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Fluorous Biphasic Catalytic Oxidation of Alkenes and Aldehydes with Air and 2-Methylpropanal in the Presence of (β-Perfluoroalkylated tetraphenylporphyrin)cobalt Complexes

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A simple and facile fluorous biphasic catalytic oxidation of alkenes and aldehydes with 1 atm of air and 2-methylpropanal in the presence of the (β-perfluoroalkylated tetraphenylporphyrin)cobalt complexes [Co{TPP(C_8F_{17})$_4$}] (**Co2**) has been demonstrated for the first time. This kind of β-perfluoroalkylated tetraphenylporphyrin may be used in other catalytic applications because of its ready availability and unique properties.

Introduction

Transition metal complexes based on porphyrins have been used extensively to catalyze a range of fundamentally and practically important chemical transformations,[1] including an array of atom/group-transfer reactions such as epoxidation and hydroxylation and nitrene (aziridination and amination) and carbene (cyclopropanation and carbene insertion) transfers.[1–3] Metalloporphyrin oxidation catalysts not only constitute unique biomimetic models for cytochrome P-450 enzymes but have also practical application in oxidation reactions. Electronically and sterically modified porphyrins incorporating strongly electron-withdrawing substituents at the pyrrolic β- and/or *meso*-position have been found to be more active and stable catalysts for oxygenation reactions than related electron-donating complexes,[3] and this has been rationalized by means of computational tools and photoelectron spectroscopy.[4] Among the numerous electron-withdrawing groups, perfluoroalkyl groups are advantageous because they are inert and strongly σ-electron-withdrawing. Moreover, theoretical and electrochemical studies show that these substituents should effectively stabilize the HOMO of the porphyrin macrocycle,[4] thus increasing the porphyrin's stability toward oxidation. More importantly, introduction of perfluoroalkyl groups onto the porphyrin macrocycle can improve solubility[5] and makes metalloporphyrin complexes potentially useful catalysts in fluorous media.[6] Perfluoroalkylated porphyrins have been used for fluorous biphasic catalysis, which has appealing features such as the easy separation and recycling of the perfluorinated organometallic complexes. In addition, the high solubility of oxygen in these fluids[7] would be particularly helpful in oxidation reactions. For example, 5,10,15,20-tetrakis(heptafluoropropyl)porphyrin has been successfully used as a fluorocarbon-soluble sensitizer for the photooxidation of allylic alcohols to hydroperoxide in a fluorous biphasic system.[8]

Nevertheless, there have been only a few reports of catalytic oxidation by *meso*-perfluroalkylated porphyrins within a fluorous biphasic system.[8,9] To the best of our knowledge, hydrocarbon oxygenation reactions catalyzed by β-perfluoralkylated metalloporphyrins have never been reported, perhaps because of synthetic difficulties. In connection with our recent report on the convenient and efficient synthesis of various β- and *meso*-perfluoroalkylated porphyrins, as well as their intramolecular radical cyclizations,[10] we report here a facile fluorous biphasic catalytic oxidation of alkenes and aldehydes with 1 atm of air and 2-methylpropanal in the presence of the (β-perfluoralkylated tetraphenylporphyrin)cobalt complexes [Co{TPP(C_8F_{17})$_4$}] (**Co2**).

Results and Discussion

The best way to prepare the required β-perfluoralkylated tetraphenylporphyrin ligand H_2TPP(C_8F_{17})$_4$ (**2**) is by demetalation of its corresponding copper complex [Cu{TPP(C_8F_{17})$_4$}] (**Cu2**) with CF_3COOH (TFA)/concd. H_2SO_4. The copper complex was conveniently prepared by a Pd-catalyzed cross-coupling of the readily available (β-octabromoporphyrin)copper complex [CuTPP(Br)$_8$] (**Cu1**)[11] with $C_8F_{17}I$/Cu in good yield, as described previously.[10a] We did not try to determine the substitution pattern of H_2TPP(C_8F_{17})$_4$ (**2**) and the fluorinated chains are therefore shown at random positions. Insertion of the metal atom (Co, Ni, Fe, or Mn) into the free-base porphyrin H_2TPP(C_8F_{17})$_4$ (**2**), according to a literature pro-

