Syntheses, Structures, and Reactivities of Cobalt(III)−Alkylperoxo Complexes and Their Role in Stoichiometric and Catalytic Oxidation of Hydrocarbons

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Abstract: Although Co(III)−alkyl peroxo species have often been implicated as intermediates in industrial oxidation of hydrocarbons with cobalt catalysts, examples of discrete [LCo^{III}−OOR] complexes and studies on their oxidizing capacities have been scarce. In this work, twelve such complexes with two different ligands, L, and various primary, secondary, and tertiary R groups have been synthesized, and seven of them have been characterized by X-ray crystallography. The dianion (L^{2-}) of the two ligands *N*,*N*-bis[2-(2-pyridyl)ethyl]pyridine-2,6-dicarboxamide (Py$_3$PH$_2$, **1**) and *N*,*N*-bis[2-(1-pyrazolyl)ethyl]pyridine-2,6-dicarboxamide (PyPz$_2$PH$_2$, **2**) bind Co(III) centers in pentadentate fashion with two deprotonated carboxamido nitrogens in addition to three pyridine or one pyridine and two pyrazole nitrogens to afford complexes of the type [LCo^{III}(H$_2$O)] and [LCo^{III}(OH)]. Reactions of the [LCo^{III}(OH)] complexes with ROOH in aprotic solvents of low polarity readily afford the [LCo^{III}−OOR] complexes in high yields. This report includes syntheses of [Co(Py$_3$P)(OOR)] complexes with R = ^{t}Bu (**7**, ^{t}Bu = CMe$_3$), Cm (**8**, Cm = CMe$_2$Ph), CMe$_2$CH$_2$Ph (**9**), Cy (**10**, Cy = *c*-C$_6$H$_{11}$), ^{i}Pr (**11**, ^{i}Pr = CHMe$_2$) or ^{n}Pr (**12**, ^{n}Pr = CH$_2$CH$_2$CH$_3$), and [Co(PyPz$_2$P)(OOR)] complexes with R = ^{t}Bu (**13**), Cm (**14**), CMe$_2$CH$_2$Ph (**15**), Cy (**16**), ^{i}Pr (**17**) or ^{n}Pr (**18**). The structures of **8**−**12** and **16** have been established by X-ray crystallography. Complexes **10** and **16** are the first examples of structurally characterized compounds containing the [Co−OOCy] unit, proposed as a key intermediate in cobalt-catalyzed oxidation of cyclohexane. The metric parameters of **7**−**12** and **16** have been compared with those of other reported [LCo^{III}−OOR] complexes. When these [LCo^{III}−OOR] complexes are warmed (60−80 °C) in dichloromethane in the presence of cyclohexane (CyH), cyclohexanol (CyOH) and cyclohexanone (CyO) are obtained in good yields. Studies on such reactions (referred to as stoichiometric oxidations) indicate that homolysis of the O−O bond in the [LCo^{III}−OOR] complexes generates RO$^\bullet$ radicals in the reaction mixtures which are the actual agents for alkane oxidation. [LCo−O$^\bullet$], the other product of homolysis, does not promote any oxidation. A mechanism for alkane oxidation by [LCo^{III}−OOR] complexes has been proposed on the basis of the kinetic isotope effect (KIE) value (5 at 80 °C), the requirement of dioxygen for oxidation, the dependence of yields on the stability of the RO$^\bullet$ radicals, and the distribution of products with different substrates. Both L and R modulate the capacity for alkane oxidation of the [LCo^{III}−OOR] complexes. The extent of oxidation is noticeably higher in solvents of low polarity, while the presence of water invariably lowers the yields of the oxidized products. Since [LCo^{III}−OOR] complexes are converted into the [LCo^{III}(OH)] complexes at the end of single turnover in stoichiometric oxidation reactions, it is possible to convert these systems into catalytic ones by the addition of excess ROOH to the reaction mixtures. The catalytic oxidation reactions proceed at respectable speed at moderate temperatures and involve [LCo^{III}−OOR] species as a key intermediate. Turnover numbers over 100 and ~10% conversion of CyH to CyOH and CyO within 4 h have been noted in most catalytic oxidations. The same catalyst can be used for the oxidation of many substrates. The results of the present work indicate that [LCo^{III}−OOR] complexes can promote oxidation of hydrocarbons under mild conditions and are viable intermediates in the catalytic oxidation of hydrocarbons with ROOH in the presence of cobalt catalysts.

Introduction

Recently there has been much interest in catalytic oxidation of inexpensive hydrocarbon substrates by transition metal salts (or complexes) to commercially important products related to pharmaceuticals, flavors, fragrances, plasticizers, and polymers.[1] The development of catalysts which carry out the oxidation processes under mild conditions and with inexpensive and environmentally benign oxidants (i.e., O$_2$, H$_2$O$_2$, ^{t}BuOOH, or PhCMe$_2$OOH) is an important goal in such pursuits. Currently, Co(II), Mn(II), and Cu(II) salts are employed for these oxidation processes, and products are removed continusouly at low conversions.[1a,d,f] Other transition metal salts are added to the reaction mixtures to control product distribution. Although it is commonly accepted that the metals have a direct role in the generation of radical species responsible for initiating the oxidation reactions and in the decomposition of the alkyl hydroperoxides formed in the oxidation processes, complete mechanistic understanding in most cases is missing. Such

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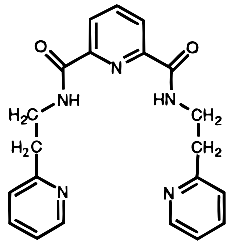
information is crucial from a fundamental standpoint and also for the improvement of the existing as well as future catalytic systems.

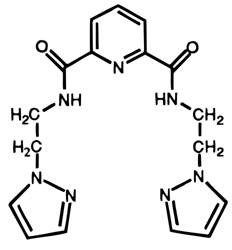
Catalytic oxidation is the preferred method for hydrocarbon oxidation since traditional stoichiometric oxidants such as permanganate and dichromate generate large amounts of toxic inorganic effluents which are difficult to dispose of.[2] Examples of industrial processes that utilize catalytic oxidation of hydrocarbons in large quantities include the Mid-Century/Amoco process where *p*-xylene is oxidized to terephthalic acid, an important precursor in the production of polyester fibers, films, and plasticizers. Another example is the Du Pont adipic acid synthesis in which cyclohexane is first oxidzed to cyclohexanol and cyclohexanone. The "ol and one" mixture is then oxidized to adipic acid[3] which is the precursor for the synthesis of nylon 6,6 and other polymers. Both of these methods employ cobalt catalysts and are performed at high pressures and temperatures. Kinetic data indicate that ROOH (R = alkyl), formed in the initial stages of these processes, reacts with the cobalt catalysts to form Co(III) alkyl hydroperoxide intermediates.[1a,d,4] The oxidation of Co(II) to Co(III) is easily observed by a change in color from pale violet or pink to dark green due to the formation of Co(III)−OOR species. Coordination of alkyl hydroperoxide to cobalt weakens the O−O bond and assists in O−O bond scission to form $RO^\bullet$ radicals under the reaction conditions. Since the oxidation of the hydrocarbons is carried out by the radicals, the industrial processes utilize different solvents and other factors (ligands) in the reaction mixtures to modulate the stability of the $[LCo^{III}-OOR]$ intermediates, the overall yields, and the product distribution.[1d,5]

To date, a handful of discrete Co(III)−alkylperoxo complexes of the formula $[LCo^{III}-OOR]$ bearing certain ligands L have been isolated and characterized.[6−15] The structures of a few these complexes have been determined by X-ray crystallography. Synthetic methods which have been employed in the syntheses of such $[LCo^{III}-OOR]$ complexes include (1) addition of excess ROOH to the $[LCo^{II}]$ precursor,[6,12,15] (2) dioxygen insertion into metal−alkyl bonds,[10,11,14] and (3) dioxygen insertion into metal ligand bonds under irradiation.[7−9,13] Only a few of these Co(III)−alkylperoxo complexes have been used to oxidize hydrocarbons[6,12,15] and the results of at least one study have indicated that the rates of decomposition of the $[LCo^{III}-OOR]$ complexes and the extent of alkane oxidation depend on L. It thus appears that a systematic study with structurally characterized $[LCo^{III}-OOR]$ complexes with different L and R will be very useful in determining how such variations affect the stability of the $[LCo^{III}-OOR]$ species and their capacities of hydrocarbon oxidation under specific conditions.

In our attempt to address these issues, we have employed two ligands, Py_3PH_2 (**1**, Py_3PH_2 = *N*,*N*-bis[2-(2-pyridyl)ethyl]pyridine-2,6-dicarboxamide) and $PyPz_2PH_2$ (**2**, $PyPz_2PH_2$ = *N*,*N*-bis[2-(1-pyrazolyl)ethyl]pyridine-2,6-dicarboxamide, H's denote dissociable amido H's in both cases) in synthesizing several Co(III) complexes of the type $[LCo^{III}-OOR]$. These alkylperoxo complexes are conveniently synthesized from $[LCo^{III}(OH)]$ precursors which in turn are obtained from $[LCo^{III}(H_2O)]^+$ complexes upon addition of 1 equiv of a base. In earlier reports, we have described the syntheses and characterization of $[Co(Py_3P)(H_2O)]ClO_4$ (**3**),[15] $[Co(Py_3P)(OH)]$ (**4**),[15] $[Co(PyPz_2P)(H_2O)][(H_3O)(PF_6)_2]^-$ (**5**),[16] and $[Co(PyPz_2P)(OH)]$ (**6**).[16] In **3** and **4**, Py_3P^{2-} (deprotonated **1**) binds cobalt in a pentadentate fashion with three pyridine nitrogens and two deprotonated amido nitrogens serving as the donors, while in **5** and **6**, $PyPz_2P^{2-}$ (deprotonated **2**) employs one pyridine nitrogen, two 2-pyrazole nitrogens, and two deprotonated amido nitrogens to bind cobalt in a similar manner. The sixth site on the Co(III) centers of these complexes is occupied by either a water molecule or a hydroxide ligand.



Py_3PH_2 (**1**)



$PyPz_2PH_2$ (**2**)

The utility of the alkylperoxo adduct of such Co(III) complexes in promoting alkane oxidation under mild conditions has already been demonstrated by us in our preliminary work with the complex $[Co(Py_3P)(OO^tBu)]$ (**7**, $^tBu = CMe_3$).[15] This structurally characterized complex of the type $[LCo^{III}-OOR]$ initiates heat-induced (70 °C) stoichiometric oxidation of cyclohexane (CyH) in dichloromethane to form cyclohexanol and cyclohexanone. In this paper, we describe the synthesis and reactivity of a series of Co(III)−alkylperoxo complexes of the type $[LCo^{III}-OOR]$. The complexes are $[Co(Py_3P)(OOR)]$ with R = Cm, (**8**, Cm = CMe_2Ph), CMe_2CH_2Ph (**9**), Cy (**10**, Cy = c-C_6H_{11}), ^iPr (**11**, $^iPr = CHMe_2$) or ^nPr (**12**, $^nPr = CH_2CH_2CH_3$), and $[Co(PyPz_2P)(OOR)]$ with R = ^tBu (**13**), Cm (**14**), CMe_2CH_2Ph (**15**), Cy (**16**), ^iPr (**17**), or ^nPr (**18**). The structures of **8**−**12** and **16** have been established by X-ray crystallography. It must be emphasized here that complexes **10** and **16** are the first examples of structurally characterized compounds contain-

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ing the [Co−OOCy] unit, proposed as a key intermediate in the cobalt-catalyzed oxidation of cyclohexane.[1a,d,g,17] The metric parameters of **7**−**12** and **16** have been compared with those of other reported $[LCo^{III}-OOR]$ complexes. The extent of *stoichiometric* oxidation of CyH by **7**−**18** under selected conditions has been determined, and the mechananism of hydrocarbon oxidation has been discussed in detail. Variations in the oxidizing capacities of the $[LCo^{III}-OOR]$ complexes with different L and R have been investigated; the effects of solvents on the yields and the distribution of the oxidation products have been explored with selected $[LCo^{III}-OOR]$ complexes; and finally, the results of *catalytic* oxidation of CyH by the $[LCo^{III}-OOR]$ complexes in the presence of excess alkyl hydroperoxide are presented.

