Organometallics **1999,** *18,* 438−446

Mechanism of Palladium−Carbon Bond Oxidation: Dramatic Solvent Effect

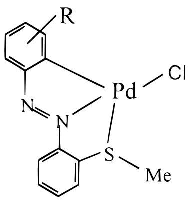
Kaliappan Kamaraj and Debkumar Bandyopadhyay*

Department of Chemistry, Indian Institute of Technology, New Delhi-110016, India

Received August 31, 1998

Pentafluoroiodosylbenzene (C_6F_5IO) selectively oxidizes Pd−C bonds of a series of cyclopalladated 2-(alkylthio)azobenzene complexes. The kinetics of oxygen atom insertion into the Pd−C bond of one representative compound has been studied in detail to understand the mechanism of this reaction. At 20 °C Pd−C bond oxidation takes place smoothly in acetonitrile at a rate of 0.08 M^{-1} s^{-1}, whereas this reaction does not proceed in solvents such as dichloromethane and chloroform. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for this reaction are 55.5 ± 3.5 kJ/mol and −75.7 ± 11.5 eu, respectively. Among other oxidants, hydroperoxy radical (for example, t-BuOO$^{\bullet}$) is found to be extremely efficient, whereas the highly electrophilic oxoiron(IV) porphyrin cation radical (oxene) is incapable of oxidizing the Pd−C bond. Oxene, however, selectively oxidizes the thioether functionality. These observations suggest that nucleophilic attack of the oxidant molecule on palladium(II) could be the most crucial step prior to Pd−C bond oxidation. A large negative value of $\Delta S^{\ddagger}$ supports an associative mechanism, and a smooth reaction in polar solvent supports a polar intermediate structure. Hydroperoxides, in the presence of a catalytic amount of iron(III) porphyrin chloride, selectively oxidizes the Pd−C bond. This observation, coupled with the fact that oxene oxidizes the thioether functionality, indicates that oxene may not be the major reactive intermediate in hydroperoxide oxidations. On the basis of these experimental results, we have attempted to draw a plausible mechanism of Pd−C bond oxidation.

Introduction



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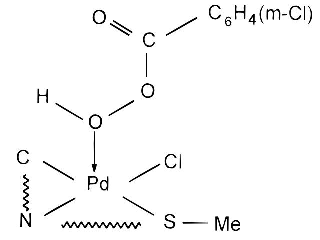
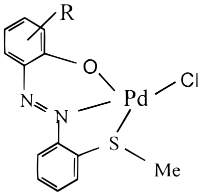


[I]



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Oxygen atom insertion into Pd−C bonds of a series of cyclopalladated azo compounds by peracids and iodosylbenzene has been achieved successfully.[1−4] Oxidative cleavage of M−C bonds (M = Pd, Pt) and stereoselective product formation from the reaction of M−C-bonded compounds with peracids are remarkable.[5−7] Oxygenation of cyclopalladated *N*,*N*-dimethylbenzylamine compounds by inorganic and organic peroxides has also been thoroughly investigated.[8,9] Preliminary kinetic studies on the oxidation of type **1** compounds by MCPBA have revealed the possible existence of the intermediate compound **[I]** prior to the formation of the Pd−C bond oxidized product **2**. In similar oxygenation of cyclopalladated *N*,*N*-dimethylbenzylamine compounds by inorganic and organic peroxides, nucleophilic end-on attack of the metal center on the O−O bond of the oxidant to give transient Pd(IV) has been proposed.[8] Herein we describe the reactions of type **1** compounds with C_6F_5IO, oxene, t-BuOO$^{\bullet}$ radical, and t-BuOOH + F_{20}TPPFeCl. Regioselective oxidation of two distinctly different parts of the same molecule by oxidants of variable electrophilicity is found to be very useful in getting further insight into the mechanistic aspects of this Pd−C bond oxidation.

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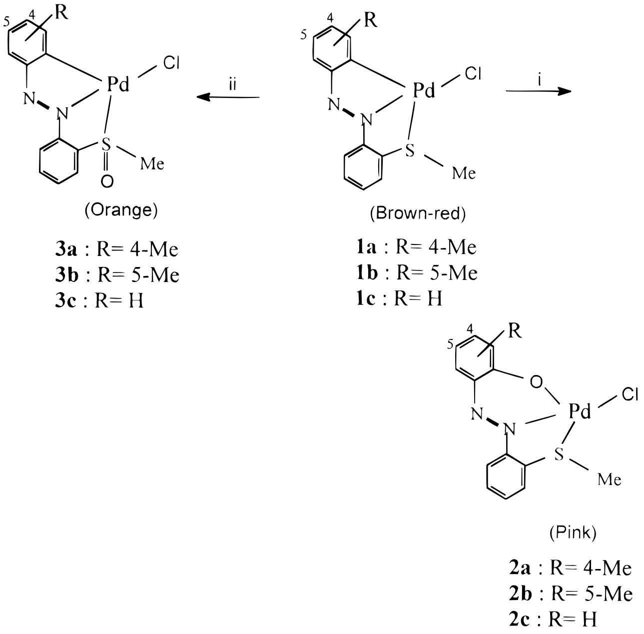
10.1021/om980731w CCC: $18.00

Table 1. Oxidation of 1a−c by Various Oxidants at 30 ± 2 °C[a]

entry no.	substrate	oxidizing system	solvent	product (% yield)
1	**1a**	C_6F_5IO	CH_3CN	**2a** (93)
2	**1b**	C_6F_5IO	CH_3CN	**2b** (76)
3	**1c**	C_6F_5IO	CH_3CN	**2c** (80)
4	**1a**	t-BuOO$^•$	CH_2Cl_2	**2a** (70)
5	**1b**	t-BuOO$^•$	CH_2Cl_2	**2b** (76)
6	**1c**	t-BuOO$^•$	CH_2Cl_2	**2c** (80)
7	**1a**	t-BuOO$^•$	CH_2Cl_2−MeOH (2:3)	**2a** (53)
8	**1b**	t-BuOO$^•$	CH_2Cl_2−MeOH (2:3)	**2b** (64)
9	**1c**	t-BuOO$^•$	CH_2Cl_2−MeOH (2:3)	**2c** (76)
10	**1a**	F_{20}TPPFeCl + t-BuOOH	CH_2Cl_2−MeOH (2:1)	**2a** (50)
11	**1b**	F_{20}TPPFeCl + t-BuOOH	CH_2Cl_2−MeOH (2:1)	**2b** (52)
12	**1c**	F_{20}TPPFeCl + t-BuOOH	CH_2Cl_2−MeOH (2:1)	**2c** (56)
13	**1a**	F_{20}TPPFeCl + C_6F_5IO	CH_2Cl_2	**3a** (73)
14	**1b**	F_{20}TPPFeCl + C_6F_5IO	CH_2Cl_2	**3b** (81)
15	**1c**	F_{20}TPPFeCl + C_6F_5IO	CH_2Cl_2	**3c** (73)
16	**1a**	F_{20}TPPFeCl + C_6F_5IO	CH_2Cl_2−MeOH (2:3)	**3a** (66)
17	**1b**	F_{20}TPPFeCl + C_6F_5IO	CH_2Cl_2−MeOH (2:3)	**3b** (83)
18	**1c**	F_{20}TPPFeCl + C_6F_5IO	CH_2Cl_2−MeOH (2:3)	**3c** (80)

[a] Details are given in the Experimental Section.

