

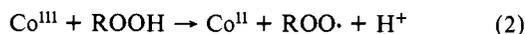
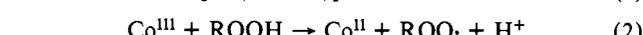
Cobalt(III) Alkylperoxy Complexes. Synthesis, X-ray Structure, and Role in the Catalytic Decomposition of Alkyl Hydroperoxides and in the Hydroxylation of Hydrocarbons

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Contribution from Laboratoire d'Oxydation, Institut Français du Pétrole, 92502 Rueil-Malmaison, France, and Laboratoire de Cristalochimie, Université Louis Pasteur, 67070 Strasbourg Cédex, France. Received September 24, 1984

Abstract: Novel cobalt(III) alkylperoxy complexes with the general formula $\text{Co}(\text{R}''\text{BPI})(\text{OCOR}')(\text{OOR})$ [type I, $\text{R}'' = \text{H}$, Me ; $\text{BPI} = 1,3\text{-bis}(2'\text{-pyridylimino})\text{isoindoline}$, $\text{R}' = \text{Me}$, Ph , $t\text{-Bu}$; $\text{R} = t\text{-Bu}$, CMe_2Ph] and $\text{Co}(\text{BPB})(\text{OO}t\text{-Bu})(4\text{-Mepy})$ [type II, $\text{BPB} = N,N'\text{-bis}(2'\text{-pyridinecarboxamide})\text{-}1,2\text{-benzene}$] were synthesized from the reaction of alkyl hydroperoxides with their $\text{Co}(\text{II})$ precursor, and characterized by physicochemical methods. The X-ray structure of Ib ($\text{R}'' = \text{H}$, $\text{R}' = \text{Ph}$, $\text{R} = t\text{-Bu}$) revealed a distorted octahedral environment with a chelating carboxylate moiety and an apically bonded *tert*-butylperoxy group. The reactivity of cobalt(III) alkylperoxy complexes toward hydrocarbons was found to be dependent on their thermal decomposition rate, with type I complexes being the most reactive ones. Saturated hydrocarbons are oxidized by $\text{Co}(\text{III})$ *tert*-butylperoxy complexes into alcohols, ketones, and *tert*-butylperoxy products. The hydroxylation reaction preferentially occurs at the more nucleophilic C-H bonds with extensive epimerization at the hydroxylated carbon atom. Hydrocarbons having labile allylic or benzylic C-H bonds react beginning at room temperature to give a large amount of allylic or benzylic *tert*-butyl peroxide. Olefins having no allylic hydrogen atom are preferentially transformed into epoxides. The catalytic hydroxylation of alkanes by *t*-BuOOH in the presence of complexes I-III has the same characteristics as the stoichiometric reaction. The homolytic decomposition and reactivity of cobalt(III) alkylperoxy complexes is discussed in the context of the Haber-Weiss mechanism of alkyl hydroperoxide decomposition and of hydrocarbon hydroxylation by first-row transition-metal peroxides.

The cobalt-catalyzed oxidation of hydrocarbons by molecular oxygen represents one of the largest scale applications of homogeneous catalysis and is widely used in industry, e.g., for the synthesis of terephthalic acid from *p*-xylene or adipic acid from cyclohexane.² In these processes, one of the key steps is the homolytic decomposition of the in situ formed hydroperoxide autoxidation product by cobalt ions according to the well-known Haber-Weiss mechanism (eq 1-3).^{2a,3} Cobalt hydroperoxide



complexes have been postulated as intermediates in these processes on the basis of kinetic data,⁴ but they have not yet been firmly characterized. However, several cobalt(III) alkylperoxy complexes having dimethylglyoxime as ligands,⁵ e.g., $\text{Co}(\text{dmgH})_2(\text{py})(\text{OOR})$ or Schiff base,⁶ e.g., $\text{Co}(\text{salen})(\text{OO}t\text{-Bu})$, have been synthesized, and some of them have been characterized by an X-ray crystal structure,^{5a,6a} but the reactivity of such compounds toward hydrocarbons is almost unknown.

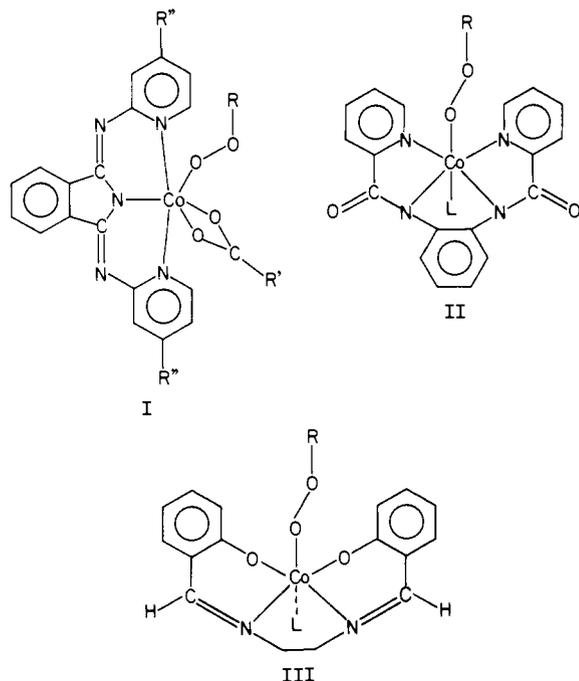
We have recently shown that vanadium(V) peroxo, e.g., $(\text{Pic})\text{VO}(\text{O}_2)\cdot 2\text{H}_2\text{O}$,⁷ and alkylperoxy complexes, e.g., (dipic)-

$\text{VO}(\text{OO}t\text{-Bu})\cdot \text{H}_2\text{O}$,⁸ as well as chromium(VI) peroxo complexes, e.g., $\text{Cr}(\text{O}_2)_2\cdot \text{Ph}_3\text{PO}$,⁹ hydroxylate hydrocarbons in a homolytic way. This contrasts with the known heterolytic oxidizing properties of second- and third-row transition-metal peroxides (e.g., Mo^{VI} , W^{VI} , Rh^{III} , Ir^{III} , Pd^{II} , Pt^{II}).¹⁰ We have therefore been interested in synthesizing stable but reactive $\text{Co}(\text{III})$ alkylperoxy complexes in order to develop synthetically useful catalytic hydroxylation of alkanes by alkyl hydroperoxides. Such hydroxylation reactions were previously observed by Hiatt et al. during the decomposition of alkyl hydroperoxides in refluxing alkanes in the presence of cobalt octoate¹¹ and by Mansuy et al. who used metalloporphyrins as catalysts for the hydroxylation of alkanes by *tert*-butyl and cumyl hydroperoxide at room temperature.¹² A significant increase in selectivity in the decomposition of cyclohexyl hydroperoxide to cyclohexanol and cyclohexanone in the presence of transition-metal (particularly cobalt) complexes of 1,3-bis(pyridylimino)isoindoline derivatives ($\text{R}''\text{-BPIH}$) has recently been reported in a patent by researchers at Du Pont.¹³

