Hydroxylation of Alkanes and Arenes using Molecular Oxygen†

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A novel μ-oxo binuclear iron complex [$\{Fe(HBpz_3)(hfacac)\}_2O$] was found to be effective for dioxygen hydroxylation of alkanes and arenes including pentane and benzene in the presence of Hhfacac and Zn powder.

We recently reported the dioxygen oxidation of alkanes by a catalytic system composed of the μ-oxo binuclear iron complex [$(HBpz_3)Fe(OAc)_2(O)Fe(HBpz_3)$] **1**, $MeCO_2H$ (proton donor) and Zn powder (electron donor).[1] The system is of interest not only as a catalytic system for alkane hydroxylation but also as a plausible model for oxidation reactions catalysed by methane monooxygenase which is known to contain a binuclear iron site.[2] In our continuing efforts to develop a more effective catalyst, we have now found that the novel μ-oxo binuclear iron complex

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† Abbreviations used: $HBpz_3$ = hydrotris-1-pyrazolylborate, Hhfacac = hexafluoroacetylacetone.

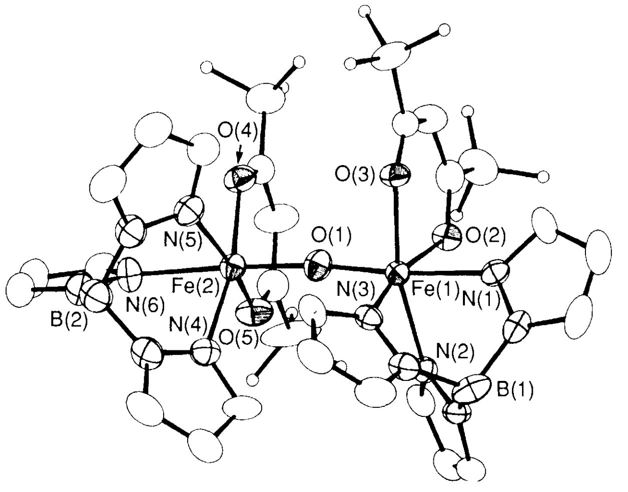
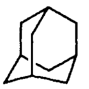
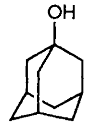
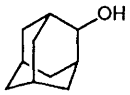
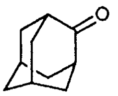
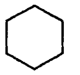
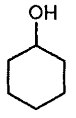
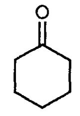
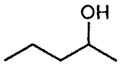
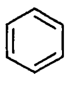
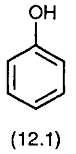
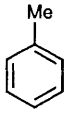
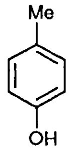
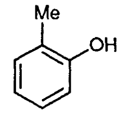
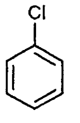
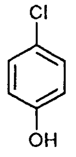
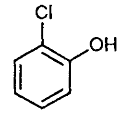


Fig. 1 ORTEP view of **2** (30% probability ellipsoids). Fluorine atoms are indicated as small spheres for clarity. Selected bond distances (Å) and angles (°): Fe(1)–O(1) 1.774(7); Fe(1)–O(2), 2.070(6); Fe(1)–O(3), 2.083(6); Fe(1)–N(1), 2.167(8); Fe(1)–N(2), 2.108(8); Fe(1)–N(3), 2.082(8); Fe(2)–O(1), 1.778(7); Fe(2)–O(4), 2.071(6); Fe(2)–O(5), 2.060(7); Fe(2)–N(4), 2.095(8); Fe(2)–N(5), 2.102(9); Fe(2)–N(6), 2.209(9); Fe(1)–O(3)–Fe(2), 169.4(4); A Fe(1) · · · Fe(2), 3.537(2).

Table 1 Oxidation of alkanes and arenes by **2**–Hhfacac–Zn powder using molecular dioxygen[a]

Substrate	Products (T.N.)		
	 (46.6)	 (1.7)	 (trace)
	 (4.5)	 (0.2)	
	 (21.0)		
	 (12.1)		
	 (6.3)	 (2.7)	
	 (2.2)	 (0.7)	

[a] The yields are given as turnover numbers (T.N.) based on **2**. Reactions conditions: 1 atm O_2; reagents in 20 ml of CH_2Cl_2, at 25 °C for 30 h; [**2**], 7.5 × 10^{-2} mmol dm^{-3} (1.5 μmol); [Hhfacac], 21.3 mmol dm^{-3} (0.43 mmol); Zn powder, 0.5 g; substrate, 1.66 mmol.