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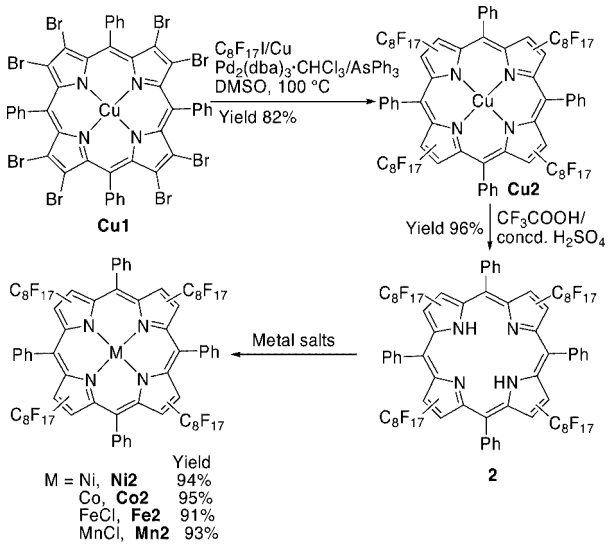
cedure,[12] afforded the corresponding metalloporphyrins. Although the fluorine load of these metalloporphyrins (F ≈ 55%) is lower than that required to make these fluorous biphasic oxidation catalysts soluble in perfluorocarbons (F > 60%)[6] (and Pozzi[13] has reported that the introduction of four C_8 perfluoroalkyl tails at the periphery of a tetraarylporphyrin is not sufficient to ensure its solubility in perfluorocarbons), they readily dissolve in perfluorodecalin, although not in CH_3CN, CH_2Cl_2, acetone, or alcohols, as determined by visual tests. The remarkably high fluorous affinity of **M2** (M = Cu, Ni, Co, Fe, Mn) for perfluorocarbons is probably related to their increasing electroneutrality upon introduction of a perfluoroalkyl chain at the β-positions because the very low dielectric constants of perfluorocarbons diminishes the solubilization of charged complexes, even though they are highly fluorinated.[14] Indeed, we found that the solubility of **M2** (M = Cu, Ni, Co) in perfluorocarbons is higher than that of **M2** (M = Fe, Mn) because of the cationic nature of the latter. The present results also confirm that the fluorine load alone is not sufficient to be able to predict the solubility of a molecule, and other features such as the number, length, and position of the R_F substituents must be taken into account.[14] In contrast, these (β-perfluoralkylated tetraphenylporphyrin)metal complexes [M{TPP(C_8F_{17})$_4$}] (**M2**; M = Cu, Ni, Co, Fe, Mn) are very soluble in diethyl ether, making the workup convenient, and this can be ascribed to their favorable interaction with the R_F tails.[13] The partition coefficient of **Co2** in perfluorodecalin/CH_3CN (1:1, v/v) is very high at 20 °C; it cannot be detected by UV/Vis spectroscopy in the CH_3CN layer, despite its characteristic absorption at 435 nm, after stirring a solution of **Co2** in perfluorodecalin with CH_3CN (1:1, v/v) for 2 h. We therefore took advantage of the preferential solubility of **M2** (M = Cu, Ni, Co, Fe, Mn) in perfluorodecalin for their isolation from the reaction mixture and for the fluorous biphasic catalytic oxidation of alkenes and aldehydes (Scheme 1).

Using styrene as a model substrate, we first evaluated the catalytic oxidation activity of various (β-perfluoralkylated tetraphenylporphyrin)metal complexes [M{TPP(C_8F_{17})$_4$}] (**M2**; M = Cu, Ni, Co, Fe, Mn). The results are summarized in Table 1. The reactions were carried out at room temperature in flasks carefully shielded from direct sunlight. A solution of the complex in perfluorodecalin was added to a solution of styrene in CH_3CN containing a twofold excess of 2-methylpropanal, as a sacrificial reducing agent,[15] with respect to the styrene. The resulting biphasic mixture was vigorously stirred under 1 atm of air. After completion of the reaction, the two layers were easily separated and the CH_3CN layer was analyzed by GC. In the absence of **M2** the styrene did not react. Although the fluorous biphasic oxidation can go smoothly in the presence of various **M2** complexes, [Co{TPP(C_8F_{17})$_4$}] (**Co2**) was found to be the most efficient catalyst. The suitable loading of catalyst was 0.4 mol-%. It is worth mentioning that air is a safe, clean, and freely available oxidant, although the use of 1 atm of air in most aerobic oxidation systems is still limited as pure oxygen or a high pressure of air under severe reaction conditions is generally required in order to maintain the activity of the metal catalysts. Our catalytic system is more convenient and efficient and uses air instead of pure oxygen.



Scheme 1. Synthesis of various (β-perfluoralkylated tetraphenylporphyrin)metal complexes [M{TPP(C_8F_{17})$_4$}] (**M2**).