Experimental Section

Materials. Synthetic protocols for the ligands **1**[18] and **2**[19] and the two precursors **4**[15] and **6**[16] have been reported by us previously. Tetramethylammonium hydroxide pentahydrate, *tert*-butyl hydroperoxide (TBHP) 70%, cumene hydroperoxide 80%, hydrogen peroxide 50%, silver trifluoroacetate, cyclohexyl iodide, 2-propyl iodide, 1-propyl iodide, 2-methyl-1-phenyl-2-propanol, lithium bromide, HBr 48%, and anhydrous ethylene glycol were procured from Aldrich Chemical Co. The *tert*-butyl hydroperoxide, cumene hydroperoxide, and hydrogen peroxide were further dried over anhydrous $MgSO_4$. All other reagents were used without further purification. All solvents were dried and distilled before use.

Synthesis. Safety Notes. *Caution!* Although no problems were encountered handling the alkyl hydroperoxides employed in this study, alkyl hydroperoxides are potentially explosive and should be handled in small amounts with great care.

Preparation of Compounds. Syntheses of Alkyl Hydroperoxides (ROOH). Cyclohexyl hydroperoxide (CyOOH), 2-propyl hydroperoxide (^{i}PrOOH), 1-propyl hydroperoxide (^{n}PrOOH), and 2-methyl-1-phenyl-2-propyl hydroperoxide ($PhCH_2CMe_2OOH$) were synthesized from cyclohexyl iodide, 2-propyl iodide, 1-propyl iodide, and 2-methyl-1-phenyl-2-propyl bromide,[20] respectively, by following the method of Cookson and Davies.[21] The general procedure is as follows. A batch of 11.32 mmol of alkyl halide was mixed with 22.64 mmol of dry H_2O_2[22] in 40 mL of anhydrous dichloromethane at 0 °C. The addition of 11.32 mmol of silver trifluoroacetate to this mixture resulted in the precipitation of the corresponding silver halide. The mixture was stirred at 0 °C for 2 h, and then it was filtered. The filtrate was washed three times with 40 mL of 7.5% (w/v) aqueous sodium bicarbonate. For CyOOH, ^{i}PrOOH, and ^{n}PrOOH, the dichloromethane layer was collected and evaporated to 5 mL. The solution of the alkyl hydroperoxide in dichloromethane thus obtained was then used in the synthesis of the [LCoOOR] complex (vide infra) without further purification. In the case of $PhCH_2CMe_2OOH$, the solution of the alkyl hydroperoxide in dichloromethane was evaporated, and the crude product was purified by chromatography on silica column using 5% ethyl acetate/hexanes as the eluant. The final product in this case was a white crystalline solid. The concentrations of the other hydroperoxides in solution were determined by the method of Banerjee and Budke.[23] Typical percent yields for the alkyl hydroperoxides were as follows: CyOOH (23%), ^{i}PrOOH (25%), ^{n}PrOOH (28%), and $PhCH_2CMe_2OOH$ (80%).

General Procedure for the Synthesis of $[LCo^{III}-OOR]$ Complexes. A batch of 0.5 mmol of either $[Co(Py_3P)(OH)]$ or $[Co(PyPz_2P)(OH)]$ was dissolved in 10 mL of dichloromethane under ambient conditions and to this was added approximately 2−5 mmol of ROOH. The mixture was stirred at room temperature in the dark in a stoppered 50-mL round-bottom flask. After 2 h of stirring, 15 mL of diethyl ether was added, and the solution was filtered. The filtrate was then stored at 4 °C. Crystals of the $[LCo^{III}-OOR]$ complex appeared within 48 h. The crystals were collected and washed with anhydrous diethyl ether. A typical percent yield was 85% based on $[LCo^{III}(OH)]$. All the $[LCo^{III}-OOR]$ complexes gave satisfactory elemental analyses. The complexes for which crystal structures are presently missing were identified by their NMR spectra. These clean NMR spectra (vide infra) exhibited only the expected resonances, and the proper intensities were recorded for all the peaks.

Selected spectroscopic data for the $[LCo^{III}-OOR]$ complexes are listed below. The complete list has been submitted as part of the Supporting Information.

Spectroscopic Data: ν_{CO} (KBr, cm^{-1}); electronic absorption spectrum, λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$) in dichloromethane. $[Co(Py_3P)(OOCm)]$ (**8**): 1600; 640 (sh, 141), 250 (21 000). $[Co(Py_3P)(OOC(CH_3)_2CH_2Ph)]$ (**9**): 1598; 630 (175), 315 (sh, 10 000), 270 (sh, 16 700), 248 (21 000). $[Co(Py_3P)(OOCy)]$ (**10**): 1594; 625 (sh, 76), 335 (sh, 7000), 270 (sh, 12 000), 248 (sh, 16 500). $[Co(Py_3P)(OO^{i}Pr)]$ (**11**): 1599; 635 (sh, 86), 340 (sh, 8600), 300 (sh, 9600), 270 (sh, 13 000), 245 (sh, 15 400). $[Co(Py_3P)(OO^{n}Pr)]$ (**12**): 1603; 630 (sh, 90), 540 (sh, 244), 318 (5800), 250 (sh, 18 700). $[Co(PyPz_2P)(OO^{t}Bu)]$ (**13**): 1594; 635 (165), 305 (sh, 5800), 250 (sh, 10 600). $[Co(PyPz_2P)(OOCm)]$ (**14**): 1597; 630 (sh, 149), 320 (sh, 7000), 280 (sh, 10 600), 250 (sh, 16 500). $[Co(PyPz_2P)(OOCMe_2CH_2Ph)]$ (**15**): 1602; 625 (204), 545 (sh, 216), 320 (14 000), 250 (sh, 28 000). $[Co(PyPz_2P)(OOCy)]$ (**16**): 1601; 600 (sh, 85), 325 (5500), 250 (sh, 7900). $[Co(PyPz_2P)(OO^{i}Pr)]$ (**17**): 1602; 610 (sh, 109), 535 (sh, 180), 325 (5700), 250 (sh, 10 160), 225 (26 000). $[Co(PyPz_2P)(OO^{n}Pr)]$ (**18**): 1602; 600 (sh, 86), 330 (sh, 4900), 250 (sh, 9500).

Physical Measurements. Infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrophotometer. Absorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer. ^{1}H NMR spectra were monitored on a Varian 500 MHz Unity Plus instrument interfaced with a Sun OS 4.1.3 computer. Standard organic product analyses were performed on a Hewlett-Packard 5890 series II plus gas chromatograph equipped with a flame-ionization detector (FID) and heliflex AT-1701 (30 m × 0.25 mm o.d.; film thickness, 0.25 μ) capillary column (Alltech).

Oxidation of Hydrocarbon Substrates. Stoichiometric oxidation proceeded as follows: In a typical reaction, ∼5 mg (8 μmol) of the $[LCo^{III}-OOR]$ complex was dissolved in 1 mL of 1:1 CH_2Cl_2/CyH in a 2-dram screwcap vial with a Teflon seal, and the mixture was kept in a constant-temperature bath for a certain number of hours. Following a rapid cooling period, the mixture was filtered through a 0.45-μm Acrodisc nylon filter, and the products were analyzed by gas chromatography. Toluene or cyclooctane (internal standard) and excess triphenyl phosphine were added to the products before GC analyses. Products were identified and quantitated by comparison with authentic samples.

Catalytic oxidation proceeded as follows: The mixtures of $[LCo^{III}-OOR]$ complexes, ROOH, and cyclohexane were placed in thick-walled screwcap glass bottles (volume: 115 mL) stoppered with Teflon seals and kept in a constant-temperature bath for a certain number of hours. After rapid cooling, the mixtures were filtered through 0.25-μm Acrodisc nylon filters, and triphenylphosphine was added to the filtrates to decompose unreacted peroxides. The oxidation products were then analyzed as above.

X-ray Data Collection and Structure Solution and Refinement. Brown plates of **8** were obtained by slow cooling of a dichloromethane/diethyl ether solution of **8** at 4 °C. There are no solvent molecules in the unit cell, and the O3−O4 bond is well ordered. Light brown-red dichroic needles of $[Co(Py_3P)(OOCMe_2CH_2Ph)]\cdot 0.6CH_2Cl_2$, $\mathbf{9}\cdot 0.6CH_2Cl_2$, were obtained by slow cooling of a dichloromethane/diethyl ether solution of **9**. In the crystal lattice, the dichloromethane molecule is disordered. Two dichloromethanes occupying the same site were

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Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for [Co(Py$_3$P)(OOCMe$_2$Ph)] (**8**), for [Co(Py$_3$P)(OOCy)]·0.5Et$_2$O·0.2CH$_2$Cl$_2$ (**10**·0.5Et$_2$O·0.2CH$_2$Cl$_2$), Co(Py$_3$P)(OO^{i}Pr)]·H$_2$O(**11**·H$_2$O), and [Co(PyPz$_2$P)(OOCy)]·2CHCl$_3$ (**16**·2CHCl$_3$)

	complex **8**	complex **10**	complex **11**	complex **16**
formula	$C_{30}H_{30}N_5O_4Co$	$C_{29.2}H_{37.4}N_5O_{5.5}Cl_{0.4}Co$	$C_{24}H_{28}N_5O_5Co$	$C_{25}H_{30}N_7O_4Cl_6Co$
(mol wt)	(583.52)	(619.55)	(525.44)	(764.21)
cryst color, habit	brown plate	red-brown plate	red-brown needle	red block
T, K	130 (2)	130 (2)	130 (2)	169 (2)
cryst system	orthorhombic	triclinic	triclinic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	9.714 (2)	10.6894 (13)	9.5636 (9)	8.902 (3)
b, Å	15.593 (3)	12.1421 (13)	11.6891 (10)	10.133 (2)
c, Å	17.391 (3)	13.2428 (9)	12.1806 (13)	19.135 (4)
α, deg	90	65.004 (8)	90.502 (8)	99.42 (2)
β, deg	90	66.415 (8)	110.190 (7)	102.57 (2)
γ, deg	90	69.388 (9)	107.581 (7)	99.38 (2)
V, Å^3	2634.3 (9)	1392.6 (2)	1208.5 (2)	1626.2 (8)
Z	4	2	2	2
d_{calcd}, g cm^{-1}	1.471	1.478	1.444	1.557
abs coeff, μ, mm^{-1}	5.496	5.60	5.951	1.063
GOF^a on F^2	1.033	1.052	1.045	1.110
R1,^{b} %	4.70	6.48	6.94	5.69
wR2,^{c} %	9.15	16.74	15.00	13.67

^{a} GOF $= [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ (M = no. of reflections, N = no. of parameters refined). ^{b} R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{c} wR2 $= [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

located. These were refined with site occupancy of 0.37 and 0.23 for sets "A" and "B" of the atoms Cl(1), Cl(2), C(32), and hydrogen atoms at calculated postitions. Thermal parameters for these atoms were kept isotropic. All other non-hydrogen atoms were refined with anisotropic thermal parameters. Red-brown plates of [Co(Py$_3$P)(OOCy)]·H$_2$O·0.5Et$_2$O·0.2CH$_2$Cl$_2$, **10**·H$_2$O·0.5Et$_2$O·0.2CH$_2$Cl$_2$, were obtained when a solution of **10** in a mixture of dichloromethane and regular (not anhydrous) diethyl ether was stored at 4 °C for 48 h. The diethyl ether solvent of crystallization could not be completely resolved partly because it shares a site with a dichloromethane and partly because of a center of symmetry. The overall shape, however, indicates that it is a diethyl ether molecule. The molecule of water in the structure is hydrogen bonded to the complex. It is well-behaved, and the hydrogen atoms show up on a difference map. The other region which is a mix of 0.2 dichloromethane and 0.5 diethyl ether is best described as disordered. The two chlorine atoms have the right separation for a molecule of CH$_2$Cl$_2$; however, the carbon atom cannot be observed. Red-brown needles of [Co(Py$_3$P)(OO^{i}Pr)]·H$_2$O, **11**·H$_2$O, were obtained by slow cooling of a dichloromethane/diethyl ether solution of **11** which also contained some water. Red plates of [Co(Py$_3$P)(OO^{n}Pr)]·1.5CH$_2$Cl$_2$·0.5H$_2$O, **12**·1.5CH$_2$Cl$_2$·0.5H$_2$O, moderately suitable for X-ray analysis, were obtained by slow cooling of a solution of **12** in dichloromethane/diethyl ether/water. Although the structure was refined to R = 13%, reliable metric parameters were obtained for this complex. In the asymmetric unit, there are two molecules of the complex, three molecules of dichloromethane, and one water molecule. The two complexes differ mainly in the orientation of the peroxyl groups. One of the three molecules of dichloromethane is badly disordered and could not be modeled except as an ad hoc mixture of chlorine atoms. The U values of these atoms were refined after their location on a final difference map. Occupancies were as follows: Cl (5A), 0.40; Cl (5B), 0.40; Cl (5C), 0.40; Cl (5D), 0.25; Cl (5E), 0.25; Cl (5F), 0.15; Cl (5G), 0.15. Red blocks of [Co(PyPz$_2$P)(OOCy)]·2CHCl$_3$, **16**·2CHCl$_3$, were obtained by slow cooling of a chloroform/diethyl ether solution of **16**. There are two chloroform molecules in the unit cell, one being slightly disordered. The chloroform molecules are hydrogen bonded to a carbonyl oxygen and to the oxygen of the coordinated peroxo group that is directly bonded to the Co(III) center (H25···O1 = 1.97 Å and H26A···O4 = 2.32 Å).