Scheme 1[a]



[a] Reagents: (i) C_6F_5IO in CH_3CN, or t-BuOO$^•$ or $F_{20}TPPFe^{III}Cl$ + t-BuOOH in CH_2Cl_2−MeOH. (ii) $F_{20}TPPFe^{III}Cl$ + C_6F_5IO in CH_2Cl_2.

Results

The compounds chosen for the present study are shown in Scheme 1. All these compounds were independently prepared and spectroscopically characterized as previously described.[1b,d] Cyclopalladated compounds **1a−c** react smoothly with C_6F_5IO in CH_3CN to give Pd−C bond oxidized products **2a−c** in high yields. This reaction does not proceed in solvents such as CH_2Cl_2 and $CHCl_3$. Alcoholic solvents play an interesting role in this oxidation reaction. We have followed the kinetics of this reaction in CH_3CN, and the role of one alcoholic solvent (CF_3CH_2OH) has been studied in detail. The second reagent (t-BuOO$^•$ radical) is extremely efficient in oxidizing **1a−c** to **2a−c** in CH_2Cl_2. Alcoholic solvent reduces the efficiency of this reagent. The third reagent (PFeCl + t-BuOOH) is selective for Pd−C bond oxidation in CH_2Cl_2−MeOH mixed solvent. In CH_2Cl_2 the reaction is too slow (vide infra), and in neat MeOH the reaction mixture becomes a mess in 5 min. The fourth reagent (PFeCl + C_6F_5IO) does not oxidize the Pd−C bond, but it selectively oxidizes **1a−c** to **3a−c** (path ii, Scheme 1). In this reaction we have not observed any significant solvent effect. Full details of these reactions are given under different subheadings, and the results are summarized in Tables 1 and 2.

A. Reaction of C_6F_5IO. Cyclopalladated compounds **1a−c** react smoothly with C_6F_5IO in acetonitrile solvent to give **2a−c** in high yields (Table 1, entries 1−3). The transformation of **1a** has been monitored thoroughly. In a typical kinetic experiment a strong solution (10−50 μL) of C_6F_5IO in CF_3CH_2OH was added to a CH_3CN solution (1.5 mL) of **1a** in a sealed quartz cuvette at a desired temperature. The cuvette was vigorously shaken before it was placed into the thermostated cell holder of a spectrophotometer. One representative spectral change of **1a** for such a reaction mixture is given in Figure 1. Absorbances at 420 and 510 nm were recorded at 20 s intervals until at least 80% of the total reaction was over. The rate of reaction was determined by a least-squares fit of the observed data to an equation of

$$A_t = \sum_{i=1}^{n} A_i e^{-k_i t} + A_\alpha \qquad (1)$$

type (1), where A_t is the absorbance at time t, n is the number of discrete exponentials, and A_α is the absorbance at infinite time. Least-squares analysis of all data files, however, were best fitted with $i = 1$, and the rates measured at 420 and 510 nm (tested for more than one data file at each temperature) agreed within 1.5−2.0%. This implies that Pd−C bond oxidation is a single-exponential process. Standard plots of these pseudo-first-order rates did not show any simple relationship with oxidant concentrations. For example, plots of (i) k_{obs} vs [oxidant] and (ii) k_{obs} vs [oxidant]^2 were all distinctly nonlinear (Figures 2 and 3). With great surprise we observed that small (10−50 μL) but variable quantities of trifluoroethanol (TFE) added to the CH_3CN solution of **1a** in different kinetic experiments during variable oxidant data collections were primarily responsible for all such nonlinear plots. Thus, each experiment, having fixed concentrations of **1a** and C_6F_5IO, was repeated with systematic variation of TFE (up

Table 2. Kinetic Data for the Oxidation of 1a with C_6F_5IO in Acetonitrile[a]

entry no.	temp (°C)	$10^3[C_6F_5IO]$ (M)	$[CF_3CH_2OH]$ (M)	10^4k_{obs} (s^{-1})	$10^4k_{obs(0)}$ (s^{-1})	k (M^{-1} s^{-1})
1	20	3.907	0.2691	2.8662	4.02 ± 0.07	0.0836 ± 0.007
2			0.3565	2.4153		
3			0.4427	2.1023		
4			0.5278	1.7079		
5		5.915	0.2691	4.4216	6.08 ± 0.17	
6			0.3565	3.7061		
7			0.4427	3.1257		
8			0.5278	2.7764		
9			0.6119	2.1211		
10		7.688	0.3565	4.7774	6.97 ± 0.47	
11			0.5278	4.0911		
12			0.6119	3. 204		
13			0.6949	2.8503		
14		9.573	0.4427	5.9611	8.94 ± 0.05	
15			0.5278	5.4128		
16			0.6119	4.8256		
17			0.6949	4.2723		
18	25	4.035	0.1806	6.5321	10.16 ± 0.05	0.134 ± 0.003
19			0.2691	4.7215		
20			0.3565	3.0002		
21			0.4427	1.2260		
22		6.0725	0.2691	7.3643	12.92 ± 0.01	
23			0.3565	5.5478		
24			0.4427	3.7994		
25			0.5278	2.0035		
26		8.309	0.3565	7.7032	15.68 ± 0.07	
27			0.4427	5.7986		
28			0.5278	3.8263		
29			0.6119	2.0017		
30		10.301	0.4427	9.1706	18.66 ± 0.06	
31			0.5278	7.3514		
32			0.6119	5.5610		
33	30	4.191	0.1806	7.8059	11.14 ± 0.11	0.1803 ± 0.006
34			0.2691	6.3107		
35			0.3565	4.7064		
36			0.4427	3.0092		
37		6.245	0.2691	9.3240	15.01 ± 0.84	
38			0.3565	7.7200		
39			0.4427	5.2540		
40			0.5278	3.2020		
41			0.6119	2.4427		
42		8.213	0.3565	9.8326	18.11 ± 0.10	
43			0.5278	5.1717		
44			0.6119	3.2754		
45			0.6949	1.8328		
46		10.000	0.4427	10.821	21.77 ± 0.90	
47			0.5278	08.040		
48			0.6119	06.302		
49			0.6949	04.310		
50	35	4.133	0.1806	16.166	20.17 ± 0.65	0.2750 ± 0.07
51			0.2691	14.541		
52			0.3565	12.029		
53			0.4427	9.7921		
54			0.5278	8.8761		
55		6.159	0.2691	22.641	28.77 ± 0.66	
56			0.3565	20.401		
57			0.4427	18.780		
58			0.5278	16.008		
59			0.6119	14.914		
60		7.533	0.3565	26.527	34.57 ± 0.75	
61			0.4427	24.301		
62			0.5278	23.200		
63			0.6119	20.791		
64			0.6949	18.760		
65		9.974	0.5278	27.571	36.05 ± 2.3	
66			0.6119	25.300		
67			0.6949	23.806		
68			0.7768	23.414		

[a] Concentration of **1a**: (1.8−2.2) × 10^{-4} M in all experiments.