This paper reports on the synthesis and characterization of novel cobalt(III) alkylperoxy complexes with the general formula $\text{Co}^{\text{III}}(\text{R}''\text{BPI})(\text{OCOR}')(\text{OOR})$ [type I: $\text{R}'' = \text{H}$, Me ; $\text{R}' = \text{Me}$, Ph , $t\text{-Bu}$; $\text{R} = t\text{-Bu}$, CMe_2Ph] for which the X-ray crystal structure of Ib ($\text{R} = t\text{-Bu}$, $\text{R}' = \text{Ph}$, $\text{R}'' = \text{H}$) has been determined. These complexes I were found to be reactive for the stoichiometric hydroxylation of alkanes and to be catalysts for the hydroxylation of alkanes by alkyl hydroperoxides. The reactivity of complexes I was compared to that of $\text{Co}^{\text{II}}(\text{BPB})(\text{OO}t\text{-Bu})(4\text{-Mepy})$ (type

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II) prepared here for the first time [BPB = *N,N*-bis(2'-pyridylcarboxamide)-1,2-benzene] and to that of known Co(salen)(OO-*t*-Bu)L (type III; L = no ligand or 4-methylpyridine.)

Results

1. Synthesis and Characterization of Cobalt(III) Alkylperoxy Complexes. Addition of excess alkyl hydroperoxide to a suspension of Co^{II}(R''BPI)(OCOR')(IV) precursor in CH₂Cl₂ or benzene at room temperature results in the formation of a brown-red solution and demixing of water. Removal of the solvent results in the formation of a brown-red crystalline compound with good-to-excellent yields. These compounds were characterized by elemental analysis, infrared spectroscopy, NMR, and iodometric titration and correspond to the formula Co^{III}(R''BPI)(OCOR')(OOR). These complexes are soluble in most organic solvents, stable in the solid state, safe to handle, and can be stored for months in a refrigerator.

The infrared spectra of the *tert*-butylperoxy complexes (Table I) showed the characteristic OO-*t*-Bu absorptions at 2970–2980 cm⁻¹ (ν (C–H)), 1180–1190 cm⁻¹ (ν (C–C)), and 870–880 cm⁻¹ (ν (O–O)) and are dominated by the ligand bands in the 1400–1650-cm⁻¹ region. This therefore did not allow an accurate assignment to be made of the carboxylate ν (C=O) vibrations in complexes I, which would have been of great interest owing to the rather unusual bidentate chelating mode of the carboxylate ligand¹⁵ revealed by the X-ray structure of complex Ib (vide infra). NMR spectra of the complexes (Table I) exhibited a singlet at δ 0.4–0.9 ppm (reference Me₄Si) attributable to the *tert*-butyl or the *gem*-dimethyl groups of the peroxidic moieties. This corresponds to a significant upfield shift with respect to the free hydroperoxides and suggests that the alkyl group is located over the aromatic rings of the chelating ligand, as confirmed by the X-ray structure of Ib. A similar upfield shift was observed for the methyl substituents of the acetate and pivalate groups of type I complexes, suggesting a similar magnetic interaction. Iodometric titration of the alkylperoxy complexes indicated 3 electronic equiv per molecule, corresponding to one peroxidic oxygen atom (2 equiv) and the reduction of cobalt(III) to cobalt(II) (1 equiv).

The alkylperoxy complex II was obtained with good yield by treating a CH₂Cl₂ suspension of Co^{II}(BPB)·H₂O¹⁶ with *t*-BuOOH in the presence of 4-picoline. This green complex was charac-

Table I. Cobalt(III) Alkylperoxy Complexes

complex	R	R'	R''	ν (O–O), ^a cm ⁻¹	δ Me, ^b ppm
Co(R''BPI)(OCOR')-(OOR) (I)					
Ia	<i>t</i> -Bu	Me	H	880	0.47
Ib	<i>t</i> -Bu	Ph	H	875	0.52
Ic	CMe ₂ Ph	Me	H	880	0.73
Id	CMe ₂ Ph	Ph	H	875	0.68
Ie	<i>t</i> -Bu	Me	Me	880	0.50
If	<i>t</i> -Bu	Ph	Me	875	0.55
Ig	<i>t</i> -Bu	tBu	Me	885	0.43
Ih	CMe ₂ Ph	tBu	Me	870	0.73
Co(BPB)(OO- <i>t</i> -Bu)(4-Mepy)(II)				880	0.53
Co(salen)(OO- <i>t</i> -Bu)(IIIa)				880	
Co(salen)(OO- <i>t</i> -Bu)(4-Mepy)(IIIb)				875	0.87

^a Infrared spectra. KBr disk. ^b ¹H NMR spectra of the OO-*t*-Bu or the OOCMe₂Ph groups; solvent CD₂Cl₂, reference SiMe₄.

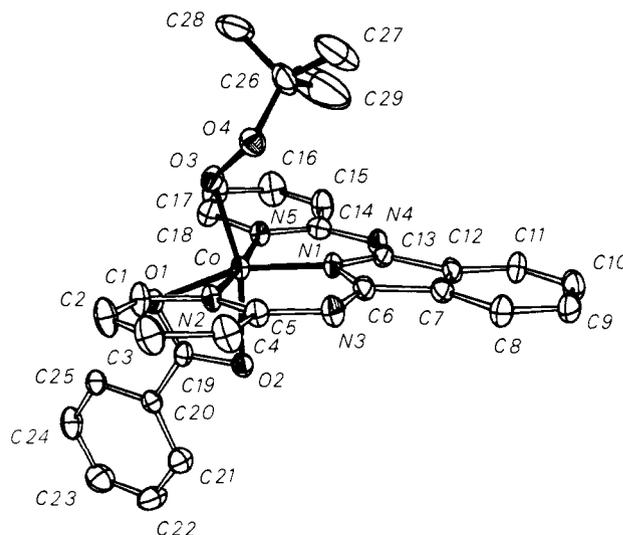


Figure 1. ORTEP plot of the molecule of Ib. Ellipsoids are scaled to enclose 50% of the electron density. Principal bond distances (Å): Co–N1, 1.845 (5); Co–N2, 1.960 (5); Co–N5, 1.950 (5); Co–O1, 1.993 (4); Co–O2, 2.045 (5); Co–O3, 1.838 (5); O3–O4, 1.444 (6); O4–C26, 1.423 (9). Selected bond angles (deg): N1–Co–N2, 91.8 (2); N1–Co–N5, 91.5 (2); N1–Co–O1, 160.6 (2); N1–Co–O2, 95.7 (2); N1–Co–O3, 101.5 (2); N2–Co–N5, 174.0 (2); N2–Co–O1, 90.4 (2); N2–Co–O2, 94.9 (2); N2–Co–O3, 87.0 (2); N5–Co–O1, 88.0; N5–Co–O2, 89.7 (2); N5–Co–O3, 87.4(2); O1–Co–O2, 64.9 (2); O1–Co–O3, 97.8 (2); O2–Co–O3, 162.6 (2); Co–O3–O4, 114.6 (3); O3–O4–C26, 111.2 (6).

terized by IR, NMR, elemental analysis, and iodometric titration.

