Cobalt Schiff Base Complex-Catalyzed Oxidation of Anilines with *tert*-Butyl Hydroperoxide

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Cobalt Schiff base complexes [Co(SB)] catalyze the oxidation of anilines (**1**) with *tert*-butyl hydroperoxide to give nitrobenzenes **2** and 4-(*tert*-butylperoxy)-2,5-cyclohexadien-1-imine derivatives **3** in yield distributions depending on the substitution mode of the substrate. 4-Alkyl- and 4-aryl-2,6-di-*tert*-butylanilines gave mixtures of **2** and **3**, where the higher the bulkiness of the 4-substituent, the higher the yield of **2**. With 2,4,6-trimethylaniline, the ratio of oxidations of the nitrogen and C-4 atoms was almost the same; but a hydrolyzed product **5** of the imine was obtained. 2,4,6-Triphenylaniline gave only **2**. Nitrobenzene derivatives were also obtained from 2,6-dialkylanilines and 4-substituted anilines. The catalytic activity of Co(SB) depended on the nature of the SB ligand: the formal potential $E°$ and steric factors seem to affect the reaction rate. Kinetic studies showed that the key step may involve hydrogen abstraction from the aniline, presumably by t-BuO$^•$ generated from homolytic decomposition of initially formed Co^{III}(SB)(OO-t-Bu). A precursor of **2** was found to be the nitrosobenzene derivative.

Introduction

Cobalt(II) Schiff base [Co^{II}(SB)] complexes are interesting compounds because of their catalytic activities in oxidation reactions.[1−4] For instance, five-coordinate Co^{II}-(SB) complexes in aprotic solvents catalyze the dioxygenase-type reactions of phenols, indoles, flavonols, and nitroalkanes.[4] In alcoholic solutions, on the other hand, Co^{II}(SB) complexes catalyze the monooxygenation of phenols, hydrazones, nitroalkanes, alkenes, and alkynes with molecular oxygen.[5] Furthermore, it has been found that Co(salen) [H$_2$salen = 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] catalyzes the *tert*-butyl hydroperoxide (TBHP) oxidation of phenols, giving (*t*-butylperoxy)-quinol ethers,[6] and of alcohols[7] and amines,[8] leading to dehydrogenation. In a general investigation of Co^{II}(SB)-catalyzed oxidation reactions, we are also interested in the oxidation of primary anilines. Ring-substituted primary anilines are normally not susceptible to the

Table 1. Co(salen)[= Co(L^1)]-Catalyzed Oxidation of 1a−d with TBHP in DCE[a]

1	reactn time (min)	conversn (%)	product yield[b] (%)		
			2	**3**	**4**
1a	160	100	30	54	9
1b	30	100		90	
1c	180	80			63
1d	60	91			79

[a] Reaction conditions: **1** (0.5 mmol), Co(salen) (0.09 mmol), TBHP (4 mmol) in 1,2-dichloroethane (DCE) (10 mL) under N$_2$ at 23 °C. [b] Isolated yield.

Table 2. Co(salen)[= Co(L^1)]-Catalyzed Oxidation of 1e with TBHP in DCE[a]

1e	reactn time (min)	conversn (%)	product yield[b] (%)		
			2	**3**	**4**
1e-1	120	100[c]			
1e-2	80	100	27	53	
1e-3	70	100	81		10
1e-4	480	92	23	65	
1e-5	110	98	13	66	
1e-6	90	100	23	67	

[a] Reaction conditions: **1** (0.5 mmol), Co(salen) (0.09 mmol), TBHP (4 mmol) in DCE (10 mL) under N$_2$ at 23 °C. [b] Isolated yield. [c] An inseparable complex mixture was obtained.

Co^{II}(SB)-promoted oxygenation with molecular oxygen[9] but were readily oxidized with TBHP mainly to give 4-(*tert*-butylperoxy)-2,5-cyclohexadien-1-imines and 2,4,6-trisubstituted nitrobenzenes.[10] The present paper deals with the details of this Co^{II}(SB)-catalyzed TBHP oxidation of anilines.

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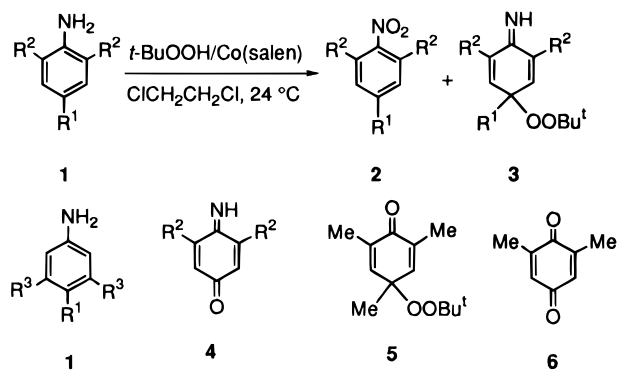(3) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.
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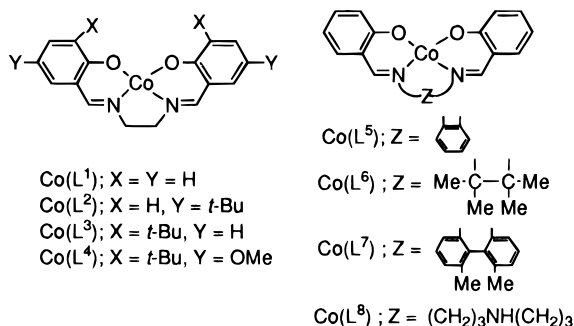
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	a	b	c	d	e-1	e-2	e-3
R^1	*t*-Bu	Me	H	OMe	4-Me$_2$NC$_6$H$_4$	4-MeOC$_6$H$_4$	Mesityl
R^2	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu	*t*-Bu

