electron transfer similar to that discussed above (Scheme III). In the Wacker-type oxidation the energy barrier for the oxidation of Pd(0) by the Fe(Pc)–oxygen complex is not very much higher than the barrier for oxidation of Pd(0) by benzoquinone. Since coordination of the quinone to Pd(0) is less important in the oxidation of olefin to ketone compared to the 1,4-oxidation of 1,3-dienes, a higher barrier for electron transfer from palladium(0) to the quinone is expected in the former reaction.

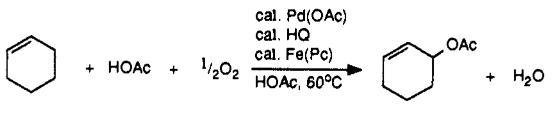
This new triple catalytic system, which allows the use of chloride-free conditions in the Wacker-type oxidation, has led to a faster and more efficient reaction, giving high yields under mild conditions.

**Aerobic Allylic Oxidations of Olefins.** It is known that olefins, in particular cyclic olefins, undergo a palladium-catalyzed oxidation by benzoquinone in acetic acid to give allylic acetates.[16,18a,30b] The reaction proceeds through a ($\pi$-allyl)palladium intermediate and the benzoquinone acts both as an oxidant and as a ligand in the system (eq 4). The use of the system $MnO_2$/catalytic amounts of benzoquinone,[11,38] mentioned above, was also successfully applied to this reaction.[16a,39] We therefore considered recycling of the hydroquinone by the oxygen/metal–macrocycle system. This would lead to a useful aerobic allylic oxidation.



(eq. 4)

Reaction of cyclohexene in acetic acid in the presence of oxygen with 5 mol % of $Pd(OAc)_2$, 20 mol % of hydroquinone, and 5 mol % of Fe(Pc) at 60 °C resulted in a smooth oxidation (eq 5). The oxygen uptake was followed and indicated >90% conversion after 2 h. The stoichiometry of these aerobic allylic oxidations becomes very simple and the only side product is water. We found that it was possible to reduce the amount of Fe(Pc) to as little as 0.5 mol% without severely changing the rate (Table III). This suggests that the reoxidation of hydroquinone to *p*-benzoquinone is not the rate-limiting step. Co(Salophen) and Co(TPP) were also efficient oxygen activators in the allylic oxidation; the latter gave a fast conversion with only 0.5 mol % (Table III). The use of Co(salen), however, gave no reaction as monitored by the oxygen uptake.



(eq. 5)

Table III. Aerobic Allylic Oxidation of Cyclohexene with a Triple Catalytic System $Pd(OAc)_2$–HQ–$ML^m$ [a]

| entry | $ML^m$ | mol % | $O_2$ uptake[b] 2 h | $O_2$ uptake[b] 4 h | % yield[c] |
|---|---|---|---|---|---|
| 1 | Fe(Pc) | 5 | 23 | | 90 |
| | | 0.5 | 13.2 | 22.0 | 78 |
| | | 0.5 | 13.0 | 23.2 | 75[d] |
| 2 | Co(TPP) | 0.5 | 16.6 | 25 | 93 |
| 3 | Co(salen) | 5 | 0 | 0 | |
| 4 | Co(salophen) | 5 | 15.4 | 20.2 | 100 |
| 5 | | 0.5 | 2.3 | 7.8 | 85 |

[a] Unless otherwise noted the reaction was performed on a 2-mmol scale in acetic acid at 60 °C with 5 mol % of $Pd(OAc)_2$ and 20 mol % of hydroquinone (HQ) in the presence of $LiOAc{\cdot}2H_2O$ (1 mmol). Workup after 4–6 h except entry 5 where the reaction was worked up after 22 h. [b] Theoretical oxygen uptake 24 mL. [c] Isolated yields. [d] 2-Methoxy-3,6-dihydroxybenzoic acid (20 mol %) was used in place of hydroquinone.

A few other hydroquinones or quinones were also tried. Chloranil gave a very slow reaction, and 2-chlorohydroquinone reacted more slowly than hydroquinone. On the other hand, the hydroquinone 2-methoxy-3,6-dihydroxybenzoic acid reacted at a rate comparable to that of hydroquinone (Table III, entry 3).