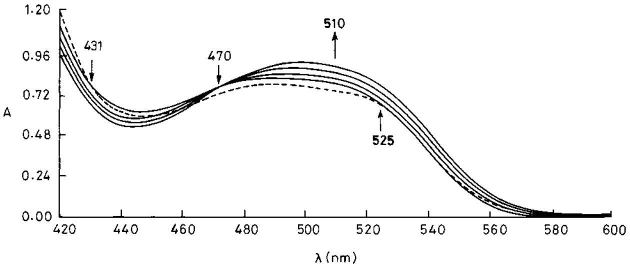


Figure 1. Change of UV−visible spectra of **1a** on its reaction with C_6F_5IO: (- - -) spectrum of **1a** (0.163 mM) in 1.5 mL CH_3CN; (—) change of above spectrum on addition of 20 μL of C_6F_5IO solution in TFE. The final oxidant concentration was 2.08 mM. Each spectrum was recorded at an interval of 2 min after mixing the two reagents at 25 °C.

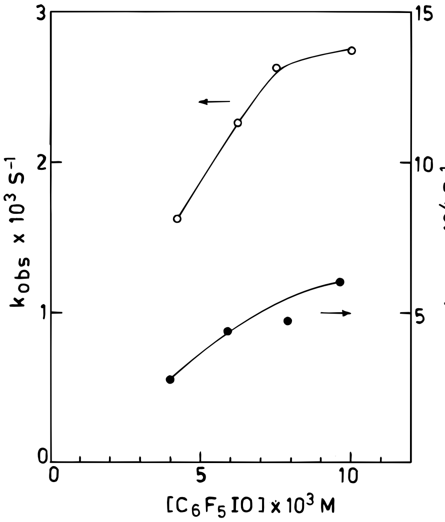


Figure 2. Plots of k_{obs} versus $[C_6F_5IO]$ for the oxidation of **1a** to **2a** in CH_3CN at (●) 20 °C and (○) 35 °C.

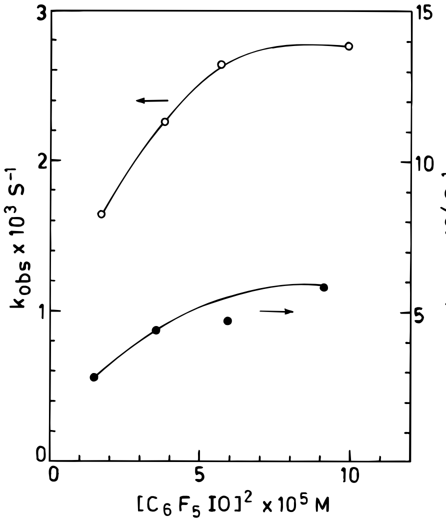


Figure 3. Plots of k_{obs} versus $[C_6F_5IO]^2$ for the oxidation of **1a** to **2a** in CH_3CN at (●) 20 °C and (○) 35 °C.

to 0.7 M) in acetonitrile and the rates of these reactions were plotted against trifluoroethanol concentrations (Figure 4).[10] The observed linear plots were extrapolated

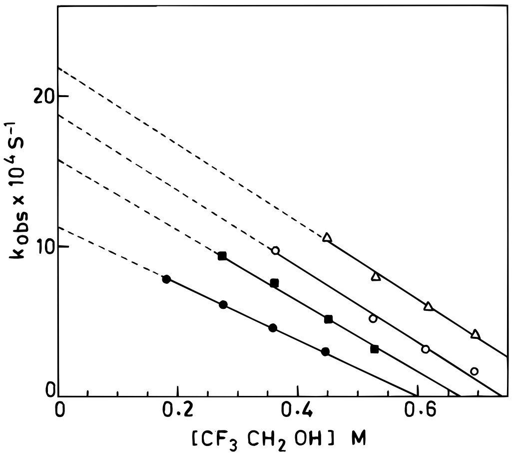


Figure 4. Plots of k_{obs} versus $[CF_3CH_2OH]$ at 30 °C. $[C_6F_5IO]$ = (●) 4.21 mM, (■) 6.2 mM, (○) 8.2 mm, and (△) 10 mM. [**1a**] = 0.18−0.22 mM in all cases.

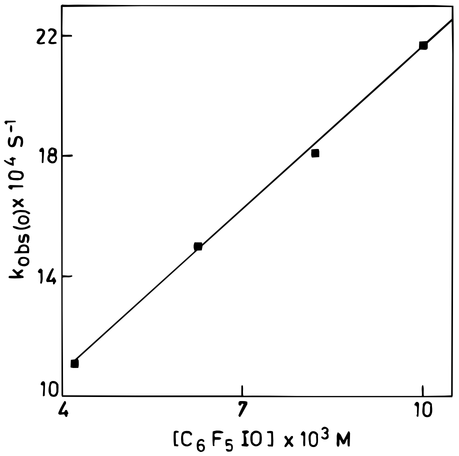


Figure 5. Plot of $k_{obs(0)}$ versus $[C_6F_5IO]$ for the oxidation of **1a** to **2a** in CH_3CN at 30 °C. [**1a**] = 0.18−0.22 mM.

to zero TFE concentrations and the intercepts on the *y* axis were taken as pseudo-first-order rates in pure acetonitrile ($k_{obs(0)}$). These $k_{obs(0)}$ values, when plotted against corresponding C_6F_5IO concentrations, gave perfectly linear plots (one representative plot is shown in Figure 5). Thus, in pure acetonitrile the rate equation could be represented by: $-d[\mathbf{1a}]/dt = k[\mathbf{1a}][C_6F_5IO]$; however, in acetonitrile containing TFE (up to 0.7 M) the rate equation becomes $-d[\mathbf{1a}]/dt = k[\mathbf{1a}][C_6F_5IO]/[TFE]$. The rates at variable temperature (20−35 °C) were similarly measured, and from standard Eyring plots, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated to be 55.5 ± 3.5 kJ/mol and −75.7 ± 11.5 eu, respectively. Solvent compositions and rate constants are summarized in Table 2. This Pd−C bond oxidation by C_6F_5IO has not been observed in CH_2Cl_2, $CHCl_3$, or TFE.