[{Fe(HBpz$_3$)(hfacac)}$_2$O] **2**, which may be prepared by ligand replacement of **1** with hexafluoroacetylacetone (Hhfacac), in the catalytic system **2**–Hhfacac–Zn powder, shows much greater activity than **1** for dioxygen hydroxylation of alkanes and arenes.

$$[(HBpz_3)Fe(OAc)_2(O)Fe(HBpz_3)]$$
$$\mathbf{1}$$
$$[\{Fe(HBpz_3)(hfacac)\}_2O] \quad [Fe(HBpz_3)_2]^+$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{3}$$

In order to improve the catalytic activity of the **1**–MeCO$_2$H–Zn powder system, we examined the effect of the electron and proton donor. During these investigations, an increase in the total yield for adamantane oxidation was noted when Hhfacac was used instead of MeCO$_2$H. Although the improvement in activity was not pronounced (*ca.* 1.5 times higher), we thought that the effect might be ascribed to formation of a new iron complex from **1** in the presence of Hhfacac which is catalytically more effective than **1**. In fact, treatment of **1** with Hhfacac in CH_2Cl_2 results in ligand replacement of acetato by hexafluoroacetylacetonato, affording the novel μ-oxo binuclear iron complex [{Fe(HBpz$_3$)(hfacac)}$_2$O] **2**. The ligand replacement reaction was accompanied by extensive decomposition to give [Fe(HBpz$_3$)$_2$]$^+$ **3**,[3] but **2** and **3** could be separated by benzene extraction of the crude product. Complex **2** was thus obtained as dark-orange crystals in 50–60% yield.‡ The structure of **2** was established by X-ray crystallography.§ As shown in Fig. 1, **2** has a binuclear structure bridged solely by the oxo ligand, with an Fe–O–Fe angle of 169°. The angle is more obtuse than that found in **1** (125°) in which the two iron atoms are bridged not only by oxo but also by two acetato ligands.[4] Each hexafluoroacetylacetonato ligand coordinates to one iron atom in a bidentate fashion.

A catalytic system composed of **2**, Hhfacac and Zn powder is effective for dioxygen oxidation of a variety of alkanes and arenes as shown in Table 1. The activity is apparently much higher than that of the system **1**–MeCO$_2$H–Zn reported previously.[1] For instance, the turnover number of adamantane oxidation obtained with the present system was 48.3, whereas the system containing **1** gave a turnover of only 2.3 under the same reaction conditions. In recent years, a number of attempts have been made to mimic enzymatic hydroxylation of alkanes.[5] However, most of the reactions were

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‡ Satisfactory elemental analyses were obtained for **2**. UV–VIS (CH_2Cl_2): λ_{max}/nm 500 (ε mol^{-1} dm^3 cm^{-1} 1710), 381 (8300) and 304 (20000); IR (KBr): ν cm^{-1}: ν_{BH} 2501; ν_{CO} 1649 and 1480 cm^{-1}.

§ *Crystal data* for **2**: M = 967.86, monoclinic, space group $P2_1/a$, a = 25.661(3), b = 11.887(2), c = 13.184(2) Å, β = 92.94(1)°, U = 4016(1) Å^3, Z = 4, D_c = 1.60 g cm^{-3}, $F(000)$ = 1936, graphite monochromated Mo-Kα radiation, λ = 0.71068 Å, μ (Mo-Kα) = 7.69 cm^{-1}. The data were collected on a Rigaku four-circle AFC-5 diffractometer using the ω-2θ scan mode with 2θ in the range 2–60°. The structure was solved by direct methods and refined by full-matrix least-squares. The final refinement used anisotropic thermal parameters for non-hydrogen atoms. No hydrogen atoms were included in the calculation. The final $R(R_w)$ values are 8.36% (8.20%) for 3921 independent reflections [$F_o > 3\sigma(F_o)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

accomplished with an oxidant such as H_2O_2 or ROOH, and only a few systems[6] are known to be effective for hydroxylation with dioxygen. Among these, our systems and Gif (and modified) systems[7] are unique since the iron complexes do not contain a porphyrin as a ligand.

Finally, it is notable that the present system is effective for dioxygen hydroxylation of not only alkanes but also arenes including benzene, because hydroxylation of benzene to phenol with dioxygen is attractive industrially.[8] Moreover, this suggests that the active species involved in the present system is distinct from that for Gif system, which does not oxidise arenes.¶

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¶ The present hydroxylation reaction may proceed *via* $^{\cdot}$OH radicals; EPR experiments with BPN (*N*-tert-butyl-α-phenyl nitrone) as a spin trapping reagent indicated formation of $^{\cdot}$OH radicals[9] in the solution under the reaction conditions.