The amount of palladium could also be reduced in the reaction. In an efficient preparative procedure we used 2 mol % of Pd(O-$Ac)_2$, 20 mol % of hydroquinone, and 2 mol % of Fe(Pc). This led to >95% conversion after 8 h and an isolated yield of 88% of 2-cyclohexenyl acetate. Cycloheptene and cyclopentene were also oxidized to the corresponding allylic acetates with high selectivity. These olefins reacted more slowly than cyclohexene.

## Conclusions

We have developed a new mild triple catalytic system consisting of $Pd(OAc)_2$, hydroquinone, and a transition-metal macrocycle. By using different reaction conditions it has been possible to develop three different types of transformations: (i) 1,4-oxidation of conjugated dienes, (ii) oxidation of terminal olefins to methyl ketones, and (iii) allylic oxidation. In all three of these oxidations Pd(II) is interacting with the substrate and acquires two electrons, which are further transferred to benzoquinone. The hydroquinone is then reoxidized to benzoquinone by the $O_2$/metal macrocycle system.[40] With this new multistep electron-transfer system the oxidation potential of oxygen has been lowered stepwise, and thus it is possible to direct the selectivity toward a desired transformation.

## Experimental Section

NMR spectra were recorded with a Varian XL-300 spectrometer (300 MHz). All NMR spectra were recorded for $CDCl_3$ solutions with tetramethylsilane as internal standard for $^1H$ NMR and $CDCl_3$ for $^{13}C$. Analytical gas chromatography was performed with a Varian 3400 GC with a FID detector, connected to a Varian 4270 computing integrator. A 30-m DB-5 J&M fused silica column was used.

Mass spectra were recorded with a Finnigan MAT Incos 50 instrument, connected to a capillary GC.

Palladium diacetate was purchased from Aldrich and used as received. 1,3-Cyclohexadiene (Aldrich) was distilled prior to use. Other chemicals and solvents were obtained from commercial sources and were, unless otherwise noted, used as received.

**Iron(II) phthalocyanine** was prepared following the procedure of Byrne, Linstead, and Lowe.[25] *o*-Cyanobenzamide (40 g) and iron filings (2 g) were combined with naphthalene (3 g) in a round-bottomed flask with a short air condenser. The mixture was stirred and heated to 250 °C for 1 h, during which an intense blue color developed. After cooling, the solid cake was broken up and washed with ether and hot acetone. The remaining solids were Fe(Pc) and iron filings; the latter stuck to the stirring bar. A second wash with hot acetone and drying yielded 7.5 g

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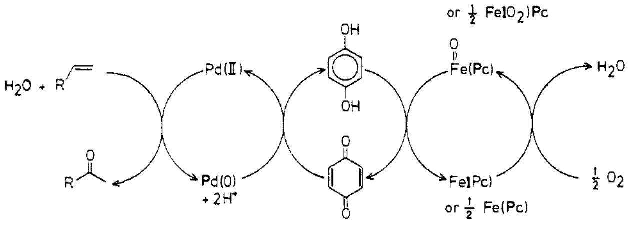
(37) It has been shown by Tsuji that internal olefins react very slowly compared to terminal olefins in Wacker-type oxidation.[15,29,31b,32]

(38) Bäckvall, J. E. *Pure Appl. Chem.* **1983**, *55*, 1669.

(39) Åkermark, B.; Hansson, S.; Rein, T.; Vågberg, J.; Heumann, A.; Bäckvall, J. E. *J. Organomet. Chem.* **1989**, *369*, 433.

(40) Electrochemical reoxidation of hydroquinone to benzoquinone in 1,4-oxidation of conjugated dienes and oxidation of terminal olefins to ketones has recently been reported.[14b,15]

**Scheme III**



of Fe(Pc). This procedure generally gave Fe(Pc) with high catalytic activity. However, we noted some variation of the catalytic activity from different batches.