For **8**−**12**, diffraction data were collected at 130 (2) K on a Siemens P4 diffractometer equipped with a Siemens rotating anode, a nickel filter, and Enraf Nonius low-temperature apparatus. Data for **16** were collected at 169 (2) K on a Siemens R3m/V diffractometer equipped with a normal-focus sealed tube and Enraf nonius low-temperature appartatus. Cu Kα radiation (λ = 1.541 78 Å) radiation was used for **8**−**12** while Mo Kα radiation (λ = 0.710 73 Å) was employed for **16**. Only random fluctuations of <1% in the intensities of two standard reflections were observed during data collection for all of the complexes. The structures were solved by direct methods (SHEXTL 5, XS, Sheldrick, 1994). All calculations were carried out on a 486/DX50 computer using SHELXTL Version 5.03 program.[24] The data were corrected for absorption effects by the use of the program XABS2.[25] Hydrogen atoms bonded to carbon were added geometrically and refined with the use of a riding model.

Machine parameters, crystal data, and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The rest of the crystallographic data has been submitted as Supporting Information.

Results and Discussion

In our earlier synthetic work,[15] we synthesized [Co(Py$_3$P)(OO^t-Bu)] (**7**) by reacting isolated [Co^{II}(Py$_3$P)] with excess ^{t}BuOOH in dichloromethane under dry dinitrogen at room temperature. Soon we discovered that this method also works for the synthesis of [Co(Py$_3$P)(OOCm)] (**8**) when ^{t}BuOOH is replaced by CmOOH. Addition of diethyl ether to the reaction mixture and cooling at 4 °C affords crystalline **8** within 48 h. Although this procedure affords **7**, **8**, and other [LCo^{III}−OOR] complexes,[6,12] it soon became clear to us that it is a suitable procedure for synthesizing [Co(Py$_3$P)(OOR)] complexes with tertiary R groups only. For secondary or primary R groups, this method is not as useful since secondary and primary alkyl hydroperoxides are less stable and decompose during the synthetic procedures. In addition, this method was found to be unsuitable for the syntheses of [Co(PyPz$_2$P)(OOR)] complexes even when tertiary R groups were employed; the desired products were not obtained in most cases.[26] Quite in contrast, all of the [Co(Py$_3$P)(OOR)] and [Co(PyPz$_2$P)(OOR)] complexes with tertiary, secondary or primary R groups can be conveniently

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(24) Sheldrick, G. SHELXTL, Version 5.03; Siemens Industrial Automation, Inc.: Madison, WI, 1994. Tables of neutral atom scattering factors, f' and f'', and absorption coefficients were taken from: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

(25) Parkins, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallogr.* **1995**, *28*, 53.

(26) In the best case, reaction of [Co^{II}(PyPz$_2$P)] with TBHP affords a crystalline solid, the NMR spectrum of which indicates that the product contains ~70% **13** along with other hitherto unknown Co(III) complex(es).

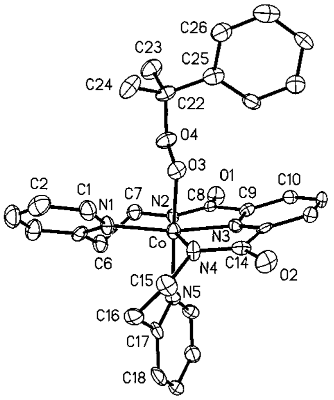

Figure 1. Thermal ellipsoid (probability level 50%) plot of [Co(Py_3P)-(OOCm)] (**8**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

$$[\mathrm{LCo^{III}(OH)}] + \mathrm{ROOH} \rightarrow [\mathrm{LCo^{III}{-}OOR}] + \mathrm{H_2O} \qquad \text{(I)}$$

synthesized by reacting the [$\mathrm{LCo^{III}(OH)}$] complexes with excess ROOH. This method of synthesis has several advantages over other methods previously used to synthesize [$\mathrm{LCo^{III}{-}OOR}$] complexes.[6−15] They are as follows: There is no change in the oxidation state of the cobalt in reaction I and hence, the transformation can be followed by ^{1}H NMR spectroscopy. The reaction involves exchange of OH^- with ROO^-, and the only byproduct is water. Thus, there is no need to purify the final product by column chromatography or other means, and crystalline materials are obtained readily. The synthesis is also a very general one, and any ROOH can be used. Also, one does not require rigorously pure ROOH for reaction I to work; solutions of partially purified ROOH in dichloromethane afford analytically pure [$\mathrm{LCo^{III}{-}OOR}$] complexes.

In the solid phase, the [$\mathrm{LCo^{III}{-}OOR}$] complexes **7**−**18** are stable for months when kept in a desiccator at room temperature. They can be recrystallized from a variety of halogenated solvents, diethyl ether, or pentane. Dissolution of the [$\mathrm{LCo^{III}{-}OOR}$] complexes in hydrocarbon substrates such as cyclohexane can be achieved by the addition of dichloromethane, acetonitrile, or excess ROOH.

Structure of [Co(Py_3P)(OOCm)] (8) and [Co(Py_3P)-($OOCMe_2CH_2Ph$)]·0.6CH_2Cl_2 (9·0.6CH_2Cl_2). Structural parameters of these two [Co(Py_3P)(OOR)] complexes containing a tertiary alkylperoxo group as R are listed in Table 2. In complexes **8** (Figure 1) and **9** (Figure S1, Supporting Information), the cobalt(III) center resides in a slightly distorted octahedral environment. In both complexes, the Py_3P^{2-} ligand is bound to the Co(III) center in a pentadentate square pyramidal fashion with three pyridine nitrogens and two deprotonated amido nitrogens as donors. This mode of coordination is similar to that of other structurally characterized metal complexes of this ligand[15,19] (also see below). The structure of **8** is well-ordered and devoid of any solvent molecule(s) of crystallization in the unit cell. The structure of **9**, however, has 0.6 molecules of CH_2Cl_2 in the unit cell. Complex **9** is the first example of a metal complex with a ligated $PhCH_2CMe_2OO^-$ group of the mechanistic probe $PhCH_2CMe_2OOH$ (MPPH)[27] as R (vide infra), that has been characterized by X-ray crystallography. The nearly identical Co−O3 bond distances of **8** and **9**,1.883(4) Å

Table 2. Selected Bond Distances (Å) and Angles (deg)

[Co(Py_3P)(OOCm)] (**8**)

Bond Distances

Co−N1	1.966(5)	N4−C14	1.346(8)
Co−N2	1.917(5)	N4−C15	1.459(8)
Co−N3	1.859(5)	N5−C17	1.364(8)
Co−N4	1.947(5)	O1−C8	1.250(7)
Co−N5	2.010(5)	O3−O4	1.485(5)
Co−O3	1.883(4)	O2−C14	1.242(7)
N1−C5	1.353(8)	O4−C22	1.443(7)
N2−C8	1.337(8)	C22−C23	1.549(9)
N3−C9	1.329(7)	C22−C24	1.517(9)

Bond Angles

N1−Co−N2	93.1(2)	N1−Co−O3	86.3(2)
N1−Co−N3	170.0(2)	Co−N2−C7	124.5(4)
N1−Co−N4	103. 1(2)	Co−N3−C9	117.1(4)
N1−Co−N5	95.4(2)	Co−N4−C14	115.1(4)
N2−Co−N3	82.2(2)	Co−O3−O4	109.2(3)
N2−Co−N4	163.7(2)	N2−C8−O1	128.1(6)
N2−Co−N5	92.6(2)	N4−C14−C13	111.7(6)
N3−Co−N4	82. 1(2)	O3−O4−C22	107.1(4)
N3−Co−N5	93.6(2)	O1−C8−C9	121.6(6)

[Co(Py_3P)(OOCy)]·H_2O·0.5Et_2O·0.2CH_2Cl_2
(**10**·H_2O·0.5Et_2O·0.2CH_2Cl_2)

Bond Distances

Co−N1	1.990(4)	Co−O3	1.891(3)
Co−N2	1.937(4)	O1−C8	1.254(6)
Co−N3	1.857(4)	O3−O4	1.460(4)
Co−N4	1.966(4)	O2−C14	1.259(6)
Co−N5	2.029(4)	O4−C22	1.425(6)

Bond Angles

N1−Co−N2	93.2(2)	N2−Co−N5	94.1(2)
N1−Co−N3	168.8(2)	N3−Co−N4	81. 7(2)
N1−Co−N4	103.8(2)	N3−Co−N5	95.4(2)
N1−Co−N5	94.9(2)	N4−Co−N5	83.6(2)
N2−Co−N3	81.7(2)	Co−O3−O4	113.6(2)
N2−Co−N4	162.9(2)	O3−O4−C22	108.5(3)

[Co(Py_3P)(OO^iPr)]·H_2O (**11**·H_2O)

Bond Distances

Co−N1	1.950(4)	Co−O3	1.887(4)
Co−N2	1.911(4)	O1−C8	1.251(6)
Co−N3	1.887(4)	O3−O4	1.446(4)
Co−N4	1.958(4)	O2−C14	1.249(6)
Co−N5	2.024(4)	O4−C22	1.423(7)

Bond Angles

N1−Co−N2	92.9(2)	N3−Co−N5	92.5(2)
N1−Co−N3	171.5(2)	N4−Co−N5	82.2(2)
N1−Co−N4	103. 2(2)	N1−Co−O3	86.7(2)
N1−Co−N5	94.7(2)	N2−Co−O3	97.3(2)
N2−Co−N3	82.0(2)	N5−Co−O3	168.1(2)
N2−Co−N4	163.7(2)	Co−O3−O4	115.3(2)
N2−Co−N5	94.4(2)	O3−O4−C22	109.2(4)
N3−Co−N4	82. 2(2)	C23−C22−C24	112.9(5)

[Co($PyPz_2P$)(OOCy)]·2$CHCl_3$ (**16**·2$CHCl_3$)

Bond Distances

Co−N1	1.944(3)	N1−N2	1.362(4)
Co−N3	1.930(3)	N6−N7	1.364(4)
Co−N4	1.844(3)	O3−C6	1.241(4)
Co−N5	1.955(3)	O1−O2	1.456(3)
Co−N7	1.971(3)	O4−C12	1.254(4)
Co−O1	1.892(3)	C22−C23	1.528(5)