2. X-ray Crystal Structure of Co(BPI)(OBz)(OO-*t*-Bu) (Ib).

Figure 1 shows an ORTEP¹⁷ plot of one molecule of Ib, the labeling scheme used, and the principal bond lengths and angles. Table II gives the atomic positional and equivalent thermal parameters for all non-hydrogen atoms. The coordination polyhedron of the cobalt atom is a distorted octahedron. Three nitrogen atoms of the BPI ligand and one oxygen atom of the benzoate moiety occupy the equatorial corners, while the second carboxylate oxygen atom and one oxygen atom of the OO-*t*-Bu group are in axial positions. The OO-*t*-Bu moiety is apically bonded to the cobalt atom as in other Co^{III} alkylperoxy complexes^{5a,6a} but contrasts with triangular VOO-*t*-Bu⁸ and bridged PdOO-*t*-Bu¹⁸ complexes. The Co–O3 length of 1.838 (5) Å is in the same range as that found in peroxy-*p*-quinolato Co^{III} (salpr) (1.854 (9) Å)^{6a} but is significantly shorter than in Co(dmgh)₂(py)(OOCMe₂Ph).^{5a} By

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Table 11. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å ²	atom	x	u	z	B, Å ^{2a}
Co	0.2411 (1)	0.21053 (6)	0.14857 (8)	3.21 (2)	C17	0.214 (1)	0.3786 (5)	-0.0479 (7)	6.4 (3)
N1	0.2176 (6)	0.1232 (3)	0.0846 (5)	3.3 (2)	C18	0.2336 (9)	0.3347 (5)	0.0305 (6)	4.0 (2)
N2	0.2935 (6)	0.1630 (4)	0.2749 (5)	3.6 (2)	N5	0.2046 (6)	0.2632 (4)	0.0258 (5)	3.6 (2)
C1	0.3386 (9)	0.2049 (5)	0.3515 (6)	4.7 (2)	O1	0.2086 (5)	0.3009 (3)	0.2147 (4)	3.6 (1)
C2	0.384 (1)	0.1803 (6)	0.4425 (6)	5.9 (3)	O2	0.0708 (5)	0.2229 (3)	0.1618 (4)	4.1 (1)
C3	0.387 (1)	0.1081 (6)	0.4601 (7)	5.9 (3)	C19	0.1026 (8)	0.2829 (5)	0.1984 (5)	3.6 (2)
C4	0.343 (1)	0.0652 (5)	0.3837 (7)	5.4 (3)	C20	0.108 (8)	0.3340 (5)	0.2172 (5)	3.6 (2)
C5	0.2983 (9)	0.0911 (5)	0.2905 (6)	3.9 (2)	C21	-0.1039 (9)	0.3121 (5)	0.2103 (7)	5.1 (3)
N3	0.2594 (7)	0.0406 (4)	0.2201 (5)	4.2 (2)	C22	-0.188 (1)	0.3622 (6)	0.2243 (9)	6.5 (3)
C6	0.2255 (8)	0.0566 (5)	0.1284 (6)	3.6 (2)	C23	-0.157 (1)	0.4308 (7)	0.2429 (9)	7.1 (3)
C7	0.1802 (8)	0.0014 (5)	0.0551 (6)	3.8 (2)	C24	-0.043 (1)	0.4527 (5)	0.2510 (0)	6.2 (3)
C8	0.1699 (9)	-0.0733 (5)	0.0634 (7)	4.9 (3)	C25	0.0437 (9)	0.4047 (5)	0.2303 (7)	4.1 (2)
C9	0.1189 (9)	-0.1086 (5)	0.0226 (8)	5.6 (3)	O3	0.3971 (5)	0.2274 (3)	0.1509 (4)	4.3 (1)
C10	0.083 (1)	0.0724 (6)	-0.1097 (7)	5.6 (3)	O4	0.4665 (6)	0.1633 (4)	0.1474 (4)	4.9 (2)
C11	0.0924 (9)	0.0001 (5)	-0.1178 (7)	4.7 (2)	C26	0.516 (1)	0.1630 (6)	0.0636 (7)	6.1 (3)
C12	0.1420 (8)	0.0368 (5)	-0.0327 (6)	3.9 (2)	C27	0.564 (1)	0.0897 (8)	0.061 (1)	11.3 (4)
C13	0.1649 (8)	0.1146 (4)	-0.0132 (6)	3.4 (2)	C28	0.600 (1)	0.2184 (8)	0.066 (1)	9.9 (4)
N4	0.1326 (7)	0.1627 (4)	-0.0794 (5)	4.0 (2)	C29	0.446 (2)	0.174 (2)	-0.024 (1)	21 (1)
C14	0.1568 (8)	0.2345 (5)	-0.0627 (6)	4.1 (2)	OW1	0.500	0.500	0.000	20 (2)*
C15	0.134 (1)	0.2799 (6)	-0.1453 (7)	5.8 (3)	OW2	-0.004 (1)	0.1392 (9)	0.725 (1)	18.0 (5)*
C16	0.160 (1)	0.3500 (6)	-0.1370 (7)	7.1 (3)	OW3	0.524 (5)	0.381 (3)	-0.095 (4)	33 (2)*

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

contrast, the O–O bond lengths in these three complexes are not significantly different at the 3 σ level. The n² chelating mode of the carboxylate is rather unusual.¹⁵

This bidentate carboxylate moiety probably causes the extensive distortion of the cobalt coordination octahedron. Whereas oxygen atom O2 is in a nearly apical position, the O1–Co–O2 bond angle of 64.9 (2)° pulls oxygen atom O1 out of the equatorial plane, leading to a N1–Co–O1 angle of 160.6 (2)°. Consequently, the two Co–O1 and Co–O2 bond lengths are different (1.993 (4) and 2.045 (5) Å, respectively). As in previously described copper(II)¹⁹ and manganese(II)²⁰ BPI complexes, the BPI ligand is distorted from planarity at the bridging nitrogen atoms. The unit cell contains seven partly disordered water molecules.

3. Thermal Decomposition of Cobalt(III) Alkylperoxy Complexes. As shown below, the reactivity of cobalt(III) alkylperoxy complexes is governed by their thermal decomposition rate. This was estimated by iodometric titration of the three oxidizing equivalents of these cobalt(III) compounds²¹ and by GC analysis of the organic decomposition products. Figure 2 shows the decomposition curves of different alkylperoxy complexes at 60 °C in benzene solution. Type I BPI complexes decomposed much more rapidly than type III salen complexes, whereas type II BPB compounds do not decompose at all under these conditions.