	e-4	e-5	e-6	f	g	h	i
R^1	4-MeC$_6$H$_4$	C$_6$H$_5$	4-ClC$_6$H$_4$	Me	Ph	H	H
R^2	*t*-Bu	*t*-Bu	*t*-Bu	Me	Ph	Et	Me

	j-1	j-2	j-3	j-4	j-5	j-6	j-7	j-8
R^1	Me$_2$N	OMe	OEt	*t*-Bu	Et	Me	H	Cl
R^2	H	H	H	H	H	H	H	H

	j-9	j-10	j-11				k	l	m
R^1	F	CN	NO$_2$			R^1	H	NO$_2$	H
R^2	H	H	H			R^3	*t*-Bu	*t*-Bu	Me

Co(L^1); X = Y = H
Co(L^2); X = H, Y = *t*-Bu
Co(L^3); X = *t*-Bu, Y = H
Co(L^4); X = *t*-Bu, Y = OMe

Co(L^5); Z =
Co(L^6) ; Z = Me·C—C·Me (Me Me)
Co(L^7) ; Z =
Co(L^8) ; Z = (CH$_2$)$_3$NH(CH$_2$)$_3$

Results and Discussion

Co(salen)-Catalyzed TBHP Oxidation of Substituted Anilines 1. A mixture comprised of an appropriate aniline **1**, Co(salen) [Co(L^1)], and TBHP in the molar ratio 1:0.2:8 in 1,2-dichloroethane (DCE) or dichloromethane (DCM) was stirred at 23 °C until the reaction was completed. Removal of the metal complex by filtration through a short neutral alumina column followed by TLC on basic alumina gave the corresponding nitrobenzene (**2**), 2,5-cyclohexadien-1-imine (**3**), and 1,4-benzoquinon-1-imine (**4**). The results are summarized in Tables 1−5.

Analytical data for compounds **2** and **3** are in good agreement with their structures (see Experimental Section). The ^{1}H-NMR signals at 1.3 ppm for the *t*-Bu group (R^2) and at 6.3 ppm for the ring protons in compounds **3** agree with those observed for 4-hydroxy-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-imines.[11] The signal at around 1.2 ppm is reasonably assigned to the *t*-BuOO group as

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Table 3. Co(salen)[= Co(L^1)]-Catalyzed Oxidation of 1f-i with TBHP in DCE^a

1	reactn time (min)	conversn (%)	product yield^b (%) 2	3	4
1f	240	100	50	46 (**5**)	
1g	40	100^c	73		
1h	60	100^c	50		
1i	60	100	52		27 (**6**)

^{a} Reaction conditions: **1** (0.5 mmol), Co(salen) (0.09 mmol), TBHP (4 mmol) in DCE (10 mL) under N$_2$ at 23 °C. ^{b} Isolated yield. ^{c} Products other than **2** were not investigated.

Table 4. Co(salen)[= Co(L^1)]-Catalyzed Oxidation of 1j with TBHP in DCM^a

1	reactn	conversn	product yield^b (%) 2	3	4
1j-1	30^c	100			
1j-2	180^d	100	30		
1j-3	180^d	94	24		
1j-4	^{d,e}	100	56		
1j-5	^{d,e}	100	27		
1j-6	360^d	100	17		
1j-7	420^d	93	26		
1j-8	1440^d	86	16		
1j-9	1440^d	100	8^f		
1j-10	1440^d	19	13		
1j-11	1440^d	38	10		

^{a} Reaction conditions: **1** (0.5 mmol), Co(salen) (0.09 mmol), TBHP (4 mmol) in DCM (10 mL) under N$_2$ at 23 °C. ^{b} Isolated yield. ^{c} An inseparable complex mixture was obtained. ^{d} Products other than **2** were not investigated. ^{e} Reaction time was not specified but more than 4 h. ^{f} Determined by GLC.

Table 5. Co(salen)[= Co(L^1)]-Catalyzed Oxidation of 1k−m with TBHP in DCM^a

1	reactn time (min)	conversn (%)	product yield^b (%) 2	3	4
1k	300^c	84	57		
1l	360^c	86	41		
1m	480^c	92	17		

^{a} Reaction conditions: **1** (0.5 mmol), Co(salen) (0.09 mmol), TBHP (4 mmol) in DCM (10 mL) under N$_2$ at 23 °C. ^{b} Isolated yield. ^{c} Products other than **2** were not investigated.

observed for 4-(*tert*-butylperoxy)-2,5-cyclohexadien-1-one compounds.[12] The assignment of the ^{13}C-NMR signals of **2** and **3** was achieved by using chemical shift increments, {^{1}H, ^{13}C}-coupled spectra, spin echo, and COSY spectra. In the case of **2**, the weak signal of C-1 bearing the nitro group reveals a characteristic triplet by coupling with protons H-3,5 (J = 9 Hz).

In the case of **1f**, no quinolimine **3** but the quinol derivative **5** was obtained, indicating that quinolimines of type **3** undergo hydrolysis under the reaction conditions, whereas with other species **3**, bearing *t*-Bu groups at the 2 and 6 positions, further hydrolysis of the imino group is hindered by the *t*-Bu groups. Similarly, **1i** does not give a quinonimine **4** but rather the hydrolysis product, i.e., quinone **6**.