Bond Angles

N1−Co−N3	93.02(12)	N1−Co−O1	87.05(12)
N1−Co−N4	171.26(13)	N3−Co−O1	100.08(12)
N1−Co−N5	102.82(12)	N4−Co−O1	86.57(12)
N1−Co−N7	93.32(13)	N7−Co−O1	169.05(11)
N3−Co−N4	82.22(12)	Co−N1−N2	122.6(2)
N3−Co−N5	163.52(12)	Co−O1−O2	117.0(2)
N3−Co−N7	90.83(14)	N3−C6−O3	127.7(3)
N4−Co−N5	82. 62(12)	O1−O2−C18	107.8(2)
N4−Co−N7	94.07(13)	O2−C18−C19	113.2(3)
N5−Co−N7	83.85(13)	O2−C18−C23	106.6(3)

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Table 3. Comparison of Structural Parameters for Crystallographically Characterized [LCo^{III}−OOR] Complexes. Bond Distances Are in Å and Bond Angles Are in deg

complex^a	Co−O	L_{trans}−Co	O−O	O−R	Co−O−O	O−O−R	ref
R = tertiary							
7	1.905 (7)	2.024 (3)	1.492 (8)	1.462 (7)	111.4 (6)	107.6 (5)	15
8	1.883 (4)	2.010 (5)	1.485 (5)	1.443 (7)	109.2 (3)	107.1 (4)	*b*
9	1.882 (5)	2.007 (7)	1.488 (8)	1.433 (10)	112.3 (4)	108.0 (6)	*b*
19	1.909 (3)	1.994 (3)	1.455 (3)	1.462 (5)	111.7 (2)	110.3 (2)	7
21	1.838 (5)	2.045 (5)	1.444 (6)	1.423 (9)	114.6 (3)	111.2 (6)	6
22	1.854 (9)	1.929 (11)	1.50 (1)	1.42 (1)	114.3 (6)	105.6 (8)	11
R = secondary							
10	1.891 (3)	2.029 (4)	1.460 (4)	1.425 (6)	113.6 (2)	108.5 (3)	*b*
11	1.887 (4)	2.024 (4)	1.446 (4)	1.423 (7)	115.3 (2)	109.2 (4)	*b*
16	1.892 (3)	1.971 (3)	1.456 (3)	1.437 (4)	117.0 (2)	107.8 (2)	*b*
20	1.897	2.013	1.455	1.451	112.6	107.2	9
23	1.856 (6)	1.973 (6)	1.437 (8)	1.42 (1)	108.7 (5)	110.0 (6)	13
R = primary							
12	1.855 (10)	1.999 (13)	1.451 (14)	1.40 (2)	118.2 (8)	107.1 (13)	*b*
12	1.856 (11)	1.994 (13)	1.46 (2)	1.40 (2)	114.0 (9)	106.2 (14)	*b*
24	1.92 (1)	2.04 (8)	1.40 (2)	1.41 (3)	120.1 (9)	117 (2)	14

^{a} **19** = [Co(dmgH)(py)(OOCm)], **20** = [Co(dmgH)(py)OOCHMePhMe)], **21** = [Co(BPI)(OCOPh)(OO^{t}Bu)], **22** = [Co(Salpr)(4-OO−(2,4,6-^{t}Bu-C_6H_2O)] (peroxy-*p*-quinolatocobalt(III) complex), **23** = *trans*(*t*-N,O(C))-[Co{OOCH(CH_3)COO-*O,O*}(tren)]BPh_4, **24** = [Co(TPP)(py)(OO-$CH_2CH{=}CH_2$)]. ^{b} This work.

and 1.882(5) Å, respectively, are slightly shorter than the same bond in **7** (1.914 Å) and [Co(dmgH)$_2$(py)(OOCm)] (**19**)[7] (1.909(3) Å, dmgH$^-$ = monoanion of dimethylglyoxime) but longer than the same bond in other structurally characterized [LCo^{III}−OOR] complexes with tertiary R groups (See Table 3).[6,11,13] Both **8** and **9** possess a short and a long Co−N(amido) bond (Co−N2, 1.917(5) Å and 1.925(8) Å, respectively; Co−N4, 1.947(5) Å and 1.977(8) Å, respectively). Such nonequivalent Co−N(amido) bond distances are also observed in **7** (1.921(3) and 1.959(3) Å respectively)[15] and other [Co(Py$_3$P)(OOR)] complexes (vide infra) but not in the parent aqua complex **3** (1.930(6) and 1.929(6) Å).[15] The Co−N(amido) bond lengths of **8** and **9** are however within the range of the Co−N(amido) bond distances for similar Co(III)−peptido complexes (1.915−1.968 Å).[15,16,28−31] The Co−N5 bond distance (the bond *trans* to the peroxide ligand -OOR with R = tertiary) is 2.010(5) Å in **8** and 2.007(7) Å in **9**. As discussed in a latter section, this distance is comparatively shorter when R = secondary or primary (Table 3). The O−O moiety in both **8** and **9** is ordered, and the O−O distances are very comparable (1.485(5) Å and 1.488(8) Å, respectively) in these two complexes with tertiary R groups. However, this O−O bond distance is longer than the O−O bond distance of **19** (1.455(3) Å) which also includes a CmOO$^-$ coordinated to a Co(III) center. Since dmgH$^-$ is a relatively weak σ-electron donor compared to Py$_3$P^{2-}, the metal center in **19** does not back-donate as much electron density to the π* orbitals of the O−O moiety of the CmOO$^-$ ligand. As a result, the O−O bond distance in **19** is shorter than that in **8**. The Co−O3−O4 bond angle (109.2(3)°) of **8** indicates that the proximal oxygen is sp^3 hybridized and the O−O bond is close to a single bond. In **9**, the same Co−O3−O4 bond angle is slightly larger (112.3(4)°) presumably due to more steric interactions from the OOR ligand.

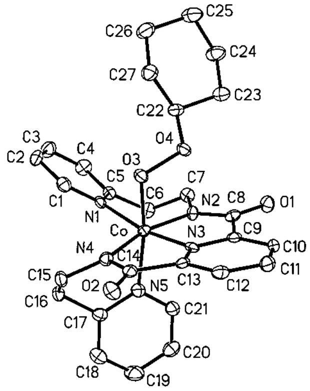

Figure 2. Thermal ellipsoid (probability level 50%) plot of [Co(Py$_3$P)(OOCy)] (**10**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

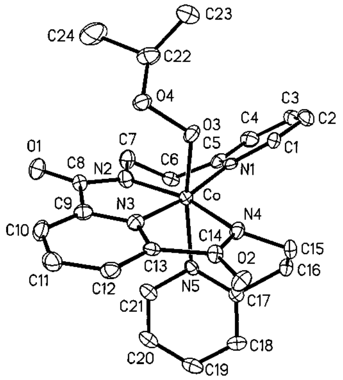

Figure 3. Thermal ellipsoid (probability level 50%) plot of [Co(Py$_3$P)(OO^{i}Pr)] (**11**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

Structure of [Co(Py$_3$P)(OOCy)]·H$_2$O·0.5Et$_2$O·0.2CH$_2$Cl$_2$ (10·H$_2$O·0.5Et$_2$O·0.2CH$_2$Cl$_2$), and [Co(Py$_3$P)(OO^{i}Pr)]·H$_2$O (11·H$_2$O). Structural parameters of these two [Co(Py$_3$P)(OOR)] complexes containing secondary alkylperoxo groups as R are listed in Table 2. The geometry around the cobalt (III) center in both **10** (Figure 2) and **11** (Figure 3) is distorted octahedral. An interesting feature of the structure of **10** is the presence of

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(28) (a) Farinas, E. F.; Tan, J. D.; Baidya, N.; Mascharak, P. K. *J. Am. Chem. Soc.* **1993**, *115*, 2996. (b) Tan, J. D.; Hudson, S. E.; Brown, S. J.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1992**, *114*, 3841. (c) Muetterties, M.; Cox, M. B.; Arora, S. K.; Mascharak, P. K. *Inorg. Chim. Acta* **1989**, *160*, 123. (d) Brown, S. J.; Hudson, S. E.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1989**, *111*, 6446. (e) Delany, K.; Arora, S. K.; Mascharak, P. K. *Inorg. Chem.* **1988**, *27*, 705 and references cited therein.

(29) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc*. **1991**, *113*, 8419.

(30) Mak, S.-T.; Wong, W.-T.; Yam, V. W.-W.; Lai, T.-F.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1991**, 1915.

(31) Ray, M.; Ghosh, D.; Shirin, A.; Mukherjee, R. *Inorg. Chem.* **1997**, *36*, 3568.

water molecules that are hydrogen bonded to the carbonyl oxygens of the complex. Such hydrogen bonding brings two molecules of the complex close to each other to form a dimeric unit with two water molecules acting as bridges (Figure S2, Supporting Information). X-ray quality crystals of **10** could only be grown from media containing small amounts of water. Rigorously dry solutions of **10** invariably afford microcrystalline materials. The molecular structure of **10** provides the metric parameters of the coordinated CyOO− moiety for the first time since, prior to this report, no metal complex with coordinated $CyOO^-$ group has been characterized by X-ray crystallography. Along the same line, complex **11** is the first example of a structurally characterized cobalt(III) complex containing a ligated $^iPrOO^-$ group.[32]

In **10**, the cyclohexyl group exists in the chair conformation. The O−O bond distance (1.460(4) Å) of the coordinated $CyOO^-$ group is similar to that observed with **11** (1.446(4) Å), and the oximato complex [Co(dmgH)$_2$(OOCHMePh-*p*-Me)] (1.455 Å) (Table 3) reported previously.[9] In these three [LCo^{III}−OOR] complexes with secondary R groups, the O−O distances fall in the range of 1.44−1.46 Å. These distances are slightly shorter than the O−O distances noted for [LCo^{III}−OOR] complexes with tertiary R groups (Table 3). The metric parameters of the Py_3P^{2-} ligand frames in **10** and **11** are very similar to those observed with **8** and **9**.

Structure of [Co(Py$_3$P)(OO^{n}Pr)]·1.5CH$_2$Cl$_2$·0.5H$_2$O (12·1.5CH$_2$Cl$_2$·0.5H$_2$O). Selected bond distances and angles for the complex **12** containing a ROO^- ligand with primary R group are listed in Table 2. In the asymmetric unit, there are two molecules of **12** with slightly different orientations of the $^nPrOO^-$ moiety (Figure S3, Supporting Information). Two slightly different O−O bond lengths (1.451(14) Å and 1.46(2) Å) are observed for these two molecules. These O−O distances are longer than the O−O distance (1.40(2) Å, Table 3) of [Co(TPP)(py)(OOCH$_2$CH═CH$_2$)][14] (TPP = tetraphenylporphyrin dianion) which also contains a primary alkylperoxo group.[33] The two slightly different orientations of the $^nPrOO^-$ group in the two molecules of **12** in the asymmetric unit are characterized by (a) the Co−O−O bond angles (118.2(8)° and 114.0(9)°), (b) the O−C−C bond angles (111(2)° and 106(2)°), and (c) the C−C−C bond angles (121(3)° and 113(2)°).

Structure of [Co(PyPz$_2$P)(OOCy)]·2CHCl$_3$ (16·2CHCl$_3$). The structure of one [LCo^{III}−OOR] complex with L = $PyPz_2P^{2-}$, namely **16**, was determined to find out the effect of the ligand L on the metric parameters of the Co−OOR moiety. The structure of **16** is shown in Figure 4, and selected bond distances and bond angles are included in Table 2. In **16**, the $PyPz_2P^{2-}$ ligand binds the cobalt(III) center in a pentadentate square pyramidal fashion with two 2-pyrazole nitrogens, one pyridine nitrogen, and two deprotonated amido nitrogens acting as donors. A similar mode of binding of this ligand has been noted in [Co(PyPz$_2$P)(H$_2$O)]$^+$ and [Cu(PyPz$_2$P)].[16,20] The cyclohexyl group of the coordinated $CyOO^-$ ligand in **16** is in the chair conformation, and the O−O bond distance (1.456(3) Å) is slightly shorter than the O−O bond distance of **10** (1.460(4) Å). Also, the Co−O−O bond angle (117.0(2)°) of the Co−OOR moiety in **16** is somewhat larger than the same bond angle in **10** (113.6(2)°).