The decompositions of Ia and Ib occur at comparable rates and reach a plateau of 0.8–1 electronic equivalent after about 120 min (Figure 2), corresponding to the complete disappearance of the initial *tert*-butylperoxy complex and the formation of (BPI)-Co^{III}(OAc)₂ (V) and *t*-Bu₂O₂ (vide infra). From the Arrhenius plots of log V_i vs. 1/TK at 40, 50, 60, and 80 °C, the activation energy $E_a = 13.2 \pm 1$ kcal mol⁻¹ was obtained for the decomposition of Ia (V_i = initial rate of decomposition).

During the decomposition of Ia, a brown precipitate mainly consisting of the Co^{III} precursor, i.e., Co^{II}(BPI)(OAc) (IVa), was formed. Filtration of this precipitate followed by evaporation of the solvent at the end of the decomposition enabled us to isolate a brown cobalt(III) complex corresponding to the formula Co^{III}(BPI)(OAc)₂ with ca. 25% isolated yield. The same compound was independently prepared from the oxidation of Co^{II}(BPI)(OAc) by peracetic acid (see Experimental Section). GC analysis of the organic solution after decomposition of Ia or Ib

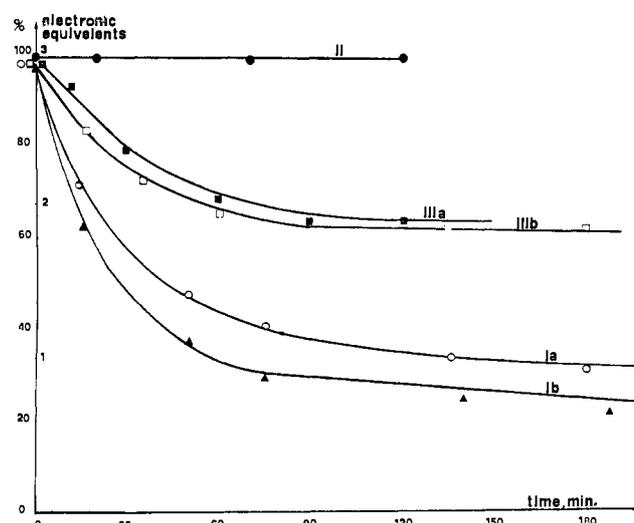
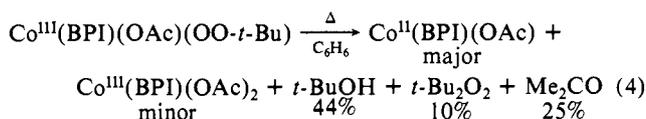


Figure 2. Decomposition curves of complexes I–III at 60 °C. Concentration, 0.048 M; solvent = benzene.

revealed the formation of *t*-Bu₂O₂ (10% yield), *t*-BuOH (44%), and acetone (25%),²² coming from *t*-BuO₂• and *t*-BuO• resulting from the homolytic scission of the cobalt(III) *tert*-butylperoxy complex (vide infra). The thermal decomposition of Ia can be summarized by eq 4.



4. Stoichiometric Oxidation of Hydrocarbons. The stoichiometric oxidation of hydrocarbons by complexes I–III was carried out in nitrogen, in the absence of solvent, or in benzene, at temperatures between 20 and 80 °C, depending on the oxidizability of the substrate. Type I Co(III) complexes are much more soluble in pure hydrocarbons than their Co(II) precursors. At the end of the oxidation of hydrocarbons by Ia or Ib in the absence of solvent, the solution becomes colorless, and the precursor Co^{II}(BPI)(OCOR) was recovered by filtration with almost quantitative yield. Three kinds of reactivity of hydrocarbons could be distinguished (Table III).

(22) Similar results were obtained with either Ia or Ib. The yields are based on the initial *tert*-Butylperoxy complex Ia or Ib.

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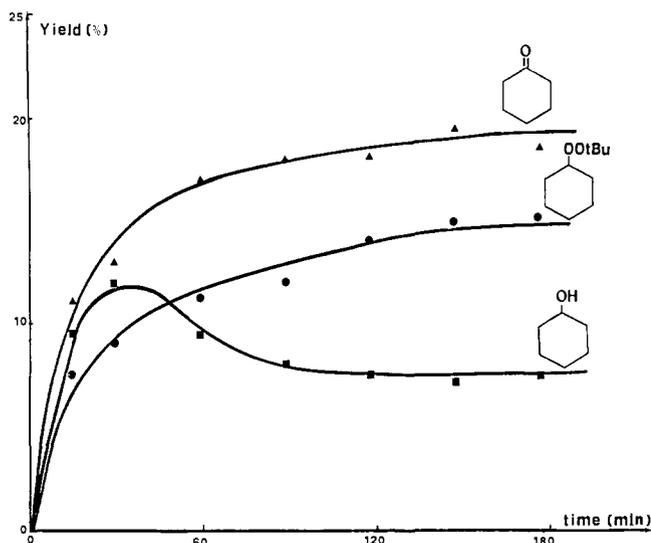


Figure 3. Stoichiometric oxidation of cyclohexane by Ia: temp. 60 °C; solvent, benzene; Ia, 0.04 M; C₆H₁₂, 5.6 M, yields are based on cobalt.

(1) Saturated hydrocarbons, e.g., cyclohexane, adamantane, *cis*-decalin, and *n*-octane, react at appreciable rates only at temperatures over 60 °C, i.e., when the decomposition of alkylperoxy complexes becomes substantial. Oxidation of cyclohexane results in the formation of cyclohexanol, cyclohexanone, and *tert*-butylperoxycyclohexane as the main products. Figure 3 shows a typical plot of oxygenated products formation vs. time when cyclohexane was oxidized by Ia in benzene at 60 °C. Cyclohexanol was mainly formed at the beginning of the reaction but progressively decreased with time at the expense of cyclohexanone, while *tert*-butylperoxycyclohexane continuously increased in a parallel way. BPI complexes Ia or Ib were found to be the most reactive toward cyclohexane (Table III) as expected from the decomposition curves shown in Figure 2. In contrast, since the BPB complex II is stable at 60 °C, it was found to be inactive, while the salen complexes IIIa or IIIb gave lower yields of oxygenated products. The hydroxylation of C–H bonds preferentially occurs at the tertiary positions as shown in the case of adamantane and *cis*-decalin. Hydroxylation of *cis*-decalin yielded *trans*-9-decalol as the main product. This indicates the formation and the substantial inversion of the *cis*-9-decalyl radical intermediate in this reaction. Cyclohexyl radicals were also revealed by the large-scale formation of cyclohexyl chloride during the oxidation of cyclohexane by Ia in the presence of CCl₄ acting as a source of chlorine atoms (entry 6).^{7,23} Hydroxylation of *n*-octane by Ia occurs in an almost statistical way, with some preference at the C-2 position, which is, however, less pronounced than in the oxidation of *n*-alkanes by Co(OAc)₃.²⁴

(2) Hydrocarbons having labile C–H bonds at the allylic (e.g., cyclohexene) or benzylic (e.g., toluene, ethylbenzene) positions react beginning at room temperature and give a large amount of allylic or benzylic *tert*-butyl peroxide, together with the formation of allyl or benzyl alcohol and carbonyl compounds. It is worthy of note that, in contrast to vanadium peroxidic complexes,^{7,8} cobalt(III) alkylperoxy complexes do not hydroxylate aromatic compounds at the ring positions.