The product distribution (Tables 1−5) is largely dependent on the nature of the substituents in **1**. For example, for **1b,d**, in which R^2 is much larger than R^1, *tert*-butylperoxylation occurs exclusively in the *para*-position to give **3b** or the hydrolysis product **4**. On the contrary, with **1e-3**, in which the size of R^1 is larger than that of R^2, the oxidation takes place predominantly at

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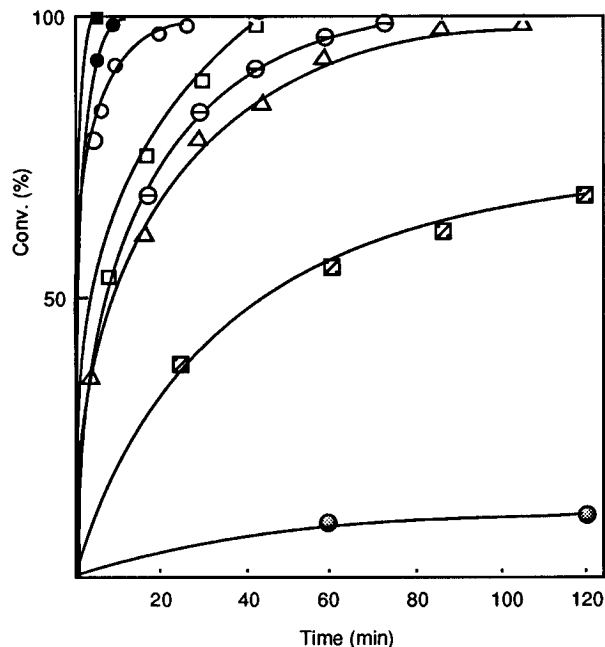
Figure 1. Comparison of catalytic activity of Co(L) in TBHP oxidation of **1a**. Conditions: **1a** (0.5 mmol), TBHP (4 mmol), DCE (20 mL), Co(L) (0.07 mmol), at 25.0 ± 0.1 °C. Key: Co(L[1]), (△); Co(L[2]), (⊖); Co(L[3]), (●); Co(L[4]), (○); Co(L[5]), (□); Co(L[6]), (■); Co(L[7]), (slashed box); Co(L[8]), (shaded circle).

the nitrogen atom to give **2e-3**. When R[2] and R[1] are of equal or comparable size (**1a**, **e-2**, **e-4**, **e-5**, **f**), the products are more homogeneously distributed among types **2** and **3**. Interestingly, **1g** (R[2] = R[1] = Ph) gives only **2g**, providing the first example of a selective formation of a nitro compound by the oxidation of the corresponding aniline. Even two large groups in the *meta*-position, as in **1k**, are sufficient to give rise to a remarkable yield of the nitro compound **2k**. 4-Monosubstituted anilines **1j** were oxidized to nitro arenes **2j**, sometimes in quite good yields, especially, if the lower conversion is considered. However, the electronic effect of the 4-substituent is clearly reflected in the isolated yields of **2**. Substrates **1j-8−j-11** with electron-withdrawing substituents show a low conversion rate and long reaction time. Occasionally, azo (e.g., from **1j-2**: 2%) or azoxy compounds (e.g., from **1j-8**: 4.5%) could be isolated from the reaction mixture in low yields. This indicates that nitroso compounds are intermediates in the reaction (see below).[13]

Effective Structure of Co(L[n]) for TBHP Oxidation. The active species in the TBHP/Co(salen) oxidation system is considered to be the *tert*-butylperoxy radical (*t*-BuOO•) or preferentially the *tert*-butoxy radical (*t*-BuO•) resulting from the homolytic cleavage of the Co−O bond in Co[III](salen)(OO-*t*-Bu) initially formed (for details see the Mechanism section).[12] Therefore, it may be expected that the more positive shift in the redox potential of Co(L[n]) results in the higher reactivity. Thus, various Co(L[n]) (*n* = 1−8) were examined for their catalytic activity in the TBHP oxidation of **1a**. It was found that the reaction rate depended on the nature of the complex (Figure 1), but the product ratio **2/3** was

always similar to that using Co(L[1]). The initial rates [(s[−1]) × 10[3]: Co(L[1]), 1.4; Co(L[2]), 1.1; Co(L[3]), 18.0; Co(L[4]), 6.3; Co(L[5]), 1.4; Co(L[6]), 26.0; Co(L[7]), 0.32; and Co(L[8]), 0.071] obtained from Figure 1 are plotted *vs* the redox potential $E°$ (Co[II]/Co[III]) (Figure 2).[14] No clearcut relation is observed; the reaction rate seems to depend not only on the formal potential, but also on the steric factor of the substituent X as well as Z in Co(L[n]). The steric factor may be attributed to the repulsion of the *t*-BuOO group in Co[III](L[n])(OO-*t*-Bu) by X (*n* = 3, 4) or by the axial Me groups of Z (*n* = 6). It may be therefore concluded that the key step of this reaction is the homolytic cleavage of the Co−O bond of the CoOOBu[t] group in Co[III](L[n])(OO-*t*-Bu) which rapidly forms in the initial stage.[15] The slow reaction with Co(L[7]) should be due to the fact that it was not readily oxidized with TBHP. The lower reactivity of Co(L[8]) is attributed to the stability of Co[III](L[8])(OO-*t*-Bu), a coordinately saturated peroxo complex, under the reaction conditions.[15]

Time Course of Co(L[6])-Catalyzed TBHP Oxidation of 1. Figure 3 shows the time-dependent TBHP oxidation of anilines **1a** and **1e-4** catalyzed by Co(L[6]), which reveals the highest catalytic activity. The time course figures for both substrates are similar to each other, showing a competitive formation of the corresponding **2** and **3**, which is indicative of the involvement of a common intermediate. Similar results in time course were obtained with other 4-arylanilines (**1e**). Table 6 summarizes the product distribution in the Co(L[6])-catalyzed TBHP oxidation of 4-arylanilines (**1e**), where the product ratio **2/3** is about 2/1, independent of the *para*-substituent. Interestingly, the product ratio is the reverse of the case with Co(L[1]). A Hammett plot of the reaction rate against σ_p gives a linear relation with $\rho = -1.2$ (Figure 4).