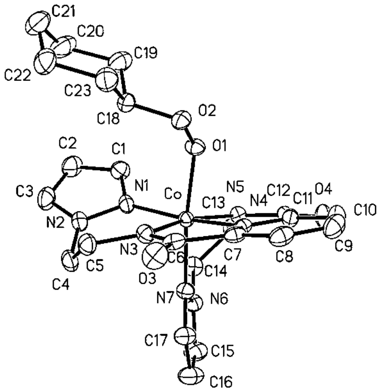

Figure 4. Thermal ellipsoid (probability level 50%) plot of [Co(PyPz$_2$P)(OOCy)] (**16**) with the atom-labeling scheme. H atoms are omitted for the sake of clarity.

^{1}H NMR Spectra of the [LCo^{III}−OOR] Complexes. The purity and integrity of the [LCo^{III}−OOR] complexes in solutions are readily evident from their ^{1}H NMR spectra. For example, the ^{1}H NMR spectra of [Co(Py$_3$P)(OO^{t}Bu)] (**7**), [Co(Py$_3$P)(OOCm)] (**8**), and [Co(Py$_3$P)(OO^{i}Pr)] (**11**) (Figure S4, Supporting Information) display all of the characteristic peaks of the coordinated Py_3P^{2-} ligand[15] in addition to peaks associated with the coordinated ROO^- moiety. The resonance patterns for the R groups of the ROO^- ligands in these complexes provide information related to the possible orientations of these groups. For example, the ^{t}Bu group of **7** resonates as a singlet (free rotation), while the two methyl groups on the isopropyl moiety (^{i}Pr) of **11** appear as two doublets, indicating fixed disposition of the two methyl groups. The two methyl groups of the coordinated $CmOO^-$ ligand of **8** also appear as two distinct peaks at 0.77 and 0.81 ppm. This nonequivalency, which is not present in PhCMe$_2$OOH, indicates that the two methyl groups are held fixed in space or move very slowly relative to the NMR time scale. The NMR spectra of **8** and **11** in CDBr$_3$ indicate that the inequivalency of the methyl groups of the cumyl moiety of **8** and the isopropyl moiety of **11** is preserved at 70 °C (temperature for the oxidation reactions, vide infra).

The majority of the [LCo^{III}−OOR] complexes with L = $PyPz_2P^{2-}$ ligand has been characterized by their clean ^{1}H NMR spectra. All of these complexes (**13**−**18**) exhibit resonances for the $PyPz_2P^{2-}$ ligand[16] as well as peaks for the coordinated ROO^- groups. Here also one notices similar peak patterns for the R groups of the coordinated peroxo units. As an example, the ^{1}H NMR spectra of [Co(Py$_3$P)(OOCy)] (**10**) and [Co(PyPz$_2$P)(OOCy)] (**16**) are compared in Figure 5. In both cases, the resonances for the cyclohexyl group appear as complicated patterns between 0.7 and 2.3 ppm.

Formation of [LCo^{III}−OOR] Complexes. That the [LCo^{III}−OOR] complexes are readily obtained from the [LCo^{III}(OH)] complexes upon addition of excess ROOH is apparent from the changes in the spectrum of [Co(Py$_3$P)(OH)] (**4**) upon addition of excess TBHP (Figure 6). In CD$_2$Cl$_2$ at 25 °C, addition of 5 equiv TBHP (dried over anhydrous MgSO$_4$) to **4** results in quantitative formation of [Co(Py$_3$P)(OO^{t}Bu)] (**7**). The reaction is clean, and there is no side product other than water. Since no broadening of any peak is noticed during the transformation, it is evident that no Co(II) species or radical(s) is generated in the reaction mixture.

Oxidation of Hydrocarbons with [LCo^{III}−OOR] Complexes. The [LCo^{III}−OOR] complexes (**7**−**18**) decompose when warmed in CH$_2$Cl$_2$ (or CHCl$_3$) above 50 °C. The presence

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[32] For the only other structurally characterized complex containing a $^iPrOO^-$ group, a platinum complex, see Ferguson, G.; Parvez, M.; Monaghan, P. K.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1983**, 267.

[33] Interestingly, the O−O bond distance in [Ge(TPP)(OOCH$_2$CH$_3$)$_2$], a complex that has two primary alkylperoxo ligands bonded to germanium, is 1.478(2) Å. See Balch, A. L.; Cornman, C. R.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2963.

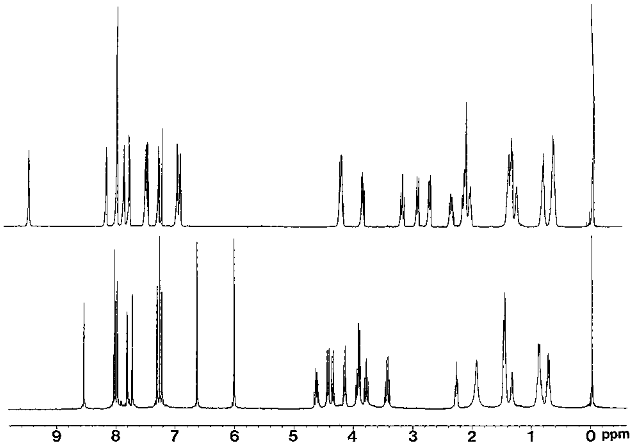

Figure 5. ^{1}H NMR spectra (500 MHz, 298 K) of [Co(Py$_3$P)(OOCy)] (**10**) (top) and [Co(PyPz$_2$P)(OOCy)] (**16**) (bottom) in CDCl$_3$.

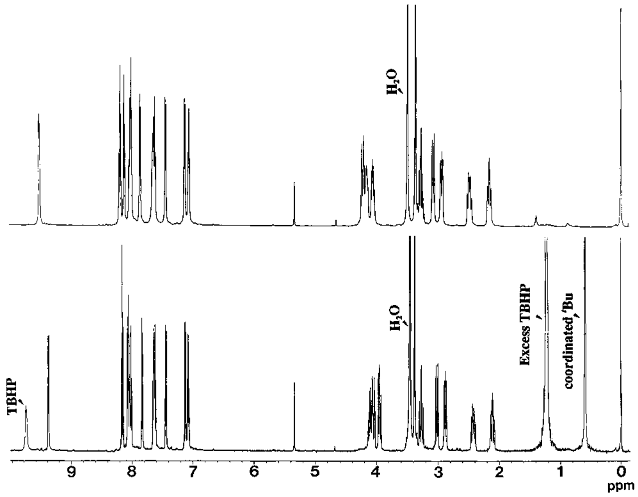

Figure 6. ^{1}H NMR spectra (500 MHz, 298 K) showing conversion of [Co(Py$_3$P)(OH)] (**4**) (top) to [Co(Py$_3$P)(OO^{t}Bu)] (**7**) (bottom) upon addition of excess TBHP in CD$_2$Cl$_2$.

Table 4. Stoichiometric Oxidation of Cyclohexane by [Co(PyPz$_2$P)(OO^{t}Bu)] (**13**)[a]

Time Profile[b,c]

time, h	% **A**	% **K**	% total
0.5	4	4	8
1.0	13	12	25
2.0	37	43	80
3.0	51	50	101
4.0	70	66	136
5.0	82	76	159
6.0	91	89	180

Temperature Profile[b,d]

T, °C	% **A**	% **K**	% total
50	0	2	2
60	5	6	11
70	37	43	80
80	82	81	163
90	81	39	120
100	71	44	115

[a] Yields based on **13** (8 μmol used). [b] Reaction mixtures consisted of 0.5 mL of CH$_2$Cl$_2$, 0.5 mL of CyH and **13**. [c] Reaction temperature was 70 °C. [d] Reaction time was 2 h.

of hydrocarbons in such solutions results in the oxidation of C−H bonds to produce the corresponding alcohols and ketones (or aldehydes). In the present study, we have determined the extent of oxidation of cyclohexane (CyH) and other hydrocarbon substrates by the [LCo^{III}−OOR] complexes. In accordance with the terminology of Mimoun,[6] these oxidations will be referred to as stoichiometric oxidations hereafter. We have also performed oxidations of CyH with the [LCo^{III}−OOR] complexes in the presence of additional ROOH. These oxidation reactions will be referred to as catalytic oxidations. In the following sections, we will first provide the results of stoichiometric oxidation of CyH by the [LCo^{III}−OOR] complexes. The discussion thereafter will focus on the general mechanism of such stoichiometric oxidations. Results of stoichiometric oxidation of hydrocarbons other than CyH will then be discussed to compare the oxidizing capacities of these complexes. And finally, we will discuss the results and mechanism of catalytic oxidation of CyH by the [LCo^{III}−OOR] complexes.

Stoichiometric Oxidation of Cyclohexane. When solutions of [LCo^{III}−OOR] complexes in CyH/CH$_2$Cl$_2$ are warmed above 60 °C, one obtains cyclohexanol (**A**) and cyclohexanone (**K**) in moderate yields within hours. The results of stoichiometric oxidations of CyH by [Co(PyPz$_2$P)(OO^{t}Bu)] (**13**) are shown in Table 4. To obtain the time profile of the oxidation reaction, a solution of 8 μmol of **13** in 1 mL of 1:1 CyH/CH$_2$Cl$_2$ was heated at 70 °C, and the yields of **A** and **K** were monitored as a function of time. The results (Table 4) reveal that oxidation of CyH is continued for over 6 h under this condition and up to 180% oxidized products (based on **13**) are obtained after 6 h. When the same reaction mixture was heated for 2 h at different temperatures, the yields of the oxidized products (Table 4) afforded a temperature profile of the oxidation reaction. No oxidation is observed below 50 °C. At 50 °C, the extent of oxidation is minimal as evidenced by the small amounts of the oxidized products (**A** = 0% and **K** = 2%). The amounts of oxidized products, however, increase significantly as the temperature is raised further and reach a maximum at 80 °C (**A** = 82% and **K** = 81%). Further increase in temperature results in diminished yields which may result from overoxidation of the oxidized products. Since all oxidation reactions by [LCo^{III}−OOR] complexes afford products derived from the OOR groups (viz, ^{t}BuOH in the case of **13**) in addition to **A** and **K**, it is evident that the oxidation of hydrocarbons is carried out by species formed during decomposition of the [LCo^{III}−OOR] complexes. This is further indicated by the fact that the rates of formation of the OOR-derived product(s) and the oxidized products from the hydrocarbon both increase with the increase in temperature. For example, when **14** (8 μmol) is used to oxidize CyH, the yields of **A**, **K**, 2-phenyl-2-propanol, and acetophenone (the last two products are derived from the [CoOOCMe$_2$Ph] moiety of **14**) for a 2 h period increase with temperature as follows: at 50 °C, **A** (2%), **K** (2%), 2-phenyl-2-propanol (3%), and acetophenone (4%); at 60 °C, **A** (10%), **K** (8%), 2-phenyl-2-propanol (22%), and acetophenone (10%); at 70 °C, **A** (36%), **K** (25%), 2-phenyl-2-propanol (46%), and acetophenone (15%).