**Tetraphenylporphyrin** (TPP) was prepared according to the method described by Lindsey:[24b] A solution of trifluoroacetic acid (0.60 g, 5.3 mmol) in 100 mL of $CH_2Cl_2$ was slowly added to a stirred solution of freshly distilled pyrrole (0.364 g, 5.4 mmol) and distilled benzaldehyde (0.577 g, 5.4 mmol) in 200 mL of dried $CH_2Cl_2$. The mixture was stirred for 1.5 h under nitrogen, during which time it turned black. *p*-Chloroanil (1.2 g, 5 mmol) was added and the mixture was refluxed for 1 h. After the mixture was cooled to ambient temperature, the volume was reduced to ca. 50 mL. The resulting black slurry was deposited on top of a column containing 200 g of dry alumina (grade 1, Fluka 507c) and the TPP was eluted with chloroform. The volume was reduced to approximately 10 mL and 2 mL of EtOH was added. The mixture was allowed to stand in the freezer overnight. Filtration and drying in vacuo over $CaSO_4$ yielded 0.42 g (50%) of TPP as purple crystals.

**Co(TPP)** was obtained by reaction of $Co(OAc)_2$ with tetraphenylporphyrin according to ref 24c.

**Salophen**, *o*-Phenylenediamine (1.8 g, 16.6 mol) was slowly added with stirring to salicylaldehyde (4.0 g, 32.8 mmol). An exothermic reaction occurred and the mixture became viscous. After 10 min of stirring, the mixture was allowed to cool down (15 min) and the product was transferred portionwise to 80 mL of ethanol with stirring. The solids were filtered off, recrystallized from ethanol, and dried in vacuo over $CaSO_4$ overnight to yield 4.6 g (88%) of salophen as yellow needles, mp 168 °C.

**Co(salophen).**[41] Salophen (1.50 g, 4.7 mmol) and $Co(OAc)_2{\cdot}4H_2O$ (1.25 g, × 7.1 mmol) were refluxed in methanol (400 mL) for 1 h, and the mixture was then allowed to stand at room temperature overnight. The brown precipitate was collected by filtration, washed with methanol and ether, and dried in vacuo at 100 °C for 10 h to yield 0.91 g (52%) of Co(salophen). This drying procedure was of importance in order to obtain material with high catalytic activity.

**General Procedure for Palladium(II)-Catalyzed Aerobic 1,4-Diacetoxylation of Conjugated Dienes, 1,4-Diacetoxy-2-cyclohexene (1). Use of Co(TPP).** Co(TPP) (50 mg, 0.07 mmol) was added to a stirred solution of $Pd(OAc)_2$ (16 mg, 0.07 mmol), $Li(OAc){\cdot}2H_2O$ (163 mg, 1.60 mmol), and hydroquinone (8 mg, 0.07 mmol) in acetic acid (2.5 mL). To the resulting slurry was added a solution of 1,3-cyclohexadiene (120 mg, 1.5 mmol) in *n*-hexane (5 mL). The reaction mixture was stirred at room temperature under 1 atm of oxygen for 18 h. The precipitate was removed by filtration and the hexane layer was collected. The remaining acetic acid phase was diluted with saturated aqueous NaCl (3 mL) and extracted with hexane/ether (1:1) (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl (3 × 3 mL) and water (3 × 3 mL) and finally 2 M aqueous NaOH (3 × 5 mL). The organic phase was dried ($MgSO_4$) and evaporated to yield 264 mg (89%) of **1** (>90% trans) as crystals. The product was characterized by comparison with an authentic sample of **1** and its cis isomer.[11a]

**Use of Fe(Pc).** $Pd(OAc)_2$ (16.8 mg, 0.075 mmol), hydroquinone (12 mg, 0.105 mmol), Fe(Pc) (43 mg, 0.075 mmol), and $LiOAc{\cdot}2H_2O$ (171 mg, 1.67 mmol) were mixed and stirred in acetic acid (3 mL) immediately followed by addition of 1,3-cyclohexadiene (120 mg, 1.5 mmol). The flask was evacuated (water aspirator) and put under atmospheric pressure of oxygen (repeated twice). The oxygen uptake was followed and after 12 h, when the gas consumption had ceased, 18 mL of oxygen had been consumed. The reaction mixture was stirred for another 6 h and worked up as described above to give 230 mg (77%) of **1** (>91% trans), which crystallized on standing.

**Use of Co(salophen).** Co(salophen) was used as described above for the Fe(Pc) procedure but replacing Fe(Pc) with Co(salophen).