Oxidation of 1a with Co[III](L[1])(OO-*t*-Bu). As mentioned above, the reactive species in the present oxidation is considered to be Co[III](L[n])(OO-*t*-Bu); therefore, the reaction of that species with **1a** was examined in the absence of TBHP. When an excess of Co[III](L[n])(OO-*t*-Bu)

1a + Co[III](L[1])(OOBu[t]) ⟶ **2a** + **3a** + [structures **7** and **8**]
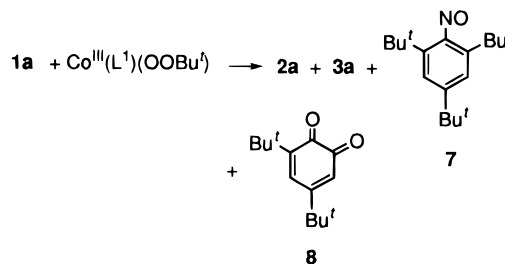
was used, 2,4,6-tri-*tert*-butylnitrosobenzene (**7**) was obtained in addition to **2a**, **3a**, and 3,5-di-*t*-butyl-*o*-benzoquinone (**8**) (Table 7). The formation of **8** is rationalized by assuming decomposition of the *ortho* isomer of **3a** giving rise to 3,5-di-*tert*-butyl-*o*-quinon-2-imine followed by hydrolysis under the reaction conditions. Compound **7** should be the intermediate of **2**, because **7** was readily oxidized with the TBHP/Co(L[1]) system to give **2** quantitatively.

Mechanism. All the results described above are rationalized by the mechanism shown in Scheme 1, which is similar to that proposed for the Co(salen)-catalyzed

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(15) For the chemical behavior of Co[III](salen)(OOBu[t]) including isolation, instability in chlorinated solvents, and thermolysis to give Co[II](salen) and *t*-BuOO•, see: Nishinaga, A.; Tomita, H.; Ohara, H. *Chem. Lett.* **1983**, 1751.
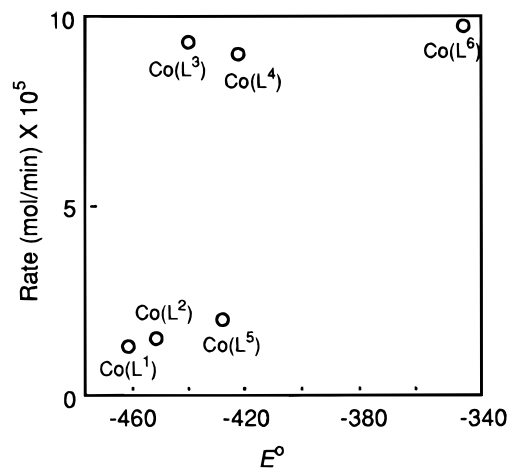
Figure 2. Plot of catalytic activity (initial rate determined from Figure 1) against the formal potential $E°$ of Co(L^n).[14]