Mechanism of Oxidation by [LCo^{III}−OOR] Complexes. In our preliminary work,[15] we suggested that [Co(Py$_3$P)(OO^{t}Bu)] (**7**) undergoes exclusive homolysis of the O−O bond when heated in a CH$_2$Cl$_2$/CyH mixture. The ^{t}BuO$^•$ radicals generated in the reaction mixture then abstract H atoms from CyH to produce cyclohexyl radicals (Cy$^•$)[34] which in the presence of dioxygen afford **A** and **K**. In the present work, we have studied

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(34) (a) Avila, D. V.; Ingold, K. U.; Lusztyk, J.; Green, W. H.; Procopio, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 2929. (b) Almarsson, O.; Bruice, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 4533 and references therein. (c) Minisci, F.; Fontana, F.; Araneo, S.; Recupero, F.; Banfi, S.; Quici, S. *J. Am. Chem. Soc.* **1995**, *117*, 226.

the oxidation of CyH and other hydrocarbons by several [LCo^{III}−OOR] complexes to collect more support for our earlier suggestion and establish the general mechanism of alkane oxidation by such species. The somewhat superior capacity of CyH oxidation by a second [LCo(OO^{t}Bu)] complex namely, [Co(PyPz$_2$P)(OO^{t}Bu)] (**13**), provided the first support to our suggestion that the ^{t}BuO$^\bullet$ radical, the common product in thermal decomposition of **7** and **13**, is a key participant in the overall oxidation process. Since the "radical strength"[35] of ^{t}BuO$^\bullet$ radical (105 kcal/mol) is sufficient to abstract H atoms from C−H bonds of higher molecular weight ($>C_4$) alkanes including CyH (95 kcal/mol),[36] the earlier suggestion of H abstraction from CyH by the ^{t}BuO$^\bullet$ radical appears quite reasonable. This H abstraction step is a crucial one since it allows the substrate hydrocarbon to enter a radical-driven oxidation pathway (vide infra).

To determine if [Co(Py$_3$P)(O$^\bullet$)], the other product of homolysis, is also capable of initiating oxidation of CyH by H atom abstraction, we employed [Co(Py$_3$P)(OOCMe$_2$CH$_2$Ph)] (**9**) as the starting oxidant. Since our results indicate that O−O bond homolysis is the preferred mode of decomposition of the [Co(Py$_3$P)(OOR)] complexes, one would expect formation of [Co(Py$_3$P)(O$^\bullet$)] and PhCH$_2$CMe$_2$O$^\bullet$ in this reaction mixture. Since the PhCH$_2$CMe$_2$O$^\bullet$ radical undergoes β-scission very rapidly ($PhCH_2CMe_2O^\bullet \rightarrow PhCH_2^\bullet + Me_2CO$, $k = 2.2 \times 10^8\ s^{-1}$ at 25 °C) to produce the PhCH$_2^\bullet$ radical in the reaction mixture and H atom abstraction from CyH by PhCH$_2^\bullet$ is very slow compared to other radical termination reactions, only small amounts of oxidation products of CyH are expected from the action of the RO$^\bullet$ fragment in the case of **9**.[27] On the other hand, if [Co(Py$_3$P)(O•)] is capable of H atom abstraction from CyH, one would expect a more significant extent of oxidation to occur. In the actual experiment, when 30 μmol of **9** in the presence of 1 mL of 1:1 CyH/CH$_2$Cl$_2$ was heated to 80 °C for 2 h, mostly PhCHO (62%) was obtained along with PhCH$_2$Cl (4%), **K** (3%), PhCH$_2$CMe$_2$OH (6%), and a trace of PhCH$_2$OH. This result clearly indicates that [Co(Py$_3$P)(O•)] is not strong enough to abstract H atoms from CyH.

The kinetic isotope effect (k_H/k_D, KIE) on CyH oxidation by the [LCo^{III}−OOR] complexes indicates that H atom abstraction from CyH is an important step. In one experiment, a solution of 30 μmol of **7** in 1 mL of 0.25:0.25:0.5 C$_6$D$_{12}$/C$_6$H$_{12}$/CH$_2$Cl$_2$ was heated to 80 °C in a sealed vial. After 2 h, the reaction was rapidly cooled to room temperature, and the oxidized products were quantitated by gas chromatography. The KIE value, calculated by dividing the total amount of undeuterated oxidized products ($C_6H_{11}OH + C_6H_{10}O$) by the amount of deuterated oxidized products ($C_6D_{11}OH + C_6D_{10}O$), came out to be 5. Interestingly, the expected k_H/k_D value at 80 °C for a system in which the C−H bond stretching in the transition state is rate limiting is 4.9.[37] Although production of **A** and **K** from CyH by the [LCo^{III}−OOR] complexes may involve several steps with more than one incident of C−H bond breaking (vide infra), a KIE value of 5 strongly suggests that H atom abstraction from CyH is a crucial step and the oxidation reactions are radical-driven. In support, Que and co-workers have observed a KIE value of 4.9 in the oxidation of cyclohexane by ^{t}BuO$^\bullet$ radicals at room temperature.[38]

Table 5. Influence of the Alkyl Group R on Stoichiometric Hydrocarbon Oxidation with [Co(Py$_3$P)(OOR)] (R = ^{t}Bu (**7**), Cm (**8**), Cy (**10**), ^{i}Pr (**11**), and ^{n}Pr (**12**))[a]

	Toluene		
	% benzaldehyde	% benzyl alcohol	% total
7	73	6	79
8	50	3	53
10	15	-	15
11	10	-	10
12	8	-	8

	Cyclododecane		
	% cyclododecanol	% cyclododecanone	
7	21	35	56
8	10	26	36
10	5	8	13
11	4	8	12
12	2	7	9

	Adamantane			
	%1-adamantanol	% 2-adamantanol	% 2-adamantanone	
7	55	8	5	67
8	50	7	1	58
10	13	2	2	17
11	20	4	2	26
12	16	2	2	20

[a] Yields based on the amount of the Co(III) complex. Reaction mixtures consisted of Co(III) complex (8 μmol), 0.5 mL of CH$_2$Cl$_2$, and 0.5 mL of substrate (toluene) or 200 mg (adamantane or cyclododecane). Reaction time was 2 h, and reaction temperature was 70 °C.

Oxidation of CyH by the [LCo^{III}−OOR] complexes afford **A** and **K** only in the presence of dioxygen. When reaction mixtures are prepared and heated in the absence of dioxygen, no O-containing product(s) is observed. For example, when a solution of 32 μmol of **7** in 1 mL of 1:1 CyH/CH$_2$Cl$_2$ was heated at 70 °C in the absence of dioxygen, the only product derived from CyH was a small amount of cyclohexyl chloride (**C**).[15] **C** presumably arises from trapping of the cyclohexyl radicals (Cy$^\bullet$) by the dichloromethane solvent.[39] Along the same line, neither benzaldehyde nor any O-containing product was obtained from the solution of **9** in 1 mL of 1:1 CyH/CH$_2$Cl$_2$ following anaerobic heating at 80 °C for 2 h. The products in this case were PhCH$_2$Cl (3%), PhCH$_2$CMe$_2$OH (2%), and a trace amount of PhCH$_2$CH$_2$Ph. The PhCH$_2$CMe$_2$OH presumably arises from H atom abstraction from cyclohexane by PHCH$_2$CMe$_2$O$^\bullet$ while PhCH$_2$CH$_2$Ph results from combination of two PhCH$_2^\bullet$ radicals (β-scission product). These results clearly indicate that the presence of dioxygen is necessary for the oxidation of CyH to **A** and **K** by the [LCo^{III}−OOR] complexes.

Collectively, the results of CyH oxidation by various [LCo^{III}−OOR] complexes confirm that upon heating, homolysis of the O−O bond of [LCo^{III}−OOR] affords RO$^\bullet$ radicals in the reaction mixtures. Since most RO$^\bullet$ radicals can initiate oxidation of saturated hydrocarbons including CyH, one expects that the present [LCo^{III}−OOR] complexes should promote oxidations of many saturated hydrocarbons at elevated temperatures. In the present study, two [LCo^{III}-OO^{t}Bu] complexes have been used to oxidize five additional hydrocarbon substrates, and the results are shown in Table 6. That the [LCo^{III}−OOR] complexes in general are good oxidizing agents for saturated hydrocarbons is evident from this table.

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(35) Barton, D. J. R.; Sawyer, D. T. In *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. J. R., Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1993; p 4.

(36) *Handbook of Chemistry and Physics*, 67th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1987; pp F178−179.

(37) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Haper and Row: New York, 1987; pp 233−235.

(38) MacFaul, P. A.; Ingold, K. U.; Wayner, D. D. M.; Que, L., Jr. *J. Am. Chem. Soc*. **1997**, *119*, 10594.

(39) Trapping of cyclohexyl radicals by halogenated hydrocarbons has been noted in cyclohexane oxidation: (a) Leising, R. A.; Kojima, T.; Que, L., Jr.. In *The Activation of Dioxygen and Homogeneous Catalytic Oxidation*; Barton, D. H. R., Martell, A. E., Sawyer, D. T., Eds.; Plenum Press: New York, 1993; pp 321−331. (b) Kim, J.; Larka, E.; Wilkinson, E. C.; Que, L., Jr. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2048.

Table 6. Stoichiometric Oxidation of Hydrocarbons by [Co(Py$_3$P)(OO^{t}Bu)] (**7**) and [Co(PyPz$_2$P)(OO^{t}Bu)] (**13**)^a: Influence of the Ligand L on the Capacity for Oxidation

complex				% total
	Cyclohexane			
	% cyclohexanol	% cyclohexanone		
7	18	34		52
13	37	43		80
	Toluene			
	% benzaldehyde	% benzyl alcohol		
7	73	6		79
13	127	14		141
	Cyclooctane			
	% cyclooctanol	% cyclooctanone		
7	16	66		82
13	20	114		134
	Adamantane			
	% 1-adamantanol	% 2-adamantanol	% 2-adamantanone	
7	55	8	5	67
13	91	15	8	114
	Cyclododecane			
	% cyclododecanol	% cyclododecanone		
7	21	35		56
13	29	56		85
	***n*-Heptane**			
	% 1-heptanol	% 2-heptanol	% 3-heptanol	
7	1	6	24	31
13	1	11	39	51

[a] Yields based on the amount of the Co(III) complex. Reaction mixtures consisted of 8 μmol of **7** or **13**, 0.5 mL of CH$_2$Cl$_2$, and 0.5 mL of substrate (in the cases of cyclohexane, toluene, cyclooctane, and *n*-heptane) or 0.2 g of substrate (in the cases of adamantane and cyclododecane). Reaction time was 2 h, and reaction temperature was 70 °C.

When analyzed in the light of what is known about the chemistry of the RO$^\bullet$ radicals,[40] the results of stoichiometric oxidation of hydrocarbons by the [LCo^{III}−OOR] complexes lead one to consider a general mechanism that we have suggested in our previous report.[15] In this mechanism, oxidation of hydrocarbons occurs through several steps involving different radical species (Scheme 1). The first step in this mechanism is the production of RO$^\bullet$ radicals from the [LCo^{III}−OOR] complexes upon heating. The RO$^\bullet$ radicals then initiate oxidation of the hydrocarbon substrate (R′H) by removing H atoms from R′H to produce R′$^\bullet$ radicals (Scheme 1, reaction 1). In the presence of dioxygen, R′$^\bullet$ reacts at diffusion-controlled rates to form peroxyl (R′OO$^\bullet$) radicals (Scheme 1, reaction 2).[40] At elevated temperatures, these peroxyl radicals can abstract an H atom from another R′H to begin a chain process that results in the accumulation of R′OOH (reactions 2 and 3).[1d] Termination of these radicals can also occur through reactions 4 through 6. Thermal decomposition of the [LCo^{III}−OOR] complexes in the presence of R′H thus promotes oxidation of R′H via an autocatalytic process involving RO$^\bullet$ and R′OO$^\bullet$. The fact that one obtains greater than 100% yields in some cases (Table 4) supports the autocatalytic nature of the oxidation reactions by [LCo^{III}−OOR] complexes.[41] The final substrate-based oxidized products result from a radical termination reaction like 6 of Scheme 1 and/or from metal-catalyzed decomposition of R′OOH that accumulates in the reaction mixture (reaction 3, Scheme 1). Thus, when CyH is used as the substrate, CyOO$^\bullet$ radicals are produced via reactions 1 and 2 and terminate via reaction 6 to give **A** and **K** as the major products of oxidation. The **A**:**K** ratio in most cases deviates from the typical 1:1 value in a Russell-type recombination[42] due to the overoxidation of **A** under the reaction conditions as well as the contribution from metal-catalyzed decomposition of CyOOH.

