Dioxygen Activation by $[Co_2(\mu\text{-OH})L]${H_3L=2,6-Bis[(2-hydroxyphenyl)iminomethyl]-4-methylphenol}, Catalysed Cooxygenation of PPh$_3$ and Alkenes, Alcohols, a Sulfide, a Sulfoxide and Diphenylacetylene

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Alkenes, alcohols, a sulfide, a sulfoxide and diphenylacetylene can be hetero-cooxygenated with PPh$_3$ catalysed by a dicobalt complex: $[Co_2(\mu\text{-OH})L]${H_3L=2,6-bis[(2-hydroxyphenyl)iminomethyl]-4-methylphenol}, to produce a single oxidation product for each substrate.

Recently, we discovered that $[Co_2(\mu\text{-OH})L]${H_3L = 2,6-bis[(2-hydroxyphenyl)iminomethyl]-4-methylphenol}[1] **1** can catalyse the oxygenation of triphenylphosphine with a turnover number of more than 20000.[2] More interestingly, we found that a range of organic substrate, including alkenes, alcohols, sulfide, sulfoxide and diphenylacetylene, can be hetero-cooxygenated with PPh$_3$. Unexpectedly, these organic substrates are oxidized to produce single product for each substrate. Alkenes are oxidized to epoxides stereospecifically, alcohols are oxidized to aldehydes for terminal alcohols, and to ketones for internal alcohols. Sulfide and sulfoxide are oxidized to sulfoxide and sulfone, respectively. Diphenyl-acetylene is converted to benzil. We now report preliminary results of this unique catalysed hetero-cooxygenation.

In a closed system, the oxygen pressure changes measured manometrically under various reaction conditions and at 353 K are shown in Fig. 1. Curve (*a*) indicates that (*E*)-stilbene does not react or reacts very slowly with O$_2$ in the presence of

1, whereas curve (*b*) shows that PPh$_3$ can easily be oxidized to PPh$_3$O in the presence of **1**. The levelling off in curve (*b*) is a result of complete oxidation of PPh$_3$. In the absence of **1**, PPh$_3$ oxidation is too slow to be detected. However, when (*E*)-stilbene is added to the solution (*b*), a new oxygen consumption curve (*c*) is observed. Levelling off is also evident in curve (*c*), due to complete oxidation of PPh$_3$. A large amount of (*E*)-stilbene is needed for the extra oxygen consumption to be observed clearly. When the (*E*)-stilbene concentration is further increased, more oxygen is consumed [curve (*d*)]. The maximum amount of O$_2$ consumed due to the presence of a large excess of (*E*)-stilbene is about twice that expected from the oxidation of PPh$_3$ alone. These experiments show clearly that (*E*)-stilbene can be catalytically cooxygenated with PPh$_3$.

To understand further this hetero-cooxygenation, a range of organic substrates were tested, and the results are collected in Table 1. The oxygen consumption curves in the presence of

Table 1 Organic substrates hetero-cooxygenated with PPh$_3$ catalysed by 1[a]

Substrate	Product[b]	$P(\text{subst.})/$ P^c
(E)-Stilbene	trans-Stilbene oxide	1.39
(Z)-Stilbene	cis-Stilbene oxide[d] (97%)[e]	1.39
(E)- and (Z) stilbene[f]	trans-Stilbene oxide (53%)[e] + cis-Stilbene oxide (47%)[e]	1.39
Cyclooctene	Cyclooctene oxide	1.23
Benzyl alcohol	Benzaldehyde	1.46
p-Methylbenzyl alcohol	p-Methylbenzaldehyde	1.39
p-Chlorobenzyl alcohol	p-Chlorobenzaldehyde	1.54
Butan-1-ol	Butanal	1.36
Butan-2-ol	Butan-2-one	1.24
Tetrahydrothiophene	Tetrahydrothiophene S-oxide	1.21
Tetrahydrothiophene S-oxide	Tetrahydrothiophene S,S-dioxide	1.16
Diphenylacetylene	Benzil	1.46