Table 1. Epoxidation of stryene under fluorous biphasic conditions catalyzed by various (β-perfluoralkylated tetraphenylporphyrin)-metal complexes [M{TPP(C_8F_{17})$_4$}] (**M2**).[a]

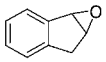
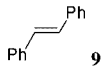
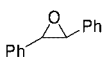
Entry	M{TPP(C_8F_{17})$_4$} (**M2**)	mol-%	Time [h]	Yield [%][b]
1	–	–	24	0
2	**Cu2**	0.4	24	0
3	**Ni2**	0.4	20	55
4	**Fe2**	0.4	24	42
5	**Mn2**	0.4	24	40
6	**Co2**	0.4	12	65
7	**Co2**	0.1	12	60
8	**Co2**	1.0	12	67

[a] Reaction conditions: styrene (1.0 mmol), 2-methylpropanal (2.0 mmol) in perfluorodecalin (5 mL) and CH_3CN (5 mL) were stirred vigorously under 1 atm of air in the dark. [b] Determined by GC using $C_{12}H_{26}$ as internal standard.

The optimized reaction conditions described above are suitable for other alkenes as well (Table 2). In general, various alkenes can be epoxidized smoothly in acceptable yield. For typical fluorous catalysis the most important aspect is the simple separation, recycling, and re-use of the catalyst. Experiments aimed at determining the extent of catalyst recyclability were carried out with stilbene. The fluorous phase was reused up to five times without apparent loss of activity (Entries 7–12).

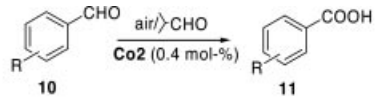
To further investigate the generality and scope of the system, the protocol was extended to simple aromatic aldehydes (Table 3). In most cases, the oxidation reaction proceeded smoothly in good yields. As expected, the reactivity of aldehydes with electron-donating substituents was higher than those with electron-withdrawing ones (Entries 2 and 3 vs. 7 and 8).

Table 2. Epoxidation of different alkenes with 1 atm of air catalyzed by [Co{TPP(C_8F_{17})$_4$}] (**Co2**) under fluorous biphasic conditions.[a]

Entry	Substrate	Product	t [h]	Yield (%)[b]
1	 **3**	 **3a**	12	65[c]
2	 **4**	 **4a**	36	68
3	 **5**	 **5a**	12	85
4	 **6**	 **6a**	24	71[c]
5	 **7**	 **7a**	20	84[c]
6	 **8**	 **8a**	24	82
7	 **9**	 **9a**	12	95
8	**9**	**9a**	12	92[d]
9	**9**	**9a**	12	93[d]
10	**9**	**9a**	12	91[d]
11	**9**	**9a**	12	88[d]
12	**9**	**9a**	12	90[d]

[a] Reaction conditions: alkene (1.0 mmol), 2-methylpropanal (2.0 mmol), and **Co2** (0.4 mol-%) in perfluorodecalin (5 mL) and CH_3CN (5 mL) were stirred vigorously under 1 atm of air in the dark. [b] Isolated yields. [c] GC yields using $C_{12}H_{26}$ as the internal standard. [d] Reaction run with the fluorous layer recovered from the previous Entry.

Table 3. Oxidation of aromatic aldehydes with 1 atm of air catalyzed by [Co{TPP(C_8F_{17})$_4$}] (**Co2**) under fluorous biphasic conditions.[a]



10 **11**

Entry	R	Product	t [h]	Yield (%)[b]
1	H (**10a**)	**11a**	10	85
2	4-Me (**10b**)	**11b**	10	74
3	4-MeO (**10c**)	**11c**	10	90
4	4-Cl (**10d**)	**11d**	12	79
5	4-Br (**10e**)	**11e**	12	80
6	2,6-Cl_2 (**10f**)	**11f**	16	91
7	4-CF_3 (**10g**)	**11g**	24	73
8	4-NO_2 (**10h**)	**11h**	36	67

[a] Reaction conditions: aldehyde (1.0 mmol), 2-methylpropanal (2.0 mmol), and **Co2** (0.4 mol-%) in perfluorodecalin (5 mL) and CH_3CN (5 mL) were stirred vigorously under 1 atm of air in the dark. [b] Isolated yields.

Conclusion

In summary, we have demonstrated for the first time a simple and facile fluorous biphasic catalytic oxidation of alkenes and aldehydes with 1 atm of air and 2-methylpropanal in the presence of the (β-perfluoralkylated tetraphenylporphyrin)cobalt complex [Co{TPP(C_8F_{17})$_4$}] (**Co2**). Because of the ready availability and unique properties of β-perfluoralkylated porphyrins, they may be applied for other catalysis reactions. Further work on this catalytic system is now in progress.