In Figure 1 we note that the isosbestic point at 470 nm is distinctly away from the spectrum of **1a** (dashed line), and the first spectrum of **1a** + oxidant intersects that of **1a** at 431 nm. This observation inspired us to look into the spectral features of **1a** in CH_2Cl_2, CH_3CN, and CH_3CN−TFE. We have not been able to detect any low-energy bands of **1a** in CH_3CN or CH_3CN−TFE solvent systems (not shown); however, there is a distinct blue shift of visible bands (Figure 6). The nature of the band shifts, the intensity of shifted bands, and the absence of any low-energy bands in coordinating sol-

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[10] The rate of this reaction in CH_3CN containing 20% TFE was immeasurably slow, and in neat TFE there was no observable C−Pd bond oxidation.

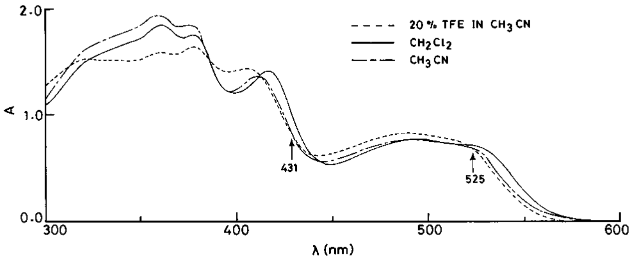

Figure 6. UV−visible spectra of **1a** in CH_2Cl_2, CH_3CN, and TFE−CH_3CN (1:4). [**1a**] = 0.16 mM.

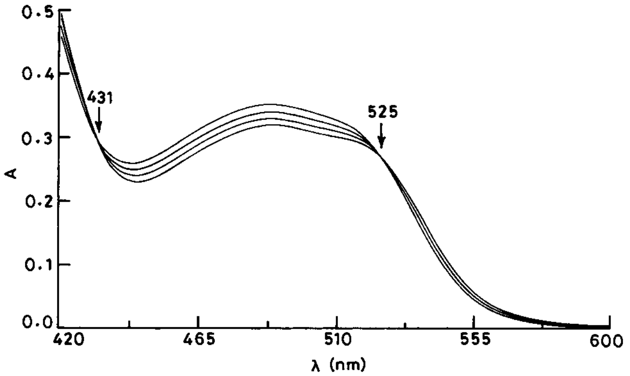

Figure 7. Change of UV−visible spectra of **1a** in CH_3CN in the presence of (i) 0.00 M (ii) 0.949 M, (iii) 1.8299 M, and (iv) 2.745 M TFE. Absorbance in the 440−510 nm increases systematically with the increase of TFE.

vents (such as CH_3CN and TFE) indicates a possible change of the square-planar palladium(II) of **1a** in CH_2Cl_2 to square-pyramidal palladium(II) in polar solvents.[11−13] At this point we have checked if there is any possibility of simultaneous chloride dissociation from **1a** in polar solvents. A 1 mM solution of **1a** in CH_3CN was found to be completely nonconducting. This solution did not show any appreciable conductivity increase even when a TFE solution (20 μL) of C_6F_5IO was added to it. This observation did not support any chloride dissociation from **1a** during its oxidation by C_6F_5IO in acetonitrile solvent. Assuming that polar solvents form adducts with square-planar palladium(II) to give square-pyramidal palladium(II), we have measured the TFE binding constant to **1a** in CH_3CN. The spectrum of **1a** in CH_3CN changes isosbestically on addition of TFE (Figure 7). We believe that this spectral change is due to the exchange of relatively loosely bound axial CH_3CN on Pd(II) by TFE. The calculated binding constant is 0.183 ± 0.015 M^{-1}. The binding constant of CH_3CN to a CH_2Cl_2 solution of **1a**, determined from a similar spectral change of **1a,** is 0.098 ± 0.005 M^{-1}.

B. Reaction of the t-BuOO$^\bullet$ Radical. The t-BuOO$^\bullet$ radical has been generated by the known reaction of t-BuOOH + C_6F_5IO, as described previously.[14,15] Neither of these two oxidants can oxidize the cyclopalladates **1a**−**c** in CH_2Cl_2; however, in the same solvent **1a**−**c** were instantaneously oxidized, by a mixture of these two reagents, to **2a**−**c** in high yields. In a typical experiment **1a** (5.15 mg, 0.013 mM) and t-BuOOH (4 μL, 0.034 mM) were dissolved in CH_2Cl_2 (2.5 mL) in a small vial (5 mL). Solid C_6F_5IO (4.07 mg, 0.0127 mM) was added to the above reaction mixture in two batches, and the reaction mixture was stirred for 4 min after each addition. Only compound **2a** and very small amount of **1a** were detected by TLC. The concentration of **2a** (0.0125 mM) in the vial was measured spectrophotometrically (yield 98.4% with respect to C_6F_5IO). In the process of isolating pure **2a** from similar reaction mixtures using a silica column, lower yields were always observed (see the Experimental Section). It has also been noted that when the reaction was carried out in methanolic solvents, inevitably the yields went down further. The isolated yields of **2a**−**c** from **1a**−**c**, respectively, in CH_2Cl_2 and methanolic solvents are given in Table 1 (entries 4−9).

C. Reaction of t-BuOOH in the Presence of Iron(III) Porphyrin Chloride. The hydroperoxides t-BuOOH and cumene hydroperoxide alone do not show any appreciable reactivity with cyclopalladates **1.** However, in the presence of iron(III) porphyrin catalyst the cyclopalladates **1a**−**c** were oxidized to **2a**−**c** only. In a typical experiment **1a** and $F_{20}TPPFe^{III}Cl$ were reacted with t-BuOOH in CH_2Cl_2−MeOH (2:1) in a small vial and the formation of **2a** was monitored by TLC. When CH_2Cl_2 was the solvent, we were able to detect the formation of **2a** only after 12 h of reaction, whereas when MeOH was the solvent, **1a** was completely destroyed within 5 min of mixing the reagents and a dark mass was the major product, wherefrom we could not detect any trace of either **2a** or **3a**. We have not attempted to characterize the dark mass, but TLC has indicated that it is composed of at least three new products. After the systematic variation of MeOH percentages in CH_2Cl_2 we observed that a 2:1 ratio of CH_2Cl_2 to MeOH was the most suitable solvent system to get a relatively clean reaction. In fact, we observed that MeOH plays a very important role in the activation of the catalyst in hydroperoxide oxidation.[16] These results are summarized in Table 1 (entries 10−12). The product selectivity remained the same for $F_{20}TPPFeCl$-catalyzed cumene hydroperoxide and hydrogen peroxide oxidations. These reactions were not studied further.