Scheme 1

Initiation

$$\mathrm{RO^\bullet + R'H \rightarrow ROH + R'^\bullet} \qquad (1)$$

Propagation

$$\mathrm{R'^\bullet + O_2 \rightarrow R'OO^\bullet} \qquad (2)$$

$$\mathrm{R'OO^\bullet + R'H \rightarrow R'^\bullet + R'OOH} \qquad (3)$$

Termination

$$\mathrm{RO^\bullet + RO^\bullet \rightarrow ROOR} \qquad (4)$$

$$\mathrm{R'OO^\bullet + R^\bullet \rightarrow R'OOR} \qquad (5)$$

$$\mathrm{R'OO^\bullet + R'OO^\bullet \rightarrow oxidized\ products} \qquad (6)$$

Finally, to confirm that the Co−O bond of the [LCo^{III}−OOR] complexes is not homolyzed upon heating, we studied the products of reactions in which the [LCo^{III}−OOR] complexes were heated in the presence of substrates such as 1,4-cyclohexadiene and 2,6-di-*tert*-butylphenol that easily afford H atoms. Without exception, these reactions afforded ROH as essentially the only product. For example, when 20 μmol of [Co(Py$_3$P)(OOCMe$_2$Ph)] (**8**) was heated at 70 °C for 2 h in 1 mL of 9:1 1,4-cyclohexadiene/MeCN under dinitrogen, PhMe$_2$COH (78%) and PhC(O)Me (2%) were formed along with PhH (530%). These products are obtained from PhCMe$_2$O$^\bullet$ via reactions II and III.

$$\mathrm{[Co(Py_3P)(OOCMe_2PH)] \rightarrow [Co(Py_3P)(O^\bullet)] + PhCMe_2O^\bullet} \qquad \mathrm{(II)}$$

$$\mathrm{2PhCMe_2O^\bullet + 1{,}4\text{-}cyclohexadiene \rightarrow 2PhCMe_2OH + PhH} \qquad \mathrm{(III)}$$

If heating of **9** had promoted homolysis of the Co−O bond, then one would have expected PhCMe$_2$OO$^\bullet$ radicals in the reaction mixture which, in the presence of excess 1,4-cyclohexadiene, would have produced PhCMe$_2$OOH as the final product. Along the same line, no CyOOH is detected when **10** and **16** were heated with 1,4-cyclohexadiene under dinitrogen atmosphere.[43] Collectively, these results confirm that homolysis of the Co−O bond does *not* occur when the [LCo^{III}−OOR] complexes are heated.

Role of the R Group on the Oxidizing Capacity of [LCo^{III}−OOR] Complexes. To investigate the effect of the R group on the ability of [LCo^{III}−OOR] complexes to promote hydrocarbon oxidation, we carried out a set of reactions in which 8 μmol of each [Co(Py$_3$P)(OOR)] (R = ^{t}Bu, Cm, Cy, ^{i}Pr, ^{n}Pr) complex was dissolved in a total volume of 1 mL of RH/CH$_2$-

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[40] (a) Walling, C. In *Free Radicals in Solution*; John Wiley & Sons: New York, 1957. (b) Howard, J. A. *Adv. Free Radical Chem.* **1972**, *4*, 49. (c) Ingold, K. U. In *Free Radicals*, Vol. 1; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; p 37.

[41] The partly autocatalytic nature of these oxidation reactions is further indicated by the fact that the yields of the oxidized products depend on the amount of the [LCo^{III}−OOR] complexes used in the reactions. The use of greater amounts of the [LCo^{III}−OOR] oxidants often results in higher amounts of the oxidized products but diminished percent of yields with respect to the amounts of the metal complexes. For this reason, we have employed the same equivalents of [LCo^{III}−OOR] complexes whenever comparisons have been made to establish trends in such oxidation reactions.

[42] Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 3871.

[43] The reaction conditions and detection procedures described here allow one to clearly identify ROOH, if present in the reaction mixtures.

Cl_2 and heated to 70 °C for 2 h. The results of these experiments are shown in Table 5. Upon close scrutiny of Table 5, it becomes apparent that for all of the hydrocarbons, [Co(Py$_3$P)(OO^{t}Bu)] is the most effective oxidant, while [LCo^{III}−OOR] complexes with R = primary alkyl groups are the least effective. Since this trend parallels the stability of the RO$^\bullet$ radicals, once more it becomes evident that the actual oxidants in all cases are RO$^\bullet$ radicals. The lifetime of the ^{t}BuO$^\bullet$ radical is longer than the CmO$^\bullet$ radical due to the slower rate of decomposition via β-scission.[27b] Secondary and primary alkoxyl radicals are susceptible to 1,2-hydrogen-atom shifts, bimolecular self-decomposition, and/or β-scission and hence have relatively shorter radical lifetimes.[44] As a result, a [LCo^{III}−OOR] complex serves as an efficient oxidant only when the RO$^\bullet$ radicals derived from it bring about H atom abstraction from the substrate (or the solvent) at a rate faster than the rate(s) of reactions that remove them from the reaction mixture in parallel pathways.

Role of Ligand L on the Oxidizing Capacity of the [LCo^{III}−OO^{t}Bu] Complexes. Shown in Table 6 are the results of stoichiometric oxidations of cyclohexane, toluene, cyclooctane, adamantane, cyclododecane, and *n*-heptane by **7** and **13**. In all cases, 8 μmol of **7** or **13** was mixed with a substrate in dichloromethane, and the solution was heated to 70 °C for 2h. The distribution of the oxidation products in each case supports Scheme 1. Close examination of the product distributions and yields of these reactions (Table 6) reveals that in all oxidation reactions, complex **13** gave more total oxidized products (alcohol, aldehyde, or ketone) than **7**. This trend suggests that the ligand L has definite influence on the overall ability of the [LCo^{III}−OOR] complexes to induce oxidation of hydrocarbon substrates.

To identify the ways L could influence the oxidative capacity of the [LCo^{III}−OOR] complexes, decomposition of **7** and **13** in the absence of substrate (in CD_2Br_2, 70 °C) was followed by ^{1}H NMR spectroscopy. The process of decomposition of the two complexes was monitored by the disappearance of the resonance of the ^{t}Bu group of the coordinated ^{t}BuOO ligand. The results indicate that **7** decomposes at a faster rate than **13**. Since ^{t}BuO$^\bullet$ radicals are responsible for H atom abstraction from the hydrocarbon substrate, it is evident that **7** affords more oxidation products, at least in the initial stage. The high concentration of the ^{t}BuO$^\bullet$ radicals, however, promotes more radical terminations, and hence, in the long run, rapid decomposition of **7** results in lower yields of the oxidized products. Quite in contrast, slower realease of ^{t}BuO$^\bullet$ radicals into the reaction mixture from **13** allows the autocatalytic oxidation reaction to proceed with a lower incidence of termination, and one obtains higher yields of the products in heat-induced oxidation reactions by **13**. The superior ability of **13** to oxidize hydrocarbon substrates is therefore derived from its greater thermal stability.

Effect of Solvent. To examine the effects of solvent polarity and the ability of the solvent to hydrogen bond on stoichiometric oxidations of cyclohexane, oxidations by **7** were carried out in 1 mL of 1:1 CyH/solv mixtures with solv = dibromomethane, acetic acid, dichloromethane, pyridine, acetone, or ethanol. Results of these oxidations are shown in Table 7. The highest yields of the oxidized products are obtained in acetic acid, a solvent with low dielectric constant.[45] When solv = dibromomethane, considerable amount of cyclohexyl bromide (CyBr) is formed in the reaction mixture due to trapping of the Cy$^\bullet$ radicals by Br atoms, and hence, lower yields of **A** and **K** are obtained. In contrast, only a trace amount of cyclohexyl chloride (CyCl) is produced when dichloromethane is used as the solvent. The larger amount of CyBr (relative to that of CyCl) in the final product presumably arises from weaker C−Br bonds in dibromomethane. Pyridine, acetone, and ethanol, the solvents with higher dielectric constants, all afford low yields of the oxidized products. Collectively, these results indicate that an increase in solvent polarity lowers the yields of the oxidized products. In general, the [LCo^{III}−OOR] complexes are more stable in solvents with low dielectric constants and hence are expected to decompose slowly and promote more oxidation in such media. Indeed, the rate of [Co(Py$_3$P)(OO^{t}Bu)] decomposition at 70 °C in CD_2Br_2 (monitored by ^{1}H NMR spectroscopy) decreases considerably when cyclohexane is added. Polar solvents, particularly those capable of H bonding, are also known to greatly accelerate the rate of β-scission of the ^{t}BuO$^\bullet$ radical by stabilizing the transition state and decreasing the rate of H atom abstraction via solvation of the ^{t}BuO$^\bullet$ radical.[40b,46,47] Since both phenomena lower the extent of oxidation by the ^{t}BuO$^\bullet$ radical, it is expected that oxidation by [Co(Py$_3$P)(OO^{t}Bu)] will afford higher yields of the oxidized products only in solvents of low polarity, and this is exactly what one observes in Table 7. We conclude that oxidation of hydrocarbons by the [LCo^{III}−OOR] complexes in general is facilitated in solvents of low polarity.

Table 7. Influence of Solvent on the Capacity for Stoichiometric Oxidation of Cyclohexane by [Co(Py$_3$P)(OO^{t}Bu)] (**7**)[a]

solvent	dielectric constant (ϵ)	% **A**	% **K**	% other	% total
dibromomethane	4.78	17	19	CyBr (30)	66
acetic acid	6.15	52	40		92
dichloromethane	8.93	18	34		52
pyridine	12.40	3	18		10
acetone	20.70	3	3		6
ethanol	24.55	6	3		9

[a] Yields based on the amount of the Co(III) complex. Reaction Conditions: 8 μmol of **7** in 1 mL of 1:1 CyH/solvent, 70 °C, 2 h reaction time.

Effect of Water. When aqueous solutions of the [LCo^{III}−OOR] complexes are allowed to sit at room temperature or heated, they are converted to the corresponding [LCo^{III}(OH)] complexes. This process can be followed by monitoring the electronic absorption spectra of the metal complexes. The conversion also generates free ROOH which is easily detected by gas chromatography.[48] Decomposition of the [LCo^{III}−OOR] complexes is therefore reaction IV which is the reverse of reaction I. One immediate consequence of reaction IV is the failure of the [LCo^{III}−OOR] oxidants to initiate oxidation of any substrate if the reaction mixture contains a significant amount of water.

$$[\mathrm{LCo^{III}{-}OOR}] + \mathrm{H_2O} \rightarrow [\mathrm{LCo^{III}(OH)}] + \mathrm{ROOH} \quad \text{(IV)}$$

Effect of Added Co(II) Salts. In industrial oxidation processes, divalent metal salts are often added to control product distribution.[1a,d,f] To investigate the effect of Co(II) salts on oxidations by the [LCo^{III}−OOR] complexes, we carried out

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(44) Fossey, J.; Lefort, D.; Sorba, J. In *Free Radicals in Organic Chemistry*; John Wiley & Sons: New York, 1995.

(45) Acetic acid also accelerates metal-catalyzed decomposition of CyOOH formed in the reaction mixture[1a,d,f] and increases the yields of **A** and **K**.

(46) Walling, C.; Padwa, A. *J. Am. Chem. Soc.* **1963**, *85*, 1593.

(47) Walling, C.; Wagner, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 3368.

(48) The presence of ROOH in such solutions was also confirmed by the use of aqueous Na_2SO_3 which is known to decompose ROOH to the corresponding alcohol (see Hock, H.; Lang, S. *Chem. Ber.* **1942**, *75*, 313).