Experimental Section

General: ^{1}H (300 MHz) and ^{19}F (282 MHz) NMR spectra were recorded with a Bruker AM-300 or Varian-360L spectrometer. Chemical shifts are reported in ppm relative to TMS as an internal standard (δ = 0 ppm) for ^{1}H NMR spectra and $CFCl_3$ as an external standard (negative for upfield) for ^{19}F NMR spectra. Deuterated solvents for NMR were purchased from Cambridge Isotope Laboratories, Aldrich, or Acros. MS and HRMS data were recorded with a Hewlett–Packard HP-5989A spectrometer and a Finnigan MAT-8483 mass spectrometer, respectively. UV/Vis spectra were measured with a Varian Cary 100 spectrophotometer. Elementary analyses were obtained with a Perkin–Elmer 2400 Series II Elemental Analyzer. TLC analysis was performed on silica gel plates and column chromatography on silica gel (mesh 300–400), which were both obtained from Qingdao Ocean Chemicals. DMSO was distilled from CaH_2. All the other solvents and chemicals were of reagent grade, purchased commercially, and used without further purification unless otherwise noted.

Synthesis of Copper Powder: $CuSO_4 \cdot 5H_2O$ (32 g, 128 mmol) was dissolved in H_2O (160 mL) and zinc powder (8 g, 123 mmol) was added in several small portions. The resulting solution was stirred for 30 min. A HCl solution (2 M, 40 mL) was then added and the mixture stirred for another 30 min. The precipitated red copper was collected by filtration under reduced pressure, washed with acetone, dried under vacuum at room temperature and kept under N_2.

General Procedure for Preparing [Cu{TPP(C_8F_{17})$_4$}] (Cu2): An oven-dried 50-mL Schlenk flask was charged with [Cu{TPP(Br_8)}] (**Cu1**; 100 mg, 1.0 equiv.), $Pd_2(dba)_3 \cdot CHCl_3$/$AsPh_3$ (10 mol-%/80 mol-%), and Cu (80 equiv. with respect to **Cu1**). The flask was then evacuated and refilled with argon (three cycles). DMSO (20 mL) and $C_8F_{17}I$ (40 equiv. with respect to **Cu1**) were then added at room temperature. The resulting mixture was stirred at 100 °C for 3 h and then allowed to reach room temperature. The reaction mixture was poured on the top of a short silica column and washed with CH_3CN under pressure; the eluate was discarded. The column was then eluted with Et_2O. The filtrate was collected and washed with water three times. The organic layer was dried with Na_2SO_4 and the solvents were evaporated to dryness. The resulting solid was purified by flash column chromatography using petroleum ether as eluent to provide the desired product **Cu2**. Yield: 146 mg (82%). MS (MALDI): m/z = 2347.0 [M$^+$]. UV/Vis (PE): λ_{max} (%) = 436 (18.9), 578 (1.2), 623 (1.0) nm. $C_{76}H_{24}CuF_{68}N_4 \cdot 5H_2O$ (2437.1): calcd. C 37.43, H 1.41, N 2.30; found C 37.00, H 1.22, N 2.00.

Demetalation of Cu2: [Cu{TPP(C_8F_{17})$_4$}] (100 mg, 1.0 equiv.) was dissolved in TFA/concd. H_2SO_4 (4:1, v/v; 4 mL) and Et_2O (4 mL) and the mixture was stirred at room temperature for 2 h, then poured carefully into ice/water and extracted with Et_2O. The organic layer was washed with saturated $NaHCO_3$ solution and water. It was then dried with Na_2SO_4 and the solvents were evaporated to dryness. The resulting solid could be used directly for the next reaction.

H_2TPP(C_8F_{17})$_4$ (2): Yield: 94 mg (96%). MS (MALDI): m/z = 2286.1 [M$^+$]. UV/Vis (PE): λ_{max} (%) = 443 (28.3), 552 (1.1), 606 (1.7), 716 (1.0) nm. HRMS (MALDI): calcd. for [$C_{76}H_{27}N_4F_{68}$]$^+$ 2287.1088; found 2287.11443. $C_{76}H_{26}F_{68}N_4 \cdot 5H_2O$ (2376.2): calcd. C 38.40, H 1.53, N 2.36; found C 37.91, H 1.06, N 1.95.