D. Reaction of C_6F_5IO in the Presence of $F_{20}TPPFe^{III}Cl$. It has been unanimously concluded that a mixture of these two reagents gives the oxoiron(IV) porphyrin cation radical (oxene).[17−19] In dichloromethane C_6F_5IO alone does not react with cyclopalladates at an appreciable rate; however, this same oxidant reacts smoothly with the cyclopalladates in same solvent but in the presence of $F_{20}TPPFe^{III}Cl$ to give exclusively **3a**−**c** within 3−4 min. In these reactions we have not detected any Pd−C bond oxidized products (**2a**−**c**), and

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any definitive role of alcoholic solvents has also not been observed, unlike other oxidizing systems (vide supra). These results are summarized in Table 1 (entries 13−18). Descriptions of the oxidations of **1a** and its platinum analogue have already appeared in preliminary form.[20]

Discussion

Selective C−Pd bond oxidation of **1a**−**c** has been achieved by three reagents: (i) C_6F_5IO, (ii) t-BuOO• radical, and (iii) F_{20}TPPFeCl + t-BuOOH. This suggests that the C−Pd bond oxygenation reaction probably proceeds through one common type of intermediate which is generated at some stage by all these three reagents. A high negative entropy of activation and a smooth reaction of **1a** with C_6F_5IO in CH_3CN is reminiscent of the oxidative addition of MeI to d^8 transition-metal ion organometallics in polar solvents. Formation of cationic intermediates and active involvement of Pt(IV), Ir(III), and Pd(IV) from the respective Pt(II), Ir(I), and Pd(II) complexes have been proposed in these reactions.[21−28] In the Pd−C bond oxidation of a series of cyclopalladated *N*,*N*-dimethylbenzylamine compounds by inorganic and organic peroxides, an oxopalladium(IV) species has been postulated as the actual oxygenating agent.[8] All these reactions are favored in polar solvents. The oxygenation of **1a** by C_6F_5IO, on the other hand, is not actually favored by all polar solvents. For example, the rate of this reaction in CH_3CN falls off with the increased percentage of TFE (Figure 4) and in neat TFE the reaction does not proceed at all.[10] Both **1a** and **2a** are neutral complexes, and in CH_3CN **1a** did not show any solution conductance. This result indicates that the possible dissociation of chloride ion from **1a** to give cationic palladium(II) and quantitative incorporation of all the dissociated chloride ions in the final product (**2a**) may not be that essential in the oxidation of **1a** to **2a** by C_6F_5IO.

A solvent molecule that can loosely bind to palladium(II) seems to be very important in facilitating oxygenation of **1a** by C_6F_5IO. This is supported by the fact that C−Pd bond oxidation does not take place in noncoordinating solvents such as CH_2Cl_2 and $CHCl_3$. Among coordinating solvents CH_3CN is suitable, and TFE is not.[10] This could be explained by the fact that TFE is a stronger ligand than CH_3CN for Pd(II) (see above). The spectrum of **1a** in CH_2Cl_2 is blue-shifted in CH_3CN (Figure 6). The nature of the band shift, the intensity change of the shifted bands, and the absence of any low-energy bands in coordinating solvents can be reasonably explained by assuming a change in the coordination sphere around palladium(II) from square planar in CH_2Cl_2 to square pyramidal in CH_3CN (or in TFE−CH_3CN), where the axial position is occupied by one CH_3CN (or TFE) molecule.[11−13] We believe that the excess TFE (up to 0.7 M), added with the oxidant solutions in the kinetic experiments, replaces the axial CH_3CN at least partially. This is supported by the fact that the binding constant of TFE with **1a** in CH_3CN (0.183 M^{-1}) is almost double that of CH_3CN with **1a** in CH_2Cl_2 (0.098 M^{-1}). This exchange causes the first spectrum of **1a** + C_6F_5IO to have an intersection at 431 nm with that of **1a** in CH_3CN (Figure 1). This proposition is again supported by the observation that an exactly similar spectral feature is observed in an independent experiment where a CH_3CN solution of **1a** is reacted with TFE (Figure 7). Distinct isosbestic points at 431 and 525 nm in Figure 7 and their exact coincidence with the intersections of the first intermediate spectrum of **1a** + C_6F_5IO−TFE adduct with that of **1a** (Figures 1 and 6) is remarkable. It has been concluded that the soliblity of iodosylbenzene in alcoholic solvent is due to the solvolysis reaction.[29,30] The coordination of the C_6F_5IO−TFE adduct through O^2 to iron(III) in the iron(III) porphyrin catalyzed oxidation of organic compounds is also known.[31] It is possible that O^2 of the C_6F_5IO−TFE adduct could be a relatively stronger donor than O^1 of TFE for palladium(II) (eq 2), and in that case exchange of axial

$$C_6F_5IO + CF_3CH_2O^1H \rightarrow C_6F_5I(O^1CH_2CF_3)(O^2H) \tag{2}$$

TFE by the C_6F_5IO−TFE adduct might proceed through an equilibrium (Scheme 2). Thus, at low concentration of TFE there is a linear decrease of rate with increased percentage of TFE in CH_3CN and at higher TFE concentration (e.g. above 20%) the C_6F_5IO−TFE adduct is such that it cannot replace the axial TFE; therefore, we do not observe any C−Pd bond oxidation in neat TFE.[10] The proposed intermediate [B] finally gives the most reactive oxopalladium(IV) species [C] in a slow rate-determining step (Scheme 2). The active involvement of Pd^{IV}=O and Ni^{IV}=O species in the corresponding palladium(II)- and nickel(II)-catalyzed oxidation of organic substrates is known.[32,33] We believe that the intermediates [B] and [C] occur simultaneously; thus, the high negative entropy of activation is actually the reflection of oxopalladium(IV) formation, and intermediate [C] is primarily responsible for oxygenation of the C−Pd bond by a complicated intramolecular process.[6,7] We believe that intermediate [C] should be highly solvated, and at least one solvent molecule will occupy the axial position, making the oxopalladium(IV) species coordinatively saturated.