(3) Alkenes having no allylic C–H bonds (e.g., norbornene, styrene) are oxidized to the corresponding epoxide as a major product. This reactivity is similar to that previously found by Kochi in the Co(acac)₃-catalyzed homolytic oxidation of norbornene and *tert*-butylethylene by O₂.²⁵

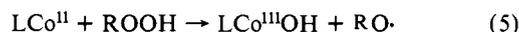
5. Catalytic Hydroxylation of Alkanes by Alkyl Hydroperoxides. Cobalt(III) alkylperoxy complexes I–III, as well as their Co(II)

precursors, catalyze the hydroxylation of alkanes by alkyl hydroperoxides, as shown in Table IV. The catalytic reaction was carried out at 80 °C in N₂ by using a 1:1000 Co/ROOH ratio in pure alkane. The catalytic activity of complexes I–III for the hydroxylation of cyclohexane and *cis*-decalin by *t*-BuOOH or PhCMe₂OOH parallels their stoichiometric oxidizing properties. BPI complexes I gave higher yields of cyclohexanol and cyclohexanone from cyclohexane, at higher ROOH conversion than complexes II, III, or cobalt(II) 2-ethylhexanoate. *tert*-Butylperoxycyclohexane was also formed as a byproduct, as in the stoichiometric reaction. The catalytic hydroxylation of *cis*-decalin results, as in the stoichiometric reactions, in the main formation of *trans*-9-decalol.

Discussion

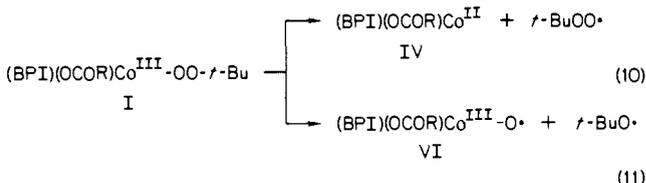
Cobalt(III) alkylperoxy complexes play a most important role as reactive intermediates in the cobalt-catalyzed decomposition of hydroperoxides, as well as in the catalytic hydroxylation of hydrocarbons by alkyl hydroperoxides. Both of these processes are of considerable industrial importance. The nature of the chelating ligand exerts a profound influence on the existence and stability of the cobalt(III) alkylperoxy complexes, and therefore on the rate of decomposition of alkyl hydroperoxides catalyzed by cobalt compounds. In effect, while BPB or salen ligands strongly stabilize the alkyl peroxy complexes, the use of BPI ligands can promote the synthesis of complexes stable enough to be accurately characterized and unstable enough to decompose and react with hydrocarbons under mild conditions.

The formation of cobalt(III) alkylperoxy complexes from the reaction of alkyl hydroperoxides with cobalt(II) complexes involves a one-electron oxidation of the metal, while the decomposition of cobalt(III) alkylperoxy complexes mainly brings back the initial cobalt(II) compound. This formation and decomposition of the alkylperoxy species occurring with a one-electron change of the metal may be associated with the two main steps of the Haber–Weiss mechanism of decomposition of alkyl hydroperoxides (eq 1 and 2). The formation of cobalt(III) alkylperoxy complexes could be interpreted by eq 5–9. This mechanism is similar to



the one proposed by Espenson for the formation of Co^{III}-(dmgH)₂(OO-*t*-Bu)Py from the reaction of *t*-BuOOH with Co^{II}(dmgH)₂py in benzene.^{5c} However, since in our case we did not observe the formation of cobalt(III) hydroxo complexes but we detected the formation of water, we presume that anion exchange occurs between the alkyl hydroperoxide and the LCo^{III}-OH species according to eq 8.

The thermal decomposition of Ia or Ib probably results from the homolytic cleavage of the Co^{III}-OO-*t*-Bu moiety, which can occur between the Co^{III}-O (eq 10) or the O–O bond (eq 11).



(11)

Among the organic products formed, di-*tert*-butyl peroxide presumably results from the direct recombination of the two *t*-BuO· or of two *t*-BuOO· radicals with evolution of O₂ from the tetraoxide formed.²⁶ *tert*-Butyl alcohol is formed by hydrogen abstraction from the medium by *t*-BuO·, and acetone results from the homolytic β-scission of *t*-BuO·.²⁷ The decomposition of complexes I proceeds differently whether it occurs in benzene or in the

(23) Bartlett, P. D.; Pincock, R. E.; Rolston, J. H.; Schindel, W. G.; Singer, L. A. *J. Am. Chem. Soc.* **1965**, *87*, 2590.

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Table III. Stoichiometric Oxidation of Hydrocarbons^a

entry	complex	temp, °C	solvent	substrate	products, ^b % yield ^c							
												
1	la	60	none		18	24	18					
2	lb	60	none		14	18	13					
3	II	60	none			<1						
4	IIIa	60	none		4.7	7.6	4.5					
5	IIIb	60	none		1	16.5	1					
6	la	60	CCl ₄ ^d		11	11		5%				
7	la	60	C ₆ H ₆	adamantane	adamantan-1-ol	adamantan-2-ol	adamantan-2-one					
8	IIIa	60	C ₆ H ₆		26	1	11					
					17	3	13					
				<i>cis</i> -decalin	<i>cis</i> -decalin-9-ol	<i>trans</i> -decalin-9-ol	decalin-1-one	decalin-2-one				
9	lb	80	none		12	43	9	11				
10	Id	80			8	30	8	8				
				<i>n</i> -octane	<i>n</i> -octan-1-ol	<i>n</i> -octan-2-ol	<i>n</i> -octan-3-ol	<i>n</i> -octan-4-ol	<i>n</i> -octan-2-one	<i>n</i> -octan-3-one	<i>n</i> -octan-4-one	
11	la	80	none		1	7	5	4.6	12	7.8	8.3	
												
12	lb	60	none		7	35	30	3				
13	lb	20			21	24	27	2				
14	la	20			32	17	23	3				
												
15 ^e	la	80	C ₆ H ₆		34							
				Ph-CH=CH ₂	PhCHO		PhCOMe					
16 ^e	la	60	C ₆ H ₆		7	15	6					
				Ph-CH ₂ -CH ₃	Ph-CH(OH)-CH ₃	Ph-C(=O)-CH ₃	Ph-CH(OO- <i>t</i> -Bu)-CH ₃					
17	lb	20	none		3.5	22	26					
18	lb	50			3.5	22.5	38					
				Ph-CH ₃	Ph-CH ₂ OH	Ph-CHO						
19	la	20	none		12	27						
		60			23	60						

^a Reaction conditions: complex, 0.04 M; time, 120 min. ^b Identified by GC-MS coupling. ^c GC determination by using various internal standards. ^d 10% CCl₄. ^e Substrate, 2 M.