**1,4-Diacetoxy-2-cycloheptene (2).** With use of the Fe(Pc) procedure, 1,3-cycloheptadiene (471 mg, 5 mmol), $Pd(OAc)_2$ (56 mg, 0.25 mmol), Fe(Pc) (142 mg), and $Li(OAc){\cdot}2H_2O$ (1.53 g, 15 mmol) in acetic acid (8.5 mL) for 48 h at room temperature afforded 0.70 g (66%) of **2** (>93% cis). The product was characterized by comparison with an authentic sample of **2** and its trans isomer.[11a]

**Aerobic 1,4-Dialkoxylation of 1,3-Cyclohexadiene. 1,4-Diethoxy-2-cyclohexene (3).** $Pd(OAc)_2$ (15 mg, 0.07 mmol), hydroquinone (42 mg, 0.39 mmol), and Fe(Pc) (45 mg, 0.08 mmol) were stirred in 99% ethanol (3.0 mL) for 5 min. The reaction vessel was quickly purged with oxygen as described above. Methanesulfonic acid ($CH_3SO_3H$) (8 $\mu$l, 0.12 mmol) was added via syringe, immediately followed by addition of diene (160 mg, 2 mmol), which was added over 3 h. The reaction was followed by the oxygen uptake and worked up after 24 h as described above to give 135 mg (54%) of *cis*-1,4-diethoxy-2-cyclohexene (**3**). The product was characterized by comparison with an authentic sample of **3**.[12]

**1,4-Dimethoxy-2-cyclohexene (4)** was prepared from 1,3-cyclohexadiene (160 mg, 2 mmol) in methanol following the same procedure as described for the preparation of **3**. The usual workup afforded 133 mg (60%) after 20 h. Spectral data of the product are in accord with those reported in the literature.[12]

The major side product of the dialkoxylation reactions, identified by GC–MS, was benzene.

**Aerobic Oxidation of Terminal Olefins to Methyl Ketones, General Procedure: Synthesis of 2-Decanone (5).** A 10-mL two-necked flask equipped with a magnetic stirring bar and septum was charged with $Pd(OAc)_2$ (17 mg, 0.076 mmol), hydroquinone (25 mg, 0.23 mmol), Fe(Pc) (43 mg, 0.076 mmol), and distilled *N,N*-dimethylformamide (1 mL). To this was added via syringe 0.12 mL of $H_2O$ and 8 $\mu$L of 60% aqueous $HClO_4$ (0.076 mmol). The reaction vessel was then carefully purged with $O_2$ with 3 pump–fill cycles (water aspirator vacuum), and 1-decene (0.21 g, 1.5 mmol) was added in six portions at 15-min intervals. The mixture was stirred at room temperature under 1 atm of $O_2$, and the oxygen uptake was measured with a buret. After 3 h (17.5 mL oxygen consumed) the reaction mixture was diluted to 15 mL with brine and extracted twice with 20 mL of pentane and once with 20 mL of pentane/ether (85:15). The combined organic layers were dried over anhydrous $Na_2SO_4$. GC analysis showed a 78% yield of ketone. The remaining olefin and ketone were separated by column chromatography over silica by pentane/ether (gradient up to 85:15) to give an isolated yield of 171 mg (73%) of 2-decanone. $^1H$ NMR analysis indicated that 2-decanone was the only oxidized product. $^1H$ NMR: $\delta$ 0.9 (t, 3 H, $CH_3$), 1.25 (m, 10 H, five $CH_2$), 1.5 (m, 2 H, $CH_2$), 2.1 (s, 3 H, $CH_3CO$), 2.4 (t, 2 H, $CH_3COCH_2$). $^1H$ and $^{13}C$ NMR analysis of the remaining olefin indicated a mixture of olefin isomerization products.

The same procedure was applied to the aerobic oxidation of the terminal olefins given in Table II, with the different reaction times indicated. The products 2-dodecanone (**6**),[31a] 2-acetonyl-2-cyclohexanone (**7**),[42] 2-phenoxy-2-propanone (**8**),[43] and 2-acetonyl-2-carbethoxycyclohexanone (**9**)[31b] are known compounds and were characterized by their spectral data.