General Procedure for Cobalt and Nickel Insertion into H_2TPP(C_8F_{17})$_4$ (2):[12a] H_2TPP(C_8F_{17})$_4$ (**2**; 100 mg, 1.0 equiv.), $M(OAc)_2 \cdot 4H_2O$ (5.0 equiv.), and DMF (10 mL) were heated at 100 °C for 1 h. The resulting mixture was cooled to room tempera-

ture, taken up in Et_2O, and transferred to a separatory funnel. The mixture was washed with water three times and the organic layer was filtered through a short silica column. The filtrate was collected and the solvents were evaporated to dryness to yield the desired products. This compound was sufficiently pure for further reactions and an analytical sample was obtained by flash column chromatography using petroleum ether as eluent.

[Co{TPP(C_8F_{17})$_4$}] (Co2): Yield: 97 mg (95%). MS (MALDI): *m*/*z* = 2343.0 [M^+]. UV/Vis (PE): λ_{max} (%) = 435 (17.5), 574 (1.3), 623 (1.0) nm. HRMS (MALDI): calcd. for $[C_{76}H_{24}N_4F_{68}Co]^+$ 2343.0232; found 2343.02415. $C_{76}H_{24}CoF_{68}N_4 \cdot H_2O$ (2361.0): calcd. C 38.65, H 1.11, N 2.37; found C 38.47, H 1.45, N 2.17.

[Ni{TPP(C_8F_{17})$_4$}] (Ni2): Yield: 96 mg (94%). MS (MALDI): *m*/*z* = 2343.0 [M^+]. UV/Vis (PE): λ_{max} (%) = 441 (28.4), 560 (1.9), 600 (1.0) nm. HRMS (MALDI): calcd. for $[C_{76}H_{24}N_4F_{68}Ni]^+$ 2343.0294; found 2343.02630. $C_{76}H_{24}F_{68}N_4Ni \cdot 1.5H_2O$ (2369.0): calcd. C38.50, H 1.15, N 2.36; found C 38.12, H 0.85, N 2.29.

General Procedure for Iron and Manganese Insertion into H_2TPP(C_8F_{17})$_4$ (2):[12b] $H_2TPP(C_8F_{17})_4$ (**2**; 100 mg, 1.0 equiv.), $MCl_2 \cdot 4H_2O$ (5.0 equiv.), 2,6-lutidine (two drops), and Et_2O/MeOH (4:1, v/v; 50 mL) were heated at 40 °C overnight. The resulting mixture was cooled to room temperature and washed with water three times. The organic layer was dried with Na_2SO_4 and the solvents were evaporated to dryness. The resulting solid was purified by flash column chromatography with petroleum ether as eluent.

[Fe{TPP(C_8F_{17})$_4$}Cl] (Fe2): Yield: 94 mg (91%). MS (MALDI): *m*/*z* = 2375.0 [M^+]. UV/Vis (PE): λ_{max} (%) = 364 (8.3), 442 (23.2), 512 (1.0), 560 (1.3) nm. HRMS (MALDI): calcd. for $[C_{76}H_{24}N_4F_{68}ClFe]^+$ 2374.9925; found 2374.99475. $C_{76}H_{24}F_{68}FeN_4$ (2340.0): calcd. C 38.41, H 1.02, N 2.36; found C 38.36, H 1.16, N 2.24.

[Mn{TPP(C_8F_{17})$_4$}Cl] (Mn2): Yield: 97 mg (93%). MS (MALDI): *m*/*z* = 2374.0 [M^+]. UV/Vis (PE): λ_{max} (%) = 446 (10.5), 496 (3.6), 610 (1.0), 680 (1.0) nm. HRMS (MALDI): calcd. for $[C_{76}H_{24}N_4F_{68}ClMn]^+$ 2373.9891; found 2374.99785. $C_{76}H_{24}ClF_{68}MnN_4$ (2340.0): calcd. C 38.43, H 1.02, N 2.36; found C 38.43, H 1.22, N 2.44.

General Procedure for the Fluorous Biphasic Catalytic Oxidation of Alkenes and Aldehydes: A 50-mL Schlenk flask was charged with an alkene or aldehyde (1.0 mmol), 2-methylpropanal (2.0 mmol), **Co2** (0.4 mol-%), perfluorodecalin (5 mL), and CH_3CN (5 mL). The resulting mixture was stirred vigorously under 1 atm of air in the dark. After completion of the reaction, the fluorous layer was recovered, washed with CH_3CN, and reused in further runs. The combined CH_3CN layers were subjected to GC analysis or flash column chromatography to yield the desired products.

Acknowledgments

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