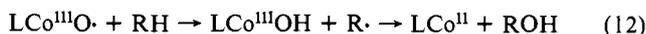
Table IV. Catalytic Hydroxylation of Alkanes by Alkyl Hydroperoxides^a

run	complex	oxidant ^b	substrate	product(s), % yield ^c			conv (ROOH) ^d	
								
20	Ia	<i>t</i> -BuOOH		33	20	6	87	
21	Ia	PhCMe ₂ OOH		39	17		100	
22	Ib	<i>t</i> -BuOOH		32	16	9	92	
23	II	<i>t</i> -BuOOH		15	17	5	40	
24	IIb	<i>t</i> -BuOOH		17	12	8	71	
25	Co(oct) ₂ ^e	<i>t</i> -BuOOH		14	11	9	78	
26	Ia	<i>t</i> -BuOOH	<i>cis</i> -decalin	<i>cis</i> -decalin-9-ol		<i>trans</i> -decalin-9-ol	decalin-1 + 2-one	96
27	Ib	<i>t</i> -BuOOH		7		27	3	96
27	Ib	<i>t</i> -BuOOH		8		31	4.5	97
28	Co(oct) ₂ ^e	<i>t</i> -BuOOH		4.5		21	3	62

^a Reaction conditions: catalyst, 10⁻³ mmol; alkane, 46 mmol; hydroperoxide, 1 mmol; temp, 80 °C; reaction time, 90 min. ^b Purity of hydroperoxides: *t*-BuOOH, 97%; PhCMe₂OOH, 80%. ^c GC yields based on hydroperoxide consumed. ^d Hydroperoxide consumption (iodometric titration). ^e Cobalt(II) 2-ethylhexanoate.

presence of reactive hydrogen substrate. In the later case, only the cobalt(II) precursor was formed, owing to the hydroxylating properties of VI (vide infra), whereas in benzene VI could further react to produce the cobalt(III) complex observed (BPI)Co(OAc)₂.

The hydroxylation of saturated hydrocarbons (e.g., cyclohexane, adamantane, *cis*-decalin, *n*-octane) by cobalt(III) alkylperoxy complexes depends on their thermal decomposition rate. In effect, since complexes II and III are relatively stable, they have no or little reactivity, whereas BPI complexes I react beyond 60 °C. The hydroxylation reaction can be attributed to the formation of Co^{III}-O· VI according to eq 11 and could occur by hydrogen atom abstraction from the substrate by VI, followed by coupling of the radical R· formed with the hydroxyl radical of the resulting Co^{III}-OH species, as suggested by Mansuy (eq 12).^{12b} Alkyl

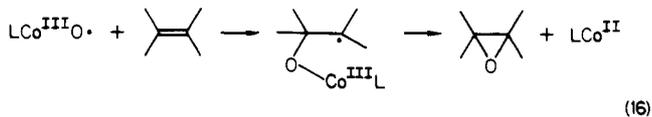
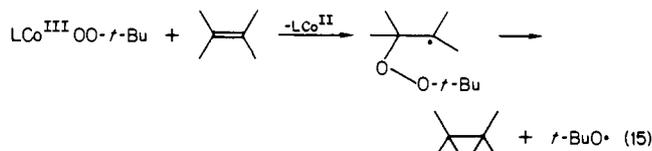


radicals R· can also be produced by hydrogen atom abstraction from the substrate by *t*-BuO· or *t*-BuOO· (eq 10, 11). *tert*-Butylperoxycyclohexane, which has also been observed in the oxidation of cyclohexane by I and III, probably results from the coupling of R· with *t*-BuOO·. The alkyl radicals R· produced in different ways are probably long-lived intermediates and can substantially epimerize before recombination, as shown by the extensive formation of *trans*-9-decalol from *cis*-decalin.

Hydrocarbons having labile allylic or benzylic hydrogen atoms (e.g., cyclohexene, ethylbenzene) react with type I complexes at room temperature and give a large amount of allylic or benzylic alkylperoxides. This could be interpreted by a hydrogen atom abstraction from the substrate by the Co(III) complex (eq 13). Reaction of the alkyl radical R· with I could provide diacyl peroxide (eq 14).



Epoxidation of olefins having no allylic hydrogen atoms (e.g.,



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(27) (a) Ingold, K. U. *Pure Appl. Chem.* **1967**, 15, 49. (b) Walling, C. *Ibid.* **1967**, 15, 69.

styrene, norbornene) by Ia could result from the homolytic addition of *t*-BuOO· (eq 15) or LCo^{III}-O· (eq 16) to the double bond, followed by homolytic cyclization, as suggested by Kochi.²⁵

Hydroxylation of alkanes by alkyl hydroperoxides in the presence of catalytic amounts of complexes I-III yields the same products as in stoichiometric oxidation by the Co(III) alkylperoxy complexes, with the same selectivity. The catalytic activity of complexes I-III also parallels their decomposition rate. It therefore appears probable that Co(III) alkylperoxy complexes are involved as active intermediates in the catalytic hydroxylation of hydrocarbons. The use of BPI complexes I as hydroxylation catalysts results in improved yields compared to conventional soluble cobalt catalysts such as Co(oct)₂. This shows that the use of appropriate ligands on cobalt can result in a major improvement in the activity and selectivity of these homolytic processes.

Experimental Section

Apparatus. Infrared spectra were recorded by a Perkin-Elmer Model 1430 and NMR spectra by a Varian CFT20. Products were identified by GC-MS coupling (Kratos Model MS80) and comparison with the mass spectra of authentic samples.

Materials. Olefins, alkanes, and alkylaromatic compounds were passed through a column containing active alumina to remove peroxidic impurities, distilled over sodium, and stored in nitrogen. *tert*-Butyl hydroperoxide (97% purity) was obtained by careful vacuum distillation of the aqueous 70% commercial solution (Akzo). Cumyl hydroperoxide (80%) and 80% *tert*-butyl hydroperoxide (Merck) were used as received for the synthesis of the alkylperoxy complexes. *tert*-Butylperoxycyclohexane,²⁸ 3-*tert*-butylperoxycyclohexene,²⁹ and 1-(phenylethyl)-*tert*-butyl peroxide³⁰ were prepared according to known procedures. The various BPI-free ligands and the cobalt(II) chelates Co(BPI)(OCOR) were synthesized according to the procedures of Siegl³¹ and Gagne.¹⁴ The Co(BPB)H₂O complex was prepared according to Chapman.¹⁶ Co(salen)(OO-*t*-Bu) (IIa) was prepared by addition of *t*-BuOOH to Co^{II}(salen) according to the procedure of Nishinaga.^{6b}

Co^{III}(BPI)(OAc)(OO-*t*-Bu) (Ia). Two milliliters of 80% *t*-BuOOH was added to a suspension of 1 g of Co(BPI)(OAc) (2, 4 mmol) in 20 mL of benzene. After 1 h of continuous stirring at 20 °C, the red solution was dried over Na₂SO₄ and concentrated in vacuo. Addition of anhydrous diethyl ether resulted in the precipitation of a red-brown complex, which was filtered, washed with an Et₂O-pentane (1:3) mixture, and dried in vacuo, yield = 1 g (83%). Anal. Calcd for C₂₄H₂₄N₅O₄Co: C, 57.04; H, 4.75; N, 13.86; O, 12.67. Found: C, 57.1; H, 4.89; N, 13.8; O, 12.65. ¹H NMR CD₂Cl₂ δ 0.47 (s, 9 H), 1.63 (s, 3 H), 7.1-8.2 (m, 10 H), 8.9 (d, 2 H).