**Aerobic Allylic Oxidation of Cyclic Olefins: 1-Acetoxy-2-cyclohexene.** $Pd(OAc)_2$ (22 mg, 0.10 mmol), hydroquinone (44 mg, 0.40 mmol), the metal macrocycle (0.01–0.1 mmol), and $LiOAc{\cdot}2H_2O$ (102 mg, 1 mmol) were stirred in acetic acid (10 mL) for 20 min. The reaction was put under an atmosphere of $O_2$ as described above and cyclohexene (164 mg, 2 mmol) was added via syringe. The reaction mixture was heated in an oil bath to 60 °C and the $O_2$ uptake was measured. When the $O_2$ uptake had ceased (usually after 2–6 h, cf. Table III), the reaction mixture was cooled to room temperature. Water (8 mL) was added and the mixture was extracted with pentane (4 × 15 mL). The combined organic extracts were washed with water (2 × 15 mL) and saturated aqueous $NaHCO_3$ (5 mL). The organic phase was dried ($MgSO_4$) and carefully concentrated to give 2-cyclohexen-1-yl acetate, which was characterizied by $^1H$ NMR and gas chromatography (results in Table III).

In a preparative procedure $Pd(OAc)_2$ (22 mg, 0.098 mmol), Fe(Pc) (56 mg, 0.098 mmol), hydroquinone (44 mg, 0.40 mmol), $LiOAc{\cdot}2H_2O$ (204 mg, 2 mmol), and cyclohexene (0.33 g, 4.0 mmol, added in two portions; second portion added after 1.5 h) were allowed to react under 1 atm of oxygen for 8 h. The usual workup afforded 0.493 g (88%) of 2-cyclohexen-1-yl acetate, the spectral data of which were in accord with those reported in the literature.[44]

**Acknowledgment.** Financial support from the Swedish Board of Technical Development and the Swedish Natural Science Research Council is gratefully acknowledged.

**Registry No.** *trans*-**1**, 78776-44-0; *cis*-**1**, 78776-45-1; **2**, 92489-91-3; **3**, 90786-01-9; **4**, 59415-77-9; **5**, 693-54-9; **6**, 6175-49-1; **7**, 6126-53-0;

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[42] Jacobson, R. M.; Raths, R. A.; McDonald, J. H., II *J. Org. Chem.* **1977**, *42*, 2545.

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**8**, 621-87-4; **9**, 24731-07-5; TPP, 917-23-7; Fe(Pc), 132-16-1; Co(TPP), 28132-69-6; Co(salophen), 39836-45-8; Pd(OAc)$_2$, 33571-36-7; Co(salen), 14167-18-1; Mn(TPP), 31004-82-7; $H_2C{=}CH(CH_2)_7CH_3$, 872-05-9; $H_2C{=}CH(CH_2)_9CH_3$, 112-41-4; $PhOCH_2CH{=}CH_2$, 1746-13-0; salophen, 118-57-0; *o*-phenylenediamine, 95-54-5; salicylaldehyde, 90-02-8; hydroquinone, 123-31-9; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 2-allylcyclohexanone, 94-66-6; 2-(ethoxycarbonyl)-2-allylcyclohexanone, 61771-75-3; 1-acetoxy-2-cyclohexene, 14447-34-8; cyclohexene, 110-83-8; 2-methoxy-3,6-dihydroxybenzoic acid, 118303-91-6.

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# Dihydrogen Complexes of Ruthenium. 2. Kinetic and Thermodynamic Considerations Affecting Product Distribution