The reaction of t-BuOO• radical with **1a** is extremely fast, where incorporation of an oxygen atom into the C−Pd bond is very specific. The yields of **2a**−**c** from **1a**−**c** in CH_2Cl_2 are higher than those in methanolic solvent. In fact, when TFE is completely avoided and the solvent is pure CH_2Cl_2,the yield of **2a** is almost

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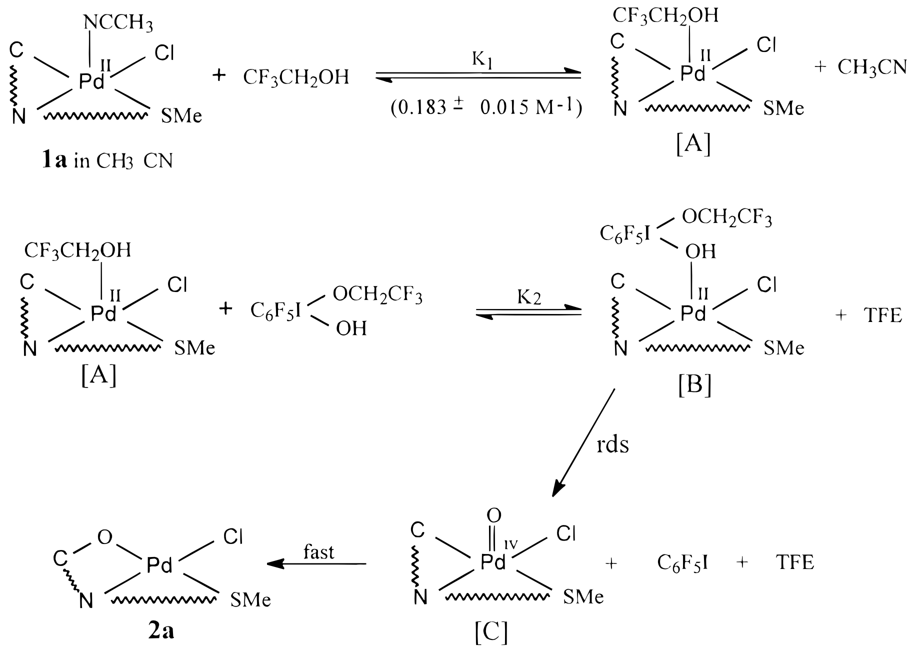
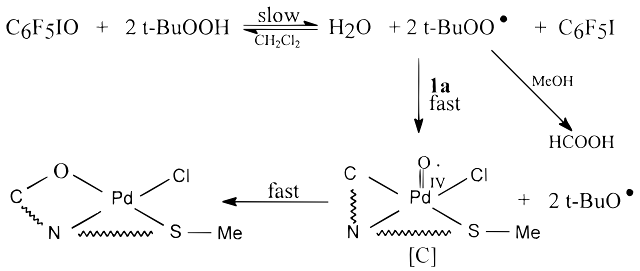
Scheme 2



Scheme 3



quantitative with respect to the terminal oxidant C_6F_5IO (vide supra). This can be explained by the possible direct attack of t-BuOO$^\bullet$ radical at Pd(II) to give an oxopalladium(IV) species (Scheme 3), which finally oxygenates the C−Pd bond by a complicated intramolecular path. Oxygenation of **1a** by t-BuOO$^\bullet$ radical to give the proposed Pd(IV) needs further studies. The t-BuO$^\bullet$ radical generated will abstract hydrogen atom from a suitable substrate at a rate of 10^8−10^9 s^{-1}.[34] Thus, in pure CH_2Cl_2 only t-BuOOH will be the possible substrate for hydrogen abstraction to produce t-BuOO$^\bullet$ radical, which will again attack **1a**. In CH_2Cl_2−MeOH solvent, the excess of MeOH will be rapidly oxidized to formic acid, and this might account for the observed lower yields of **2a**−**c** in methanolic solvents (Table 1, entries 4−9).[35]

In iron(III) porphyrin catalyzed oxidation reactions by hydroperoxides, the oxoiron(IV) porphyrin cation radical (oxene) has been proposed as the major reactive intermediate responsible for oxo transfer to substrates.[17,37] Involvement of hydroperoxide radical and oxoiron(IV) as actual oxygen transfer agents has also been claimed.[38−40] The radical path and the intermediacy of oxene in hydroperoxide oxidations are still subjects of strong debate.[17,37−43] Possible oxygen transfer from the PFe^{III} + t-BuOOH adduct to substrates has, however, been proposed in biological studies, and this has been supported by theoretical calculations.[41−43] In the present study we observed that the reaction of compound **1a** with $F_{20}TPPFe^{III}Cl$ + t-BuOOH is too slow in CH_2Cl_2. In CH_2Cl_2−MeOH (2:1) **2a** is formed selectively, but the yield is far from quantitative. A notable feature in this reaction is the fact that we did not observe any oxidation at the thioether part of **1a** (no **3a** is formed). This observation certainly indicates that oxene could not be the actual reactive intermediate responsible for oxygenation, because an authentically prepared oxene sample selectively oxidizes the thioether part of **1a**−**c** in high yields.[20] The sluggish reaction and poor yield of **2a** in this reaction does not strongly support the active involvement of t-BuOO$^\bullet$ radical, because the reaction of **1a** with authentically generated t-BuOO$^\bullet$ radical is not only very fast but also very efficient. The third possible intermediate in this oxidizing system is oxoiron(IV) porphyrin. We have generated an unambiguous sample of $PFe^{IV}{=}O$ by the reported method of Balch et al.[44] This authentic $PFe^{IV}{=}O$ does not oxidize **1a**.[20] These considerations force us to believe that the observed inefficient oxygenation of C−Pd bond in **1a** by $F_{20}TPPFe^{III}$ + t-BuOOH is possibly occurring

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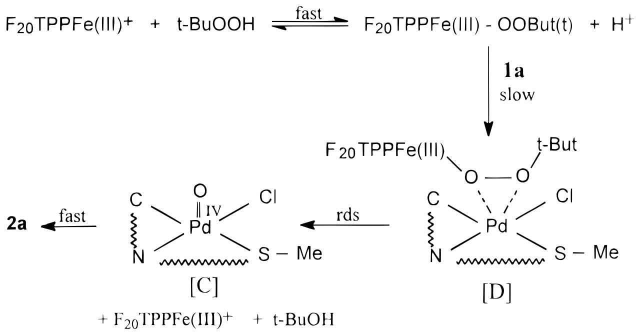
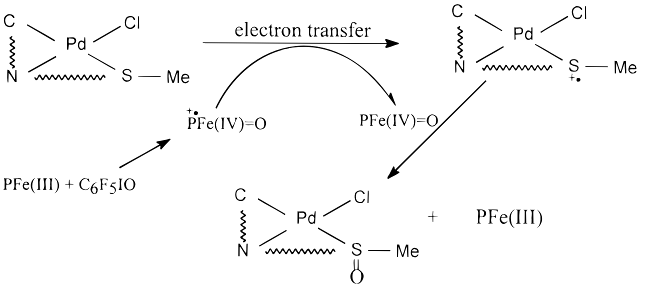
Scheme 4



Scheme 5



through the catalyst−oxidant adduct only. This adduct might approach **1a** to give the highly sterically crowded intermediate [D], as shown in Scheme 4. This will be followed by the generation of the oxopalladium(IV) species in the rate-determining step, which will finally oxygenate the C−Pd bond. The dashed line in [D] indicates the partial bond between Pd(II) and the peroxo linkage. The other possibility is that any t-BuOO$^•$ radical generated from the F_{20}TPPFe^{III}−OOBut(t) adduct by homolytic cleavage of the Fe^{III}−O bond might also be responsible for Pd−C bond oxidation. However, attack of Pd(II) on the positive oxygen bound to Fe(III) in [D] cannot be ruled out.