Co^{III}(BPI)(OBz)(OO-*t*-Bu) (Ib). Ten milliliters of 80% *t*-BuOOH was added to a suspension of Co(BPI)(OBz) (7.5 g) in 150 mL of CH₂Cl₂. After 4 h of continuous stirring at 20 °C, the red solution was

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(31) Siegl, W. O. *J. Org. Chem.* **1977**, 42, 1872.

filtered, dried over Na_2SO_4 , and concentrated in vacuo. Isolation of **1b** by the same procedure as **1a** yielded 8.3 g of a brown crystalline product (94% yield). Anal. Calcd for $\text{C}_{29}\text{H}_{26}\text{N}_5\text{O}_4\text{Co}$: C, 61.38; H, 4.58; N, 12.35; O, 11.29. Found: C, 60.35; H, 4.51; N, 12.01; O, 11.2. $^1\text{H NMR}$ (CD_2Cl_2) δ 0.52 (s, 9 H), 7–8.2 (m, 15 H), 9 (d, 2 H).

Co^{III}(BP1)(OAc)(OOCMe₂Ph) (**1c**). This complex was prepared by the same procedure as **1a** from **Co(BP1)(OAc)** (2 g) and 80% cumyl hydroperoxide (4.2 mL), yield = 1.65 g (60%). Anal. Calcd for $\text{C}_{29}\text{H}_{26}\text{N}_5\text{O}_4\text{Co}$: C, 61.36; H, 4.58; N, 12.35; O, 11.29. Found: C, 61.02; H, 4.7; N, 11.99; O, 11.24. $^1\text{H NMR}$ (CD_2Cl_2) δ 0.73 (s, 6 H), 1.54 (s, 3 H), 6.8–8.2 (m, 15 H), 8.86 (d, 2 H). During this preparation, 30% of the starting **Co(BP1)(OAc)** complex was recovered after filtration of the solution.

Complexes 1d–1h. They were prepared according to a similar procedure. Table V in supplementary material lists then elemental analysis and $^1\text{H NMR}$ spectra.

Co^{III}(BPB)(OO-*t*-Bu)(4-Mepy) (**11**). One and a half grams of **Co(BPB)·H₂O** was suspended in 35 mL of CH_2Cl_2 . Addition of 0.7 mL of 4-methylpyridine, followed by addition of 3 mL of 80% *t*-BuOOH and stirring for 30 min at 20 °C resulted in the formation of a green homogeneous solution. This solution was filtered, dried over Na_2SO_4 , and concentrated in vacuo. Addition of Et_2O resulted in the precipitation of a green complex **11**, yield 1.92 g (90%). Anal. Calcd for $\text{C}_{28}\text{H}_{28}\text{N}_5\text{O}_4\text{Co}$: C, 60.32; N, 12.57; O, 11.5; H, 5.03. Found: C, 59.32; N, 12.16; O, 11.8; H, 5.14. $^1\text{H NMR}$ (CD_2Cl_2) δ 0.53 (s, 9 H), 2.14 (s, 3 H), 7.7–8.8 (m, 15 H), 9.25 (d, 2 H).

Co^{III}(salen)(OO-*t*-Bu)(4-Mepy) (**11b**). This complex was prepared from the addition of excess 4-methylpyridine to a CH_2Cl_2 suspension of the **Co(salen)(OO-*t*-Bu)** complex prepared according to Nishinaga's procedure.⁶ After 30 min of stirring at 20 °C followed by drying over Na_2SO_4 , the complex **11b** was precipitated by addition of diethyl ether. Yield = 70%. Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{O}_4\text{N}_3\text{Co}$: C, 61.54; H, 5.9; N, 8.28; O, 12.6. Found: C, 59.3; H, 5.66; N, 8.6; O, 12.8. $^1\text{H NMR}$ (CD_2Cl_2) δ 0.87 (s, 9 H), 2.3 (s, 3 H), 3.5–4.3 (m, 4 H), 6.25–8.3 (m, 14 H).

Co(BP1)(OAc)₂(V). Addition of 1 mL of 40% peracetic acid to a suspension of 0.5 g of **Co(BP1)(OAc)** in 10 mL of CH_2Cl_2 at 0 °C resulted in the formation of a red solution. After 10 min of stirring at 0 °C, the solution was filtered, dried over Na_2SO_4 and concentrated, in vacuo. Complex **V** was obtained as a brown-red precipitate after addition of excess Et_2O , yield 0.5 g (88%). Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_5\text{O}_4\text{Co}$: C, 55.59; H, 3.79; N, 14.74; O, 13.47. Found: C, 55.01; H, 3.82; N, 14.84; O, 13.41. $^1\text{H NMR}$ (CD_2Cl_2) δ 1.5 (s, 6 H), 7–8.5 (m, 10 H), 9.15 (d, 2 H). The same complex was obtained by decomposition of **1a** in benzene, after filtration of **Co(BP1)OAc**, and evaporation of the solution.

Oxidation Procedure and Product Analysis. The hydrocarbons were stoichiometrically oxidized by complexes **1–11** in nitrogen in a Schlenk apparatus. In a typical procedure, the hydrocarbon solution was added in N_2 to the complex, and the mixture was heated to the required temperature. The evolution of the reaction was followed by GLC analysis of aliquot samples, after addition of an internal standard and reduction of the remaining complex by excess PPh_3 in order to prevent further oxidation or decomposition in the GLC column. Different columns were used depending on the analysis wanted. Column A (10% Carbowax 20 M on Chromosorb WHP, 3 m) and column B (10% FFAP on Chromosorb Q, 3 m) were used for the oxidation of olefins and alkanes. Column C (3% OV17 on Chromosorb WHP, 2 m) was used for the oxidation of aromatic compounds. The oxygenated products were identified by GLC–MS coupling and comparison of the mass spectra with those of authentic samples.

Catalytic oxidations were carried out in nitrogen by adding 1 mmol of alkyl hydroperoxide to the hydrocarbon solution—heated to the required temperature and containing 10^{-3} mmol of complex **1–11**. The evolution of the reaction was followed by GLC analysis as in the stoichiometric reaction and by iodometric titration at the end of the reaction.

The thermal decomposition of **1–11** was followed by standard iodometric titration³⁷ of aliquot samples taken from the benzene solution of the complex heated to the required temperature in nitrogen. The resulting organic products were analyzed by GLC and the complexes by elemental analysis, infrared spectroscopy, and NMR spectra.