[a] *Conditions*: [catalyst] = 4.00×10^{-3}, [PPh$_3$] = 0.1, [substrate] = 1.0 mol dm^{-3} initial O$_2$ pressure = 670 Torr; DMF solution (10 ml) at 353 K. [b] Except for (Z)-stilbene and mixed substrate, only one product is detected by TLC. [c] $P(\text{subst.})$ is the amount of oxygen pressure decrease under the reaction conditions (see footnote a) and P is the amount of oxygen pressure decrease due to phosphine oxidation. [d] Also contains 3% trans-stilbene oxide. [e] % in parentheses was determined by HPLC. [f] [(E)-stilbene] = [(Z)-stilbene] = 0.50 mol dm^{-3}.
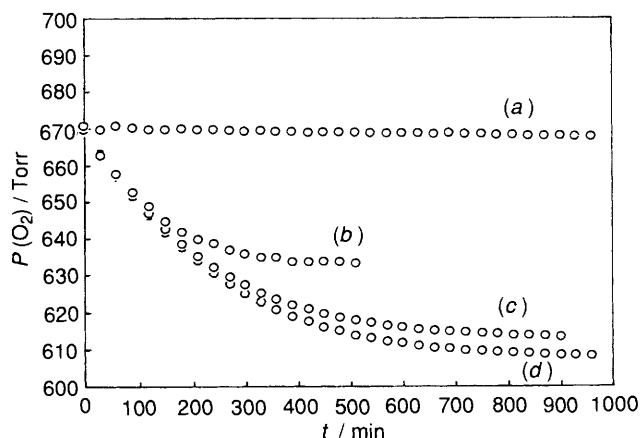
Fig. 1 Oxygen consumption under various conditions. All experiments were carried out with [catalyst] = 4.0×10^{-3} mol dm^{-3} in dimethylformamide (DMF) solution (10 ml) under O$_2$ (0.254 dm^3 at 298 K). The DMF solutions (353 K) also contained the following reactants: (a) [(E)-stilbene] = 2.0 mol dm^{-3}; (b) [PPh$_3$] = 0.1 mol dm^{-3} (c) and (d) (E)-stilbene: 1.0 and 2.0 mol dm^{-3}, respectively, were added to solution (b).

each substrate in Table 1 are similar to those for (E)-stilbene shown in Fig. 1, having a similar general shape, but the extra oxygen consumption may vary with the substrate for similar substrate concentrations. The oxidation products were isolated by preparative TLC (Merck 60H) and identified by mass and NMR spectroscopy. (E)-Stilbene, (Z)-stilbene and cyclooctene are oxidized to their corresponding epoxides stereospecifically. Terminal alcohols, such as n-butanol, benzyl alcohol and its derivatives, are oxidized to aldehydes, and no further oxidation to acid was observed. Butan-2-ol is oxidized to butan-2-one, tetrahydrothiophene was oxidised to its S-oxide, which in turn was oxidised to the S,S-dioxide, and diphenylacetylene was oxidized to the diketone. One striking feature in these oxidation reactions is that only one product is isolated for each organic substrate, except for the reaction of

(Z)-stilbene, and further analysis by TLC (Merck plastic sheet silica gel 60F$_{254}$) confirmed that only one oxidation product produced besides PPh$_3$O was produced.† A control experiment with an artificial mixture showed that impurity levels of 0.5% could easily be detected by our TLC procedure. In the case of (Z)-stilbene, no isomerization to (E)-stilbene was observed. The presence of 3% of trans-stilbene oxide in the product is due to the presence of 3% of (E)-stilbene in the (Z)-stilbene starting material. No isomerization of cis-stilbene oxide to the trans-isomer was observed under our conditions.