oxidation of phenols with TBHP.[12] Co^{III}(L^n)(OO-*t*-Bu) formed rapidly in an early stage of the reaction decomposes to yield *tert*-butylperoxy radicals *t*-BuOO$^•$ which give further *tert*-butyloxy radicals *t*-BuO$^•$ (Scheme 1, eqs 1−4).[15] The resulting oxygen radical can react with **1** in the following ways: (i) abstract a single electron to give a cation radical, followed by a fast proton transfer, or (ii) abstract a hydrogen atom. Both pathways differ only in the time delay of the proton transfer and finally lead to the same result, i.e., formation of the aminyl radical **9**, which may be written formally as eq 5 (Scheme 1). As we have shown earlier,[16ab] electrochemical oxidation of sterically hindered aniline **1**, on the time scale of cyclic voltammetry, first leads to cation radical (one-electron transfer), which may be further oxidized to a dication at higher potential (second one-electron transfer). In the presence of a base, the cation radical rapidly deprotonates to the neutral aminyl **9**.[16c] For the deprotonation of the cation radical in the absence of a base, a positive ρ-value was observed for the plot of log k *vs* σ.[16c] Since the rate of the oxidation of **1e** (log v_X/v_H *vs* σ_p) reveals a *negative* ρ-value (Figure 4), the rate determining step should here involve electron transfer from **1** by *t*-BuO$^•$. However, since *t*-BuO$^-$ formed is a strong base, a rapid deprotonation of the cation radical to the neutral aminyl **9** will occur. If we pursue the oxidation reaction of **1a** directly in the ESR cavity, only a broad, unresolved ESR signal can be observed, which does not show the HFS of the corresponding aminyl radical.[17a] This is not unexpected, since the aminyl radical is immediately trapped by an excess of *t*-BuOO$^•$. The case is similar to the formation of **9** from **1** by *t*-BuO$^•$ radicals produced by photolysis of di-*tert*-butyl peroxide, where *t*-BuO$^•$ radicals (in the absence of *t*-BuOOH) rapidly trap **9**.[17b] The fast followup reaction of the resulting aminyl radical **9** with *tert*-butylperoxy radical should give **3** (Scheme 1, eq 8) and an unstable *N*-(*tert*-butylperoxy)aniline **10** which would be readily converted to **7**, a good radical scavenger (Scheme 1, eq 6). This is supported by the fact that the
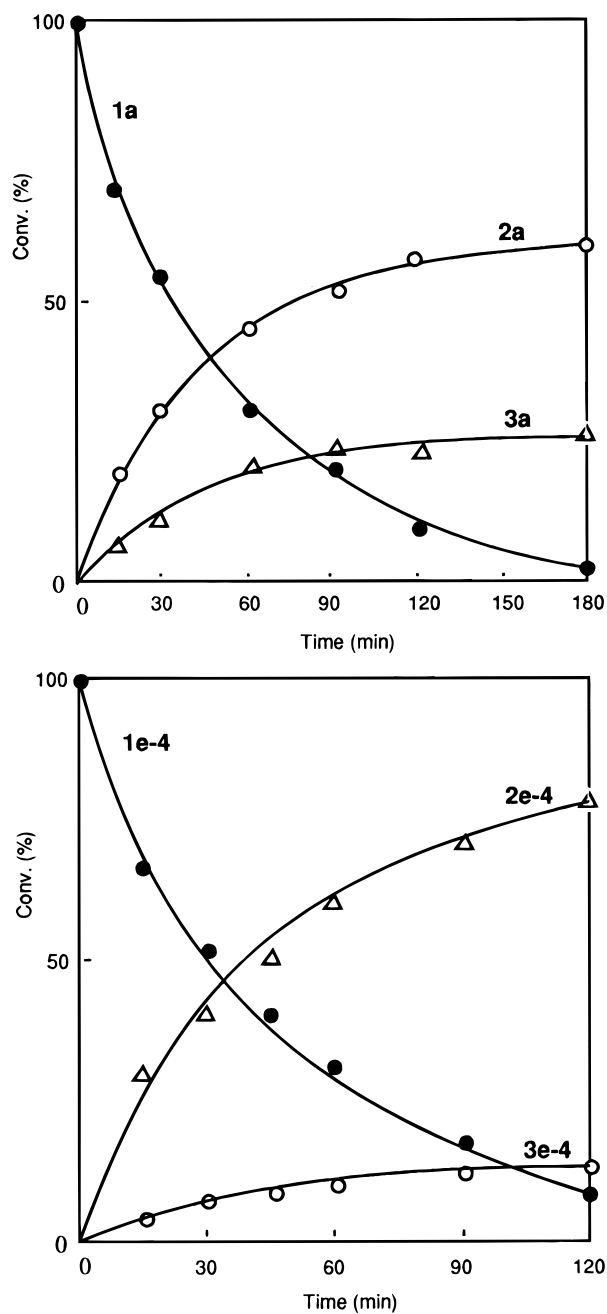
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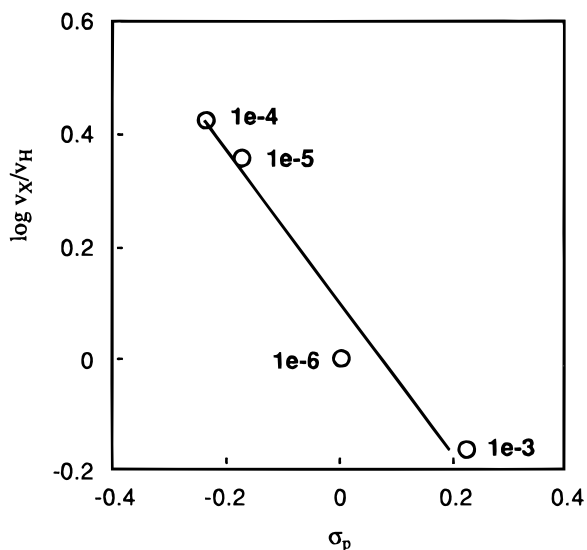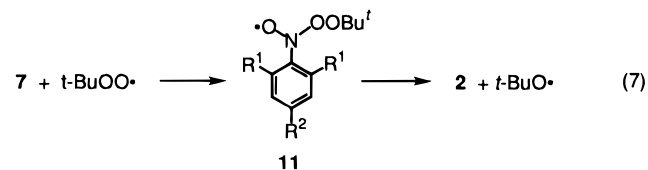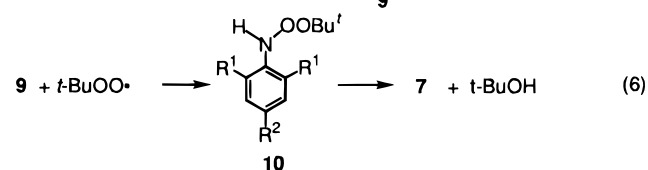

Figure 3. Time-dependent TBHP oxidation catalyzed by Co(L^6). Conditions: **1** (0.5 mmol), Co(L^6) (0.07 mmol), TBHP (4 mmol) in DCE (100 ml) at 0 ± 0.1 °C. Conversion was followed by ^{1}H NMR.