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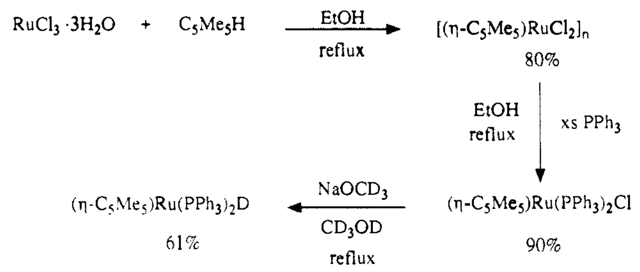
**Abstract:** Cationic ruthenium dihydrogen complexes of the form $[(\eta\text{-}C_5H_5)Ru(L)(L')(\eta^2\text{-}H_2)]BF_4$ (L = CO, L′ = PCy$_3$ (**1a**), PPh$_3$ (**2a**), PMe$_2$Ph (**3a**), PMe$_3$ (**4a**)) have been prepared by protonation of the corresponding neutral hydrides. Carbonyl free derivatives such as $[(\eta\text{-}C_5H_5)Ru(\overset{\frown}{P\,P'})(\eta^2\text{-}H_2)]BF_4$ ($\overset{\frown}{P\,P'}$ = 1,2-bis(dimethylphosphino)ethane (dmpe) (**5a**), (1,1-dimethyl-2,2-diphenylphosphino)ethane (dmdppe) (**6a**), (*R*)-(+)-1,2-bis(diphenylphosphino)propane ((*R*)-prophos) (**8a**), bis(PPh$_3$) (**9a**)) were similarly prepared. Pentamethylcyclopentadienyl analogues $[(\eta\text{-}C_5Me_5)Ru(\overset{\frown}{P\,P'})(\eta^2\text{-}H_2)]BF_4$ ($\overset{\frown}{P\,P'}$ = dmdppe (**7a**), (PPh$_3$)$_2$ (**10a**)) and $[(\eta\text{-}C_5Me_5)Ru(CO)(PCy_3)(\eta^2\text{-}H_2)]BF_4$ (**11a**) have also been prepared. Identification of these species as dihydrogen complexes is based upon observation of substantial H-D coupling (22-32 Hz) in the $^1$H NMR spectra of the HD analogues, prepared by protonation of the corresponding deuterides. In every case studied in detail, the kinetic product of the protonation reaction is the dihydrogen complex, but an intramolecular isomerization occurs to give variable amounts of the transoid dihydride form at equilibrium. The composition of the equilibrium mixture and the rate at which the equilibrium is obtained depend upon the ligand environment. Facile rotation of the coordinated H$_2$ ligand in the ruthenium complexes is established by the study of chiral complexes. The coordinated H$_2$ in these complexes is substantially activated toward heterolytic cleavage. In the case of **5a**, the measured p*K*$_a$ is 17.6 (CH$_3$CN), with the dihydrogen form deprotonated more rapidly than the dihydride.

## Introduction

Although numerous reports of $\eta^2$-dihydrogen complexes have appeared in recent literature,[1] the chemistry of cationic half-sandwich complexes with pseudo-octahedral coordination has received relatively little attention. The exceptional stability of these $\eta^2$-dihydrogen complexes of ruthenium not only facilitates their study, but the rich and relatively well developed syntheses of ($\eta^5$-cyclopentadienyl)ruthenium halides[3] (and to a lesser extent the hydrides) allows for systematic variation in the ligand environment. Thus these complexes offer a unique opportunity to study the physical and chemical properties of coordinated dihydrogen as a function of the ligand environment about a metal center.

**Scheme I**



In this paper, we report on several complexes of the general form $[(\eta\text{-}C_5R_5)Ru(L)(L')(\eta^2\text{-}H_2)]BF_4$ (L, L′ = CO and various phosphine ligands, vide infra), which are conveniently prepared by protonation of the corresponding neutral hydrides. These cationic complexes exist as rapidly equilibrating mixtures of the dihydrogen complex and the corresponding transoid dihydride form. The equilibrium composition and the rate at which equilibrium is obtained have been studied in detail in several cases and are found to be highly dependent on the ligand environment. The coordinated H$_2$ in these cationic complexes is highly activated toward heterolytic cleavage, with the dihydrogen form deprotonated in preference to the dihydride form. A preliminary account of portions of this work has been previously communicated.[4]

## Results

**Synthesis of Dihydrogen Complexes.** Syntheses of the neutral ruthenium hydrides of the type CpRu(L)(L′)H (L = CO; L′ = PR$_3$; Cp = $\eta^5$-cyclopentadienyl) patterned after the report by Humphries and Knox for the PPh$_3$ complex[5] (**2**) allow for the convenient preparation of these hydrides from Ru$_3$(CO)$_{12}$, cy-

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(1) For a comprehensive account of the development of this field, see: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120-128. Since the review by Kubas several additional dihydrogen complexes have been reported.[2]

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