The extra oxygen consumption due to the presence of the organic substrate can be taken as a measure of the relative oxidizability of the substrate. The results in Table 1 indicate clearly that alkenes, alcohols and diphenylacetylene have comparable reactivity, but the reactivity of tetrahydrothiophene and its S-oxide is lower. Since a large amount of substrate is needed for the hetero-cooxygenation to take place, it is obvious that PPh$_3$ is a much better substrate than any in Table 1. However, it should be noted that, in contrast to our system, Read's group[5a,b] have reported that in Rh^I-catalysed hetero-cooxygenation of oct-1-ene and PPh$_3$, excess of PPh$_3$ is not oxidized in the absence of octene. The relative reactivities of benzyl alcohol and its p-methyl derivative show that an electron-donating substituent retards the reaction. A similar electronic effect can also be inferred from the reactivities of stilbenes and cyclooctene. The electron-withdrawing phenyl groups in stilbene enhance its reactivity relative to cyclooctene which has electron-donating alkyl groups attached to the double bond. It is noteworthy that (E)- and (Z)-stilbene have the same reactivity, which was confirmed by the mixed substrate data in Table 1. When a mixture of equal amounts of (E)- and (Z)-stilbene is used as substrate, the excess of O$_2$ consumed is the same as in experiments with pure (E)- or (Z)-stilbene with the same total concentration, with the product distribution being the sum of oxidation products of the individual substrates. The product distribution from (Z)-stilbene [containing 3% (E)-stilbene] oxidation is also consistent with the finding that (E)- and (Z)-stilbene have the same reactivity.

One possible reaction pathway is that PPh$_3$ and the organic substrate are oxygenated simultaneously through an intermediate in which the substrate, PPh$_3$, O$_2$ and the dicobalt catalyst are bonded together to form a cyclic intermediate. One would then expect that the bonding and geometry in the intermediate would differ for each substrate, leading to different reactivities. The results in Table 1 show this is not the case. Therefore, a pathway involving simultaneously oxidation of PPh$_3$ and the substrate is highly unlikely. However, such a multi-reactant intermediate has been postulated in hetero-cooxygenation. For example, it was proposed by Read's group[5] that in [RhCl(PPh$_3$)$_3$]-catalysed hetero-cooxygenation of alkenes or cycloalkenes with PPh$_3$ or a second alkene residue, an intermediate with both substrates and O$_2$ coordinated to the Rh^I centre was formed. Another plausible reaction pathway is that a reactive intermediate is formed after PPh$_3$ is oxidized by O$_2$, which is a potent oxidant which can

oxidize PPh_3 and the substates. Since the reactive intermediate is formed only after PPh_3 is oxidized the extra O_2 consumption due to the substrate would be expected not to exceed that due to PPh_3 oxidation alone. The stereospecificity of the alkene epoxidations can easily be accounted for by invoking a concerted transfer of oxygen from the reactive intermediate to the alkene. A possible reactive intermediate is a $Co^{IV}=O$ species, which has been proposed[3,4] previously in the oxidation of organic substrates, or an oxo-bridged dicobalt species.

The hetero-cooxygenation of PPh_3 and alkenes can also be catalysed by Rh^I complexes.[5] However, the Rh^I-catalysed reactions are quite different from the reaction catalysed by 1. For example the major alkene oxidation products are ketones instead of epoxides, and side products accompanied ketone formation, e.g. heptanal in the oxidation of oct-1-ene, and cyclooct-2-en-1-one from cyclooctene. Furthermore, the Rh^I catalyst lifetime is rather limited.

High-valent Cr,[6,7d] Mn[8–10,7d] and Fe[7,11,12] porphyrin complexes are known to epoxidize alkenes. The active catalysts are believed to be metal–oxo complexes. These epoxidation reactions are characterized by the following features that are in direct contrast with the epoxidation reactions in the hetero-cooxygenation. First, the metal–oxo porphyrin complexes are more reactive towards electron-rich alkenes. This contrasting behaviour can be taken as chemical evidence that a $Co^{IV}=O$ species is not the reactive intermediate. Secondly, cis-alkenes are more reactive than trans-alkenes, as in cytochrome P-450 chemistry. Thirdly, side products were found in the epoxidation reactions, e.g. the trans-alkene and trans-alkene oxide from the cis-alkene. Also, benzaldehyde was found when styrene or stilbene is epoxidized. Finally, N-alkylation occurs in parallel with epoxidation in the Fe^{III}–porphyrin-catalysed reaction. This leads to catalyst deactivation.

In summary, $[Co_2(\mu\text{-OH})L]$ is an efficient hetero-cooxygenation catalyst for PPh_3. Important features of this cooxygenation are: (i) the long life of the catalyst; (ii) the formation of a single oxidation product; (iii) the similar oxidizability of (E)- and (Z)-stilbene; (iv) the stereospecific epoxidation of alkenes. The detailed mechanism of this hetero-cooxygenation is being studied.

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