Table 6. Co(L^6)-Catalyzed TBHP Oxidation of 1e group^a

| **1** | reactn time (min) | conversn (%) | product yield^b (%) | |
			2	**3**
1e-3	45	100	69	31
1e-4	15	100	68	32
1e-5	30	100	76	24
1e-6	30	100	64	36

^{a} Reaction conditions: **1** (0.5 mmol), Co(L^6) (0.07 mmol), TBHP (4 mmol) in DCE (10 mL) under N$_2$ at 23 °C. ^{b} Determined by ^{1}H NMR.

addition of TBHP to a solution of **9** in benzene prepared by the oxidation of **1a** with PbO$_2$ under nitrogen gave a mixture containing **2**, **3**, and **7** in a ratio of 4:3:2. The final formation of **2** may be reasonably understood by assuming a reaction of **7** with *tert*-butylperoxy radical via
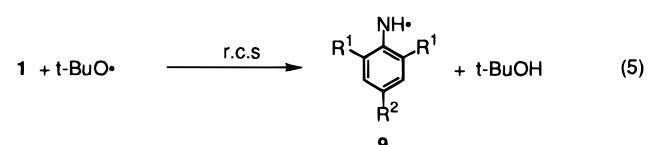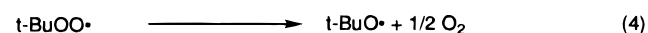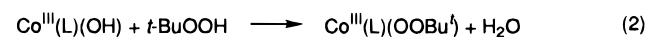
Figure 4. Hammett plot of reaction rate in Co(L[6])-catalyzed TBHP oxidation of the **1e** group against σ_p ($\rho = -1.2$).

Table 7. Reaction of Co[III](L¹)(OO-*t*-Bu) with 1a[a]

			product yield[b] (%)			
[Co]/[**1a**]	reactn time (min)	conversn (%)	**2**	**3**	**7**	**8**
1	15	35	14	4		
3	17	53	27	10	3	2
5	20	68	21	14	15	6

[a] Reaction conditions: **1a** (0.5 mmol), Co(L¹)(OO-*t*-Bu) in DCE (10 mL) at 23 °C. [b] Isolated yield.

Scheme 1

$$\text{Co}^{II}(\text{L}) + t\text{-BuOOH} \longrightarrow \text{Co}^{III}(\text{L})(\text{OH}) + t\text{-BuO}\cdot \quad (1)$$

$$\text{Co}^{III}(\text{L})(\text{OH}) + t\text{-BuOOH} \longrightarrow \text{Co}^{III}(\text{L})(\text{OOBu}^t) + \text{H}_2\text{O} \quad (2)$$

$$\text{Co}^{III}(\text{L})(\text{OOBu}^t) \longrightarrow \text{Co}^{II}(\text{L}) + t\text{-BuOO}\cdot \quad (3)$$

$$t\text{-BuOO}\cdot \longrightarrow t\text{-BuO}\cdot + 1/2\ \text{O}_2 \quad (4)$$

(5)

(6)

(7)

(8)

**11** (Scheme 1, eq 7). In fact, the reaction of **7** with TBHP in the presence of Co(L¹) in dichloromethane in a separate experiment proceeded rapidly to give **2a** in quantitative yield as described above, although **7** was unsusceptible to TBHP itself.[17c]

Some aspects of this mechanism are supported by electroanalytical results. The redox potentials of the Co[II](L[n])/[Co[III](L[n])]+ couple (varying between −480 and −340 mV) are at far negative positions from those of 4-arylanilines **1e** (varying between 420 and 578 mV),[17] suggesting that no significant electron transfer takes place from **1** to [Co[III](L[n])]+. This is not due to the steric effect of the substituents because the oxidation potentials of the examined 2,6-unsubstituted anilines range between 41 mV (**1j-2**; in DMF, *vs* FeCp₂/FeCp₂+) and 937 mV (**1j-10**).[18a] Actually, no reaction took place when **1e** was mixed with [Co[III](L¹)]+ in any solvent, leading to the conclusion that a direct interaction between the catalyst and the substrate can be excluded in the case of the anilines used in this work.[18b]

Experimental Section

General Procedures. Cobalt complexes Co(L[n]) were synthesized by known methods: complexation using Co(OAc)₂·4H₂O of the appropriate Schiff bases, which were prepared by condensation of the corresponding diamines and salicylaldehyde derivatives, Co(L¹),[19] Co(L²),[20] Co(L³),[21] Co(L⁴),[22] Co(L⁵),[23] Co(L⁶),[24] Co(L⁷),[25] Co(L⁸).[26] Starting anilines **1a**[27] and **1h−k,m** are commercially available, and **1b**,[11] **1e**,[11] **1c**,[28] **1d**,[29] and **1l**[28] were synthesized according to known methods.

Co(L¹)-Catalyzed Oxidation of Anilines 1. To a solution of **1** (0.5 mmol) in 1,2-dichloroethane (DCE) or dichloromethane (DCM) (10 mL) containing Co(L¹) (0.07 mmol) was added TBHP (4 mmol; 514 mg of 70% TBHP in aqueous solution)dropwise under nitrogen. The original brown color of the solution turned dark brown. After the reaction was completed as monitored by TLC, the mixture was filtered through a column of alumina (6 g) eluted with DCE or DCM (50 mL in total). Evaporation of the eluent followed by TLC separation of the resulting mixture gave products **2−4**. The results are given in Tables 1−5. New spectral and analytical data of the products are given below. Assignments denoted by asterisks are tentative.

2a   **2e**
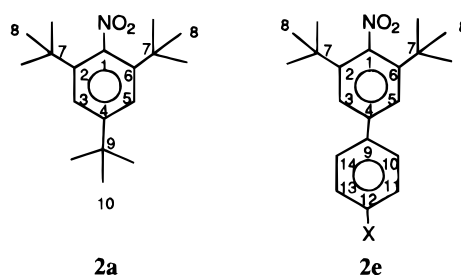
(18) (a) Förster, S. unpublished results. Dissertation, University of Tübingen, 1996, to be published. (b) The strong donator *N,N*-dimethylaniline (*E*° = −300 mV) is directly oxidized by [Co[III](L¹)]+ to give the radical cation (Wurster salt) as detected by ESR. Stahl, H. Dissertation, University of Tübingen, 1995.
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2a: mp 197−199 °C (lit.[28] mp 205−206 °C); IR (KBr) 1531, 1379 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.31 (s, 18H), 1.22 (s, 9H), 7.37 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 147.34 (C1), 140.37 (C2/6), 123.76 (C3/5), 151.57 (C4), 36.54 (C7), 31.48 (C8), 35.36 (C9), 31.48 (C10). Anal. Calcd for C$_{18}$H$_{29}$NO$_2$: C, 74.18; H, 10.03; N, 4.81. Found: C, 74.29; H, 9.84; N, 4.65.