The oxoiron(IV) porphyrin cation radical (oxene), generated by the known reaction of F_{20}TPPFe^{III}Cl + C_6F_5IO in CH_2Cl_2, selectively oxidizes **1a** to **3a**. This result suggests that if oxopalladium(IV) formation is crucial for C−Pd bond oxidation, outer-sphere electron transfer from palladium(II) to the oxidant molecule may not be the case. The synthesis and characterization of stable palladium(IV) from the novel reaction of H_2O with the corresponding palladium(II) compound strongly support this proposition.[45] It seems that oxopalladium(IV) formation from the corresponding palladium(II) compound proceeds through an inner-sphere electron-transfer mechanism, and in that case prior coordination of the actual oxidant molecule to palladium(II) should be very crucial. It is obvious that initial coordination of the oxygen atom of oxene to palladium(II) is almost impossible, due to strong steric repulsion, and as a result no oxopalladium(IV) is generated and therefore C−Pd bond oxidation is not observed. Oxygenation at the sulfur center of **1a** might be explained by an outer-sphere electron transfer mechanism similar to that proposed for the oxidation of alkenes (Scheme 5) by oxene. A similar mechanism has been proposed for the iron(III) porphyrin catalyzed oxidation of organic sulfides to sulfoxides by iodosylbenzene.[46]

Conclusions

The selective oxygenation of C−Pd bonds in cyclopalladated azo compounds can be achieved in high yield by C_6F_5IO or t-BuOO$^•$ radicals. Such oxygenation by t-BuOOH in the presence of PFe^{III}Cl (where P is the porphyrin dianion) is also possible, but further studies are needed for standardization of the method. In the oxygenation of the C−Pd bond of neutral cyclopalladates by C_6F_5IO−TFE in CH_3CN, the initial coordination of the solvated oxidant molecule to palladium(II) seems to be the most crucial step. It is proposed that the actual oxygenating species, oxopalladium(IV), is formed from the palladium(II)−oxidant adduct. The generalization of this proposition needs further studies. The highly electrophilic oxoiron(IV) porphyrin cation radical (oxene) does not oxygenate the C−Pd bond; thus, selective C−Pd bond oxygenation by PFe^{III}Cl + t-BuOOH has indicated that the proposed hypothesis of oxene intermediacy in such oxidizing systems need further studies and a review of earlier literature. In our studies we proposed that oxygen transfer takes place from the catalyst−oxidant adduct itself, well before any oxene is even formed in the medium.

Experimental Section

General Considerations. CH_2Cl_2 and CH_3CN were dried over $CaCl_2$ and were freshly distilled from P_2O_5. MeOH was dried over CaO and was purified further as reported by Perrin.[47] CF_3CH_2OH, t-BuOOH (87%), and F_{20}TPPFe^{III}Cl were purchased from Aldrich Chemical Co. and were used without further purification. The organopalladium compounds **1a**−**c**, **2a**−**c**, and **3a**−**c** were all prepared according to the literature procedure.[2,4] Pentafluoroiodosylbenzene (PFIB) (*Caution!* potentially explosive[48]) was prepared according to the literature procedure.[49] UV−vis spectral measurements were taken with a Perkin-Elmer λ_{2s} spectrometer, interfaced with a 486 digital computer. The cell holder of the spectrophotometer was connected to a Julabo F-30 temperature regulator. Absorbances at 420 and 510 nm were recorded against time by using PECSS software developed by Perkin-Elmer.

Determination of Active Oxygen. (a) C_6F_5IO. About 80−100 mg of solid C_6F_5IO and 1.0 g of dry ice was taken into an Erlenmeyer flask containing 100 mL of water and 2.0 g of KI. Glacial CH_3COOH (5 mL) was added to this mixture; the flask was quickly stoppered and was kept in the dark for 30 min. The liberated iodine was titrated with standardized thiosulfate solution using starch as indicator. A 1.0 mL amount of 0.1 N thiosulfate was taken to be equivalent to 0.0155 g of pure C_6F_5IO.

(b) t-BuOOH. An aliquot of hydroperoxide was taken into an Erlenmeyer flask and diluted to 10 mL with MeOH. About 1.0 g of dry ice was added and the flask swirled to sweep out O_2. Prior to the complete disappearance of dry ice, 1.0 mL of saturated aqueous KI, 5 mL of glacial CH_3COOH containing

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10 mM $FeCl_3$, and 100 mL of H_2O were added. The flask was quickly stoppered and was placed in the dark for 30 min. The liberated iodine was titrated with standardized thiosulfate solution using starch as indicator. A 1.0 mL amount of 0.1 N thiosulfate was taken to be equivalent to 0.004506 g of pure t-BuOOH.

Kinetic Experiments. A standard solution of **1a** ((1.8−2.2) × 10^{-4} M) was prepared in dry CH_3CN. An aliquot (1.5 mL) of this solution was transferred into a quartz cuvette of 1 cm path length (low volume) and was thermostated. Known volumes (0−80 μL) of TFE was added to the cuvette, followed by a standard PFIB solution in TFE (10−50 μL). The final concentrations of oxidant and TFE in such reaction mixtures are given in Table 2. The cuvette was shaken vigorously and was immediately placed inside the thermostated cell holder of the spectrophotometer. The changes in absorbance at 420 and 510 nm were recorded at 20 s intervals until about 80% of the reaction was over. The final absorbances (A_α) were collected when the change of absorbance remained almost constant. In these kinetic experiments we have never encountered any problem with the turbidity of reaction mixture and the yields of **2** calculated from observed A_α measurements were in the range of 98 ± 2% based on **1a**. In earlier experiments, standard solutions of C_6F_5IO in TFE were added in variable quantities (10−50 μL) to CH_3CN (1.5 mL) solutions of **1a** in the cuvette. Thus, with the variation of C_6F_5IO, the variation of TFE was also incorporated simultaneously, which resulted in the nonlinear plots shown in Figures 2 and 3.