Table 8. Catalytic Oxidation of Cyclohexane with Cobalt Complexes and Alkyl Hydroperoxides[a,b,c]

	Reaction Mixture Composition			Yield of Products[d]				
complex	complex mass (μmol)	ROOH (mmol)	CyH (mmol)	CyOH (μmol)	CyO (μmol)	P[e] (μmol)	total (μmol)	t.n.[f]
				TBHP				
4	25	10	60	1428	1661	174	3263	131
6	25	10	60	1518	1824	169	3511	140
7	25	10	60	1331	1518	145	2994	120
13	25	10	60	1452	1763	174	3389	136
4	120	30	200	5032	4890	570	10492	87
6	120	30	200	4992	5706	930	11628	97
7	120	30	200	5272	3994	942	10208	85
13	120	30	200	6720	5522	628	12870	114
				CmOOH[g]				
4	25	10	60	1617	1100		2717	109
6	25	10	60	1558	1121		2680	107
4	120	30	200	5701	2781		8482	71
6	120	30	200	6040	3413		9453	79
7	120	30	200	5531	3165		8696	72
13	120	30	200	5843	3023		8866	74

[a] Reaction mixtures were prepared under ambient conditions. [b] Reaction conditions: 80 °C, 4 h. [c] For each product, the identity and yield were determined by comparison with those of an authentic sample and with cyclooctane as internal standard. [d] Yields of three runs of each reaction were within ±5%. [e] P = CyOO^{t}Bu. [f] Turnover numbers were obtained by dividing the total mass of the oxidized products by the catalyst mass. [g] $PhCMe_2OH$ and $PhC(O)CH_3$ are obtained in all of these reactions.

stoichiometric oxidation of CyH by **7** and **13** in the presence and absence of Co^{2+}. When 8 μmol **7** was dissolved in 1 mL of 1:1 CyH/CH_2Cl_2 and heated at 70 °C for 2 h, **A** (18%) and **K** (44%) are formed with an **A**/**K** ratio of 0.41. When the same reaction was carried out in the presence of 20 μmol of $Co(OAc)_2 \cdot 4H_2O$, **A** (88%) and **K** (57%) are formed in higher amounts and the **A**/**K** ratio changed noticeably to 1.63. Similarly, oxidation of CyH by **13** (8 μmol) in 1 mL of 1:1 CyH/CH_2Cl_2 at 70 °C for 2 h afforded **A** (40%) and **K** (57%) with an **A**/**K** ratio of 0.7. Addition of 20 μmol $Co(OAc)_2 \cdot 4H_2O$ to the same reaction mixture resulted in formation of **A** (80%) and **K** (48%) in the ratio of 1.64. Thus in both cases, addition of the Co(II) salt results in more oxidized products and an enhancement in the formation of **A** relative to **K**. This result strongly suggests that CyOOH is produced in the reaction mixture (reactions 2 and 3 of Scheme 1). When a Co(II) salt is added, it reacts with CyOOH to form CyO$^\bullet$ and Co(III)OH. Abstraction of H atoms from the substrate (CyH) by CyO$^\bullet$ then affords CyOH, and the new Cy$^\bullet$ radical generated in this step promotes more oxidation to improve the overall yields of the oxidized products.

Fate of [LCo^{III}−OOR] after Single Turnover in Stoichiometric Oxidation. Stoichiometric oxidation reactions with the [LCo^{III}−OOR] complexes are not as messy as one expects in a typical radical-driven autoxidation process. The colors of the reaction mixtures indicate that rapid degradation of the cobalt complexes does not occur in most cases. To determine the fate of the [LCo^{III}−OOR] complexes in stoichiometric oxidations, we dissolved **7** in 1 mL of 1:1 d_{12}-cyclohexane/d_2-dichloromethane at 70 °C, and the decomposition of the complex was followed by monitoring the disappearance of the ^{t}Bu peak at 0.56 ppm. At the end of decomposition, as evidenced by the complete disappearance of the peak for the coordinated OO^{t}Bu group, diethyl ether was added to the reaction mixture to precipitate the cobalt-containing end product. The electronic absorption and ^{1}H NMR spectrum of this precipitate were identical to those of authentic [Co(Py$_3$P)(OH)] (**4**). A similar experiment with **13** afforded [Co(PyPz$_2$P)(OH)] (**6**) at the end of stoichiometric oxidation of CyH. In both cases, the [LCo^{III}(OH)] species were isolated in nearly quantitative amounts. These results clearly indicate that decomposition of the [LCo^{III}−OOR] complexes in the presence of hydrocarbon substrate affords the [LCo^{III}(OH)] species as the final product.

Catalytic Oxidation of Hydrocarbon Substrates by [LCo^{III}−OOR] Complexes. The fact that the [LCo^{III}−OOR] complexes are converted into the [LCo^{III}(OH)] complexes after single turnover in oxidation reactions prompted us to design catalytic systems based on these complexes in conjunction with excess ROOH. That this goal has been accomplished in the present study is indicated by the results included in Table 8. Catalytic oxidations have been observed with [LCo^{III}(OH)] (**4**,**6**) and [LCo^{III}−OOR] (**7**,**13**) complexes in the presence of excess TBHP and $PhCMe_2OOH$ (CmOOH). Scale-ups of the catalytic oxidations have been achieved by the use of more catalysts and/or more ROOH with little loss in efficiencies. More than a gram of total oxidized products can be obtained in such reactions within 4 h and at a moderate temperature of 80 °C. The catalysts remain active for over 10 h, and as high as 150 turnovers are obtained at longer (6−8 h) periods of time. Control reactions with soluble Co(II) salts afford much smaller amounts of oxidized products under identical conditions. Interestingly, when the catalytic oxidation of CyH with [Co(PyPz$_2$P)(OH)] and TBHP is allowed to continue for 12 h, adipic acid (∼10% of the total oxidized product, quantitated as dimethyl adipate) is obtained as one of the products. This indicates that **A** and **K**, produced initially in these catalytic oxidations, could be further oxidized in the same reaction vessel.

The results of the catalytic oxidation reactions by the [LCo^{III}−OOR] complexes can be rationalized on the basis of Scheme 1. Here the RO$^\bullet$ radicals formed during initial homolysis of the O−O bond of the [LCo^{III}−OOR] complexes abstract H atoms from both CyH and excess TBHP (or CmOOH). The reaction mixtures in these cases therefore contain an abundance of ^{t}BuOO$^\bullet$ (or CmOO$^\bullet$) radicals that serve two purposes, namely, (a) they act as secondary sources for RO$^\bullet$ radicals (reaction V)

$$^t\mathrm{BuOO}^\bullet \rightarrow {}^t\mathrm{BuO}^\bullet + {}^1/_2\,\mathrm{O}_2 \qquad \text{(V)}$$

$$^t\mathrm{BuO}^\bullet + {}^t\mathrm{BuOO}^\bullet \rightarrow {}^t\mathrm{BuOO}^t\mathrm{Bu} + {}^1/_2\,\mathrm{O}_2 \qquad \text{(VI)}$$

$$2\ {}^t\mathrm{BuOO}^\bullet \rightarrow {}^t\mathrm{BuOOOO}^t\mathrm{Bu} \rightarrow {}^t\mathrm{BuOOO}^t\mathrm{Bu} + {}^1/_2\,\mathrm{O}_2 \qquad \text{(VII)}$$

which in turn promote formation of more **A** and **K** via formation of $Cy^{\bullet}$ radicals (reaction 1 of Scheme 1) in the reaction mixtures, and (b) they provide additional O_2 in the reaction mixture (reactions V−VII) and increase yields of **A** and **K** via reactions 2 and 6 of Scheme 1.[34,49]

The catalytic oxidation reactions with $[LCo^{III}(OH)]$ and $[LCo^{III}{-}OOR]$ complexes are noteworthy for more than one reason. Inspection of Table 8 reveals that the overall conversion of CyH to CyOH and CyO is about 10% within 4 h in all cases. The colors of the reaction mixtures indicate that the $[LCo^{III}{-}OOR]$ species are regenerated during these oxidations. At longer reaction times, slow decomposition of the cobalt complexes to black residue(s) is also noted. Unlike the Du Pont process, corrosive constituents such as acetic acid are not required in such oxidations, and the *same* catalyst can be used for oxidation of *many* substrates. Also, the oxidation reactions proceed at respectable speed at moderate temperatures. It will be interesting to find out whether unreacted CyH could be separated from the reaction mixture and then recycled to design an efficient homogeneous catalytic system for alkane oxidation based on these cobalt complexes. Such studies are in progress in this laboratory.

To date, several groups have reported oxidation of hydrocarbons by ROOH in the presence of cobalt salts.[1] In most cases, the results have been rationalized in terms of some or all of the reactions included in Scheme 1 and the intermediacy of $[L_nCo^{III}{-}OOR]$ species. However, prior to this report, very few $[L_nCo^{III}{-}OOR]$ species had been structurally characterized and their exact role(s) in the overall oxidation remained somewhat speculative. In the present work, we have employed a series of structurally characterized $[LCo^{III}{-}OOR]$ complexes with two different L's and many different R groups in the oxidation of several hydrocarbons and identified the various factors that govern the decomposition of these intermediates and their capacity of alkane oxidation. No other group has undertaken this task before. The results of the present work clearly indicate that $[L_nCo^{III}{-}OOR]$ intermediates, if formed in the reaction mixture, break down quite readily to provide $RO^{\bullet}$ radicals and continue the oxidation process. The notion that such complexes are dead-end species is therefore not correct. Also, the overall activities of the $[LCo^{III}{-}OOR]$ complexes described in this account suggest that such complexes can be utilized in carrying out oxidation of C−H bonds under *mild* conditions.

Summary and Conclusions

The following are the principal results and conclusions of this investigation.

(i) Reactions of $[LCo^{III}(OH)]$ with ROOH in aprotic solvents of low polarity afford $[LCo^{III}{-}OOR]$ complexes in nearly quantitative yields. This procedure is clean, convenient, and works for primary, secondary, and tertiary R groups.

(ii) The structures of several $[LCo^{III}{-}OOR]$ complexes indicate, for the first time, that the O−O bond distances in these complexes do not change significantly with R groups.

(iii) When warmed (60−80 °C) in aprotic solvents of low polarity, $[LCo^{III}{-}OOR]$ complexes undergo O−O bond homolysis and afford $RO^{\bullet}$ radicals in solution. If alkanes are present in such solutions, oxidation of alkane C−H bonds is observed. These oxidation reactions are promoted by $RO^{\bullet}$ radicals and are autocatalytic to some extent. The $[LCo^{III}{-}O^{\bullet}]$ unit, the other product of homolysis, is not capable of promoting alkane oxidation. The results of hydrocarbon oxidation by various $[LCo^{III}{-}OOR]$ complexes point toward a mechanism of oxidation that is also supported by the known reactions of $RO^{\bullet}$ and $ROO^{\bullet}$ radicals.

(iv) In stoichiometric oxidation of alkanes, more oxidation is observed with $[LCo^{III}{-}OOR]$ complexes containing tertiary R groups. The extent of oxidation also depends on L. Thus, $[LCo^{III}{-}OOR]$ complexes with $L = PyPz_2P^{2-}$ afford higher yields of the oxidized products compared to the yields of similar complexes with $L = Py_3P^{2-}$.

(v) Stoichiometric oxidation of alkanes by $[LCo^{III}{-}OOR]$ complexes proceeds to a significant extent in aprotic solvents of low polarity. The presence of water in the oxidation medium impedes oxidation via conversion of $[LCo^{III}{-}OOR]$ to $[LCo^{III}(OH)]$.

(vi) In stoichiometric oxidation reactions, $[LCo^{III}{-}OOR]$ complexes are converted to $[LCo^{III}(OH)]$ at the end of one turnover.

(vii) Oxidation of cyclohexane by $[LCo^{III}{-}OOR]$ or $[LCo^{III}(OH)]$ can be made catalytic by the addition of excess ROOH to the reaction mixtures. Grams of oxidized products are obtained in such oxidation reactions within hours at 80 °C.

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Supporting Information Available: Computer-generated thermal ellipsoid plot (50% probability level) of **9** (Figure S1), hydrogen-bonding scheme in the structure of **10** (Figure S2), molecular structure of **12** (Figure S3), ^1H NMR spectra of **7**, **8**, and **11** in $CDCl_3$ (Figure S4); spectroscopic data for **8**−**18**, crystal structure data for **8**−**12** and **16** including atomic coordinates and isotropic thermal parameters, bond distances and angles, anisotropic thermal parameters, and H-atom coordinates (64 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(49) Milas, N. A.; Plesnicar, B. *J. Am. Chem. Soc*. **1968**, *90*, 4450.