2e-2: mp 104−105 °C; IR (KBr) 1533, 1377 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.35 (s, 18H), 3.78 (s, 3H), 6.92 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.8 Hz, 2H), 7.49 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 148.33 (C1), 141.50 (C2/6), 125.37 (C3/5), 141.73 (C4), 36.50 (C7), 31.45 (C8), 133.39 (C9), 128.67 (C10/14), 114.62 (C11/13), 159.90 (C12), 55.63 (C15). Anal. Calcd for C$_{21}$H$_{27}$NO$_3$: C, 73.87; H, 7.97; N, 4.10. Found: C, 74.20; H, 7.87; N, 3.79.

2e-3: mp 101−102 °C; IR (KBr) 1535, 1377 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.38 (s, 18H), 2.02 (s, 6H), 2.33 (s, 3H), 6.98 (s, 2H), 7.22 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 147.94 (C1), 141.17 (C2/6), 127.98 (C3/5), 141.79 (C4), 36.51 (C7), 31.50 (C8), 138.47 (C9), 136.07 (C10/14), 128.61 (C11/13), 137.48 (C12), 21.10 (C15/17), 21.28 (C16). Anal. Calcd for C$_{23}$H$_{31}$NO$_2$: C, 78.15; H, 8.84; N, 3.96. Found: C, 77.98; H, 8.74; N, 3.90.

2e-4: mp 119−120 °C; IR (KBr) 1531, 1379 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.42 (s, 18H), 2.41 (s, 3H), 7.27 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.58 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 148.73 (C1), 141.70 (C2/6), 125.85 (C3/5), 142.28 (C4), 36.72 (C7), 31.65 (C8), 141.70 (C9), 127.67 (C10/14), 130.06 (C11/13), 138.28 (C12), 21.57 (C15). Anal. Calcd for C$_{21}$H$_{27}$NO$_2$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.32; H, 8.42; N, 4.22.

2e-5: mp 80−82 °C; IR (KBr) 1531, 1377 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.43 (s, 18H), 7.39−7.55 (m, 5H), 7.61 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 148.40 (C1), 141.34 (C2/6), 125.63 (C3/5), 141.94 (C4), 36.31 (C7), 31.21 (C8), 140.71 (C9), 127.41 (C10/14), 128.93 (C11/13), 127.92 (C12). Anal. Calcd for C$_{20}$H$_{25}$NO$_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.92; H, 8.15; N, 4.11.

2e-6: mp 154−155 °C; IR (KBr) 1531, 1377 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.35 (s, 18H), 7.35 (d, J = 8.7 Hz, 2H), 7.38 d, J = 8.6 Hz, 2H), 7.49 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 148.57 (C1), 141.50 (C2/6), 125.36 (C3/5), 140.64 (C4), 36.23 (C7), 31.10 (C8), 139.00 (C9), 128.55 (C10/14), 129.01 (C11/13), 134.08 (C12). Anal. Calcd for C$_{20}$H$_{24}$ClNO$_2$: C, 69.45; H, 7.00; N, 4.05. Found: C, 69.04; H, 7.25; N, 4.21.
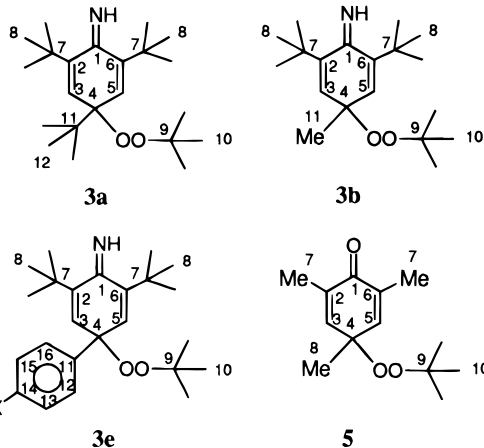
2f: mp 41−42 °C (lit.[30] mp 43−44 °C); IR (KBr) 1520, 1369 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.26 (s, 6H), 2.29 (s, 3H), 6.89 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 149.78 (C1), 129.59 (C2/6), 129.43 (C3/5), 140.30 (C4), 21.03 (C7), 17.54 (C8).

2g: mp 146−147 °C (lit.[31] mp 144−145 °C); IR (KBr) 1531, 1367 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.69 (s, 2H), 7.66−7.71 (m, 2H), 7.45−7.55 (m, 13H); ^{13}C NMR (CDCl$_3$) δ 148.70 (C1), 135.14 (C2/6), 143.06 (C4), 136.62 (C7), 138.91 (C9), 129.20, 128.93, 128.85, 128.76, 128.63, 128.25, 127.44 (7C$_{arom}$-H).

2k: mp 105−106 °C; IR (KBr) 1525, 1341 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.25 (s, 18H), 7.67 (t, J = 1.7 Hz, 1H), 7.99 (d, J = 1.7 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 148.32 (C1), 117.77 (C2/6), 152.69 (C3/5), 128.77 (C4), 35.24 (C7), 31.23 (C8). Anal. Calcd for C$_{14}$H$_{21}$NO$_2$: C, 71.46; H, 8.99; N, 5.95. Found: C, 70.75; H, 9.03; N, 6.04.