Oxygenation of 1a by PFIB. Compound **1a** (26 mg, 0.068 mmol) was dissolved in the minimum volume of CH_2Cl_2 (0.5 mL), and CH_3CN (10 mL) was added to it. A solution of PFIB (97%, 90 mg, 0.28 mmol) in TFE (1 mL) was added to the above solution over 30 s. The reaction mixture was stirred magnetically for 12 h at 33 °C and was evaporated to dryness in vacuo. The solid was dissolved in CH_2Cl_2 (4 mL), and the solution was directly added to the top of the silica gel column (10 cm × 15 cm), which was preequilibrated in petroleum ether (bp 60−80 °C). The unreacted compound was eluted from the column with CH_2Cl_2, and compound **2a** was next eluted with 1% MeOH in CH_2Cl_2. Solid compound **2a** was isolated by evaporating the solution in vacuo. The yield was 25 mg (93%).

Oxygenation of 1b and 1c by PFIB. These reactions were carried out as described for compound **1a**. The reaction of **1b** (25.4 mg, 0.066 mmol) with PFIB (97%, 94 mg, 0.29 mmol) produced 20 mg of **2b** (76% yield), and the reaction of **1c** (20 mg, 0.054 mmol) with PFIB (93 mg, 97%, 0.29 mmol) produced 16.8 mg of **2c** (80% yield). The total reaction times of these reactions were optimized by monitoring the reaction mixtures by TLC.

Oxygenation of 1a by t-BuOO$^•$ Radical. Compound **1a** (11.2 mg, 0.0292 mmol) was dissolved in CH_2Cl_2 (5 mL). To this solution was added t-BuOOH (87%,8 μL, 0.069 mmol), followed by solid PFIB (97%,11.4 mg, 0.0367 mmol). The reaction mixture was magnetically stirred until the solution became clear (3−4 min). The reaction mixture was directly added to the top of a silica gel column (10 cm × 15 cm) which was preequilibrated with petroleum ether (bp 60−80 °C). The unreacted compound (0.5 mg) was eluted from the column by CH_2Cl_2; pure **2a** was eluted with 1% MeOH in CH_2Cl_2 and the solid product (7.8 mg) was isolated by evaporating the solvent in vacuo. The yield was 70% with respect to the amount of starting material reacted. In a separate experiment similar quantities of reagents were reacted in pure CH_2Cl_2 (solid PFIB was added to a solution of **1a** and t-BuOOH in CH_2Cl_2) and the formation of **2a** was measured spectrophotometrically; the observed yield was almost quantitative with respect to PFIB (see above). The isolated yields of **2b** and **2c** from the corresponding cyclopalladates were 76 and 80%, respectively.

Oxygenation of 1a by t-BuOO$^•$ Radical in Mixed Solvent. Compound **1a** (11.64 mg, 0.0304 mmol) was dissolved in CH_2Cl_2 (2 mL). Methanol (3 mL) and t-BuOOH (87%,8 μL, 0.069 mmol) were added to this solution of **1a**, followed by addition of solid PFIB (97%, 12.0 mg, 0.0375 mmol). The reaction mixture was stirred magnetically for 3−4 min, by which time all the oxidant was dissolved and a clear solution was produced. The reaction mixture was processed as described above to get pure **2a** in 53% yield. When the same procedure was followed for compounds **1b** and **1c, 2b** and **2c** were obtained in 64% and 76% yields, respectively.

Catalytic Oxygenation of 1a by t-BuOOH. Compound **1a** (11.21 mg, 0.029 mmol) and $F_{20}TPPFe^{III}Cl$ (1.0 mg, 0.94 μM) were degassed under argon for 15 min in a small vial. Deoxygenated CH_2Cl_2 (2 mL) and MeOH (1.0 mL) were added to the above mixture. Deoxygenated t-BuOOH (3 μL, 0.026 mmol) was added to the above solution of **1a,** and the mixture was stirred for 10 min. Dry argon was passed through the solution to isolate the solid reaction mixture. The solid was dissolved in CH_2Cl_2 (1.0 mL), and the solution was directly added to the top of the silica gel column (10 cm × 15 cm) which was preequilibrated with petroleum ether; the compounds were eluted from the column as usual. Only pure **2a** (2.5 mg) and 6.9 mg of unreacted compound were isolated from the column. On the basis of the amount reacted, the yield was 50%. By the same procedure **1b** and **1c** were converted to **2b** and **2c** in 52% and 56% yields. About 78−84% of the catalyst was recovered from the column in these reactions.

Catalytic Oxygenation of 1a by PFIB. Compound **1a** (10.9 mg, 0.0284 mmol) and $F_{20}TPPFe^{III}Cl$ (0.9 mg, 0.84 μM) were dissolved in CH_2Cl_2 (5 mL). Solid PFIB (97%, 10.3 mg, 0.032 mmol) was added to the reaction mixture. The reaction was allowed to proceed for only 4 min, by which time the solution became clear. The reaction mixture was purified by the usual column chromatography over a silica gel column. Pure **3a** was isolated from the column by 0.1% MeOH in CH_2Cl_2, and the catalyst was recovered by a 5% MeOH in CH_2Cl_2 solution. Unreacted **1a** (2 mg) and **3a** (6.76 mg) were the only major products recovered from the column. The yield of **3a** was 73%, based on the starting material consumed. A very small quantity of **2a** (<1%) was also detected. The corresponding yields of **3b** and **3c** from these reactions were 81% and 73%. The survival of the catalyst in these reactions was 50−70%.

Catalytic Oxygenation of 1a−c by PFIB in MeOH−CH_2Cl_2 (3:2). Compound **1a** (10.17 mg, 0.0265 mmol) and $F_{20}TPPFe^{III}Cl$ (1.06 mg, 0.996 μmol) were dissolved in CH_2Cl_2 (2 mL), and MeOH (3 mL) was added to the above solution. Solid PFIB (11.61 mg, 97%, 0.0363 mmol) was added to the reaction mixture, and the slurry was stirred magnetically for 4 min to get a clear solution. Dry argon was blown through the solution at high speed to obtain the solid. This was redissolved in CH_2Cl_2, and the compounds were separated by the usual column chromatography. Solid compounds were isolated by evaporating the solvents under reduced pressure. The yield of **3a** was 66%, and in this reaction 59% of the catalyst was recovered from the reaction mixture. The yields of **3b** and **3c** from **1b** and **1c** were 83% and 80%, respectively, and in these two reactions 60−70% of the catalyst was recovered.

Acknowledgment. Financial assistance from the Department of Science and Technology (No. SP/S1/F-06/93), Government of India, is acknowledged.

OM980731W