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(35) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, England, 1974; Vol IV, Table 2.6.

(36) Cromer, D. T. "International Tables for X-ray Crystallography"; The Kynoch Press: Birmingham, 1974; Vol. IV, Table 2.3.1.

X-ray Experimental Section. Suitable single crystals of **1b** were obtained by slow evaporation of ethereal solutions at 5 °C. A systematic search in reciprocal space by using a Philips PW1100/16 automatic diffractometer showed that crystals of **1b** belong to the monoclinic system.

The unit cell dimension and their standard deviation were obtained and refined at room temperature with Mo $K\alpha$ radiations ($\lambda = 0.70926$ Å) by using 25 carefully selected reflections and the standard Philips software. Final results are as follows: $\text{Co}_2\text{O}_8\text{N}_{10}\text{C}_{58}\text{H}_{52}\cdot 3.5\text{H}_2\text{O}$, M_w 1198; $a = 11.649$ (4) Å; $b = 18.549$ (6) Å; $c = 14.073$ (4) Å; $\beta = 102.54$ (2) Å; $v = 2.968$ Å³; $z = 2$; $d_{\text{calcd}} = 1.34$ g cm⁻³; $d_{\text{obsd}} = 1.33 \pm 0.02$ g cm⁻³; $\mu = 6.20$ cm⁻¹; $F_{000} = 1246$; space group $P2_1/n$.

A parallelepiped crystal measuring $0.28 \times 0.28 \times 0.14$ mm was sealed in a Lindemann glass capillary and mounted on a rotation-free goniometer head. All quantitative data were obtained from a Philips PW 1100/16 four-circle automatic diffractometer, controlled by a P852 computer, using graphite monochromated radiation and standard software. The horizontal and vertical apertures in front of the scintillation counter were adjusted so as to minimize the background counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step-scan used was $\Delta\theta = 0.9 + (\text{Mo } K\alpha_1, \alpha_2 \text{ splitting})$ with a step width of 0.04° and a scan speed of $0.024^\circ \text{ s}^{-1}$. Reflections (7640) were recorded ($4^\circ < \theta < 28^\circ$). The resulting data set was transferred to a PDP 11/60 computer, and for all subsequent computations the Enraf-Nonius SDP/V18 package was used,³² with the exception of a local data-reduction program. Three standard reflections measured every hour during the entire data collection period had a mean loss of 9% in intensity, which was corrected using a time-dependent linear interpolation function.

The raw step-scan data were converted to intensities using the Lehmann-Larsen method,³³ and then corrected for Lorentz polarization and absorption factors, with the latter being computed by the numerical integration method of Busing and Levy³⁴ transmissions factors between 0.67 and 0.91). A single data set of 2403 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved by using the heavy-atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for carbon hydrogen atoms. They were introduced into structure factor calculations by their computed coordinates ($\text{C-H} = 0.95$ Å) and isotropic temperature factors of $B_{\text{eqv}}(c) + 1$ Å² but not refined. Water hydrogen atoms could not be located. Full least-squares refinement converged to $R(F) = 0.078$ and $R_w(F) = 0.101$ ($\sigma(F^2) = (\sigma^2 \text{ counts} + (pF)^2)^{1/2}$). The unit weight observation was 1.93 for $p = 0.08$. A final difference map revealed no significant maxima. The scattering factors coefficients and anomalous dispersion coefficients come, respectively, from ref 35 and 36.

Registry No. **1a**, 96095-25-9; **1b**, 96109-48-7; **1c**, 96095-26-0; **1d**, 96095-27-1; **1e**, 96095-28-2; **1f**, 96095-29-3; **1g**, 96095-30-6; **1h**, 96095-31-7; **1i**, 96095-32-8; **11a**, 88231-26-9; **11b**, 96095-33-9; **V**, 96095-38-4; **Co^{II}(BP1)(OCOCH₃)**, 53575-79-4; **Co^{II}(BP1)(OCOC₆H₅)**, 96095-34-0; **Co^{II}(MeBP1)(OCOCH₃)**, 78065-26-6; **Co^{II}(MeBP1)(OCOC₆H₅)**, 96095-35-1; **Co^{II}(MeBP1)(OCOC(CH₃)₂)**, 96095-36-2; **Co^{II}(BPB)**, 96095-37-3; **Co(Oct)**, 136-52-7; **PhCH(CH₃)OOC(CH₃)₂**, 28047-94-1; **PhC(CH₃)₂OOH**, 80-15-9; **PhCHO**, 100-52-7; ***t*-BuOOH**, 75-91-2; **PhCOCH₃**, 98-86-2; **PhCH(OH)CH₃**, 98-85-1; **PhCH₂OH**, 100-51-6; **4-methylpyridine**, 108-89-4; **peracetic acid**, 79-21-0; **cyclohexane**, 110-82-7; **adamantane**, 281-23-2; ***cis*-decalin**, 493-01-6; **octane**, 111-65-9; **cyclohexene**, 110-83-8; **norbornene**, 498-66-8; **styrene**, 100-42-5; **ethylbenzene**, 100-41-4; **toluene**, 108-88-3; **2-adamantanol**, 700-57-2; **cyclohexanol**, 108-93-0; **cyclohexanone**, 108-94-1; **chlorocyclohexane**, 542-18-7; **octan-1-ol**, 111-87-5; **octan-2-ol**, 123-96-6; **octan-3-ol**, 589-98-0; **octan-4-ol**, 589-62-8; **octan-2-one**, 111-13-7; **octan-3-one**, 106-68-3; **octan-4-one**, 589-63-9; **2-cyclohexen-1-ol**, 822-67-3; **cyclohexene epoxide**, 286-20-4; **norbornene epoxide**, 228-74-0; **styrene epoxide**, 96-09-3; **adamantan-1-ol**, 768-95-6; **adamantan-2-one**, 700-58-3; ***cis*-decalin-9-ol**, 3574-58-1; ***trans*-decalin-9-ol**, 1654-87-1; **decalin-1-one**, 4832-16-0; **decalin-2-one**, 4832-17-1; ***tert*-butyl cyclohexyl peroxide**, 15619-54-2; **2-cyclohexenone**, 930-68-7; **3-*tert*-butylperoxycyclohexene**, 51437-25-3.

Supplementary Material Available: Elemental analysis and NMR spectra of complexes **1d–1h** (Table V), complex **1b**, distances and angles (Table Vb), positional parameters for hydrogen atoms (Table VI), thermal parameters for anisotropic atoms (u_{ij}) (Table VII), listings of structure factor amplitudes (F_o and $F_o \times 10$) (Table VIII) (17 pages). Ordering information is given on any current masthead page.

(37) An accurately measured sample of the peroxidic solution (ca. 0.1 mmol) was dissolved in a mixture of 5 mL of AcOH and 5 mL of a saturated aqueous KI solution. The mixture was heated at 80 °C in N_2 for 15 min, poured in 25 mL of H_2O , titrated with 0.1 N sodium thiosulfate in the presence of a few drops of a starch indicator solution.