2l: mp 84−85 °C; IR (KBr) 1541, 1346 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.35 (s, 18H), 8.28 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 147.31 (C1), 122.14 (C2/6), 143.65 (C3/5), 152.32 (C4), 36.81 (C7),

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30.89 (C8). Anal. Calcd for C$_{14}$H$_{20}$N$_2$O$_4$: C, 59.99; H, 7.19; N, 9.99. Found: C, 60.33; H, 7.71; N, 9.32.

3a: mp 45−47 °C; IR (KBr) 1574, 1363 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.91 (s, 9H), 1.20 (s, 9H), 1.31 (s, 18H), 6.29 (s, 2H), 9.68 (s, 1H, NH); ^{13}C NMR (CDCl$_3$) δ 168.29 (C1), 146.01 (C2/6), 134.80 (C3/5), 83.38 (C4),* 35.17 (C7), 30.82 (C8), 78.85 (C9),* 26.64 (C10),* 41.36 (C11), 25.87 (C12).* Anal. Calcd for C$_{22}$H$_{39}$NO$_2$: C, 75.59; H, 11.25; N, 4.01. Found: C, 75.78; H, 11.40; N, 4.01. The asterisks denote signals not to be assigned.

3b: mp 72−73 °C; IR (KBr) 1574, 1363 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9H), 1.27 (s, 3H), 1.30 (s, 18H), 6.20 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 167.58 (C1), 145.23 (C2/6), 134.80 (C3/5), 77.18 (C4),* 34.87 (C7), 30.64 (C8), 78.97 (C9),* 26.58 (C10), 24.68 (C11). Anal. Calcd for C$_{19}$H$_{33}$NO$_2$: C, 74.22; H, 10.82; N, 4.56. Found: C, 74.48; H, 11.22; N, 4.46.

3e-2: mp 56−58 °C; IR (KBr) 1578, 1363 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.23 (s, 9H), 1.32 (s, 18H), 3.73 (s, 3H), 6.31 (s, 2H), 6.7−7.3 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 167.64 (C1), 144.93 (C2/6), 134.33 (C3/5), 80.28 (C4),* 35.05 (C7), 30.64 (C8), 79.32 (C9),* 26.64 (C10), 133.31 (C11), 127.12 (C12/16), 113.71 (C13/15), 159.00 (C14), 55.13 (C17). Anal. Calcd for C$_{25}$H$_{37}$NO$_3$: C, 75.15; H, 9.33; N, 3.51. Found: C, 74.74; H, 9.33; N, 3.47.

3e-4: mp 55−57 °C; IR (KBr) 1574, 1365 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (s, 9H), 1.32 (s, 18H), 2.30 (s, 3H), 6.35 (s, 2H), 7.02−7.28 (m, 4H); ^{13}C NMR (CDCl$_3$) δ 167.76 (C1), 145.05 (C2/6), 134.33 (C3/5), 80.51 (C4),* 35.11 (C7), 30.70 (C8), 79.38 (C9),* 26.70 (C10), 138.32 (C11), 125.80 (C12/16), 129.02 (C13/15), 137.19 (C14), 21.10 (C17). Anal. Calcd for C$_{25}$H$_{37}$NO$_2$: C, 78.28; H, 9.72; N, 3.65. Found: C, 77.66; H, 9.61; N, 3.37.

3e-5: mp 58−59 °C; IR (KBr) 1574, 1365 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.36 (s, 18H), 1.23 (s, 9H), 6.38 (s, 2H), 7.18−7.45 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 167.76 (C1), 145.17 (C2/6), 134.45 (C3/5), 80.63 (C4),* 35.11 (C7), 30.64 (C8), 79.50 (C9),* 26.64 (C10), 141.52 (C11), 125.86 (C12/16), 128.31 (C13/15), 127.47 (C14). Anal. Calcd for C$_{24}$H$_{35}$NO$_2$: C, 78.01; H, 9.55; N, 3.79. Found: C, 77.68; H, 9.51; N, 3.66.

3e-6: mp 83−84 °C; IR (KBr) 1580, 1365 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.24 (s, 9H), 1.32 (s, 18H), 6.31 (s, 2H), 7.26 (s, 4H), 9.96 (s, 1H, NH); ^{13}C NMR (CDCl$_3$) δ 167.64 (C1), 145.64 (C2/6), 133.32 (C3/5), 80.32 (C4),* 35.12 (C7), 30.64 (C8), 79.71 (C9),* 26.66 (C10), 139.99 (C11), 127.34 (C12/16), 128.49 (C13/15), 133.32 (C14). Anal. Calcd for C$_{24}$H$_{34}$ClNO$_2$: C, 71.35; H, 8.48; N, 3.37. Found: C, 70.95; H, 8.50; N, 3.40.

5: liquid; IR (neat) 1649, 1365 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9H), 1.90 (s, 6H), 6.62 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 187.01 (C1), 134.86 (C2/6), 145.71 (C3/5), 76.05 (C4),* 23.43 (C7), 15.80 (C8), 79.62 (C9),* 26.41 (C10); MS 224 (M$^+$).

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Comparison of Catalytic Activity of Co(L^n). A DCE solution (20 mL) including **1a** (0.5 mmol), Co(L^n) (0.07 mmol), TBHP (4 mmol), and benzophenone (0.15 mmol) as an internal standard probe for the analysis was put in a water bath thermoregulated at 25.0 ± 0.1 °C. An aliquot was taken out at the interval shown in Figure 1, a sufficient amount of PPh$_3$ was added in order to stop the reaction so as to reduce the remaining TBHP, and the conversion was determined by means of a TLC scanner. The results are shown in Figure 1.