Syntheses and Stuctures of Alkyl Peroxo Adducts of β-Diketonate Cobalt(III) Complexes and Their Role in Oxidation of Hydrocarbons and Olefin Epoxidation

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To assess the oxidizing capacity of [Co(β-diketonate)$_2$(L)OOR] complexes, four such species, namely, [Co(acac)$_2$(L)(OO^{t}Bu)] (acacH = acetylacetone; L = pyridine (py) (**1**), 4-methylpyridine (4-Mepy) (**2**), 1-methylimidazole (1-MeIm) (**3**)) and [Co(dbm)$_2$(py)(OO^{t}Bu)] (**4**, dbmH = dibenzoylmethane), have been synthesized and the structures of **1**, **3**, and **4** have been determined by X-ray crystallography. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.149(2)$ Å, $b = 9.741(2)$ Å, $c = 13.067(2)$ Å, $\alpha = 84.22\ (2)°$, $\beta = 77.89(2)°$, $\gamma = 67.83(2)°$, $V = 1054.1(4)$ Å^3, and $Z = 2$. Complex **3** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.341(2)$ Å, $b = 10.485(2)$ Å, $c = 18.863(2)$ Å, $\alpha = 90°$, $\beta = 106.230(15)°$, $\gamma = 90°$, $V = 2153.6(8)$ Å^3, and $Z = 4$. Complex **4**$\cdot 1.5C_6H_6$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 14.907(5)$ Å, $b = 18.701(5)$ Å, $c = 15.207(4)$ Å, $\alpha = 90°$, $\beta = 103.52\ (2)°$, $\gamma = 90°$, $V = 4122(2)$ Å^3, and $Z = 4$. The geometry around the Co(III) center in all four complexes is distorted octahedral, and the two β-diketonate ligands are cis to each other. The Co−O and O−O bond distances in the Co−OO^{t}Bu moiety fall in the narrow ranges of 1.860(3)−1.879(2) and 1.451(3)−1.466(3) Å, respectively. Although stable in the solid state, these complexes decompose in benzene or halocarbon solutions to afford ^{t}BuOO$^\bullet$ and ^{t}BuO$^\bullet$ radicals. When alkanes like cyclohexane are present in the reaction mixture, these radicals initiate oxidation of the C−H bond. The oxidizing capacity follows the order **1** > **2** > **3** > **4**. Decomposition of the complexes in the presence of cyclohexene and an aldehyde results in selective epoxidation in high yield.

Introduction

Catalytic oxidation of inexpensive hydrocarbons by metal catalysts in conjunction with benign oxidants like O_2 and peroxides under mild conditions is an important goal in large-scale industrial processes and in syntheses of fine chemicals.[1,2] In recent years, design of industrial processes also has required inclusion of the theme of "green chemistry", which requires fewer negative impacts on the environment without losing efficiency.[1] It is quite obvious that development of new green oxidation processes as well as modification of the existing ones requires a thorough understanding of the fundamental reactions that ultimately lead to oxidation of specific substrates. Precise information on the mechanisms of these reactions and the nature of the intermediates is absolutely essential for the design of new systems that are safe, inexpensive, and versatile. To date, examples of large-scale industrial processes that utilize catalytic oxidation include the Mid-Century/Amoco process where *p*-xylene is oxidized to terephthalic acid and the DuPont adipic acid synthesis in which cyclohexane is first oxidized to cyclohexanol and cyclohexanone. The "ol and one" mixture is then further oxidized to adipic acid, which is the starting material for the production of nylon 6,6. These methods utilize a cobalt catalyst and are carried out under high pressure and temperature. The cobalt catalyst initiates the free radical autoxidation chains and also decomposes the ROOH species formed in the reaction mixtures. It is believed that both catalytic processes involve a transient Co(III)−alkylperoxide interemediate which is crucial for sustaining production of radicals and decomposition of alkyl hydroperoxides.[1a,2c,3] The oxidation of Co(II) to Co(III) is evident from the change in color of the reaction mixture from violet or pink to dark green due to formation of Co(III)−OOR species. Subsequent decomposition of such species leads to regeneration of the Co(II) catalyst and production of RO$^\bullet$ and ROO$^\bullet$, which initiate and sustain the autoxidation reactions. It is quite evident that efficient generation of such radicals under mild conditions is the key to performing catalytic oxidations at moderate temperature and pressure.

For some time, we have been involved in determination of the oxidizing capacities of structurally characterized [LCo^{III}−OOR] complexes. As part of this pursuit, we have reported the syntheses, structures, and reactivities of isolated [LCo^{III}−OOR] complexes with L = pentadentate strong-field ligands and R = CMe_3, CMe_2Ph, CMe_2CH_2Ph, $CHMe_2$, c-C_6H_{11}, and $CH_2CH_2CH_3$.[4,5] Our results have revealed that the [LCo^{III}−OOR] complexes decompose primarily by O−O bond homolysis and afford RO$^\bullet$ radicals in the reaction mixtures. When a hydrocarbon substrate is present, the RO$^\bullet$ radical abstracts an H atom

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from it and initiates autoxidation reactions. The largest amount of oxidized products is obtained when the R group in [LCo^{III}−OOR] is CMe$_3$ (^{t}Bu). To further explore the influence of the ligand (L) on the stability of the [LCo^{III}−OOR] complexes and their capacity to initiate hydrocarbon oxidation, we have recently turned our attention to the β-diketonate complexes of cobalt. The commercially available Co(II) complex of acetylacetone, [Co(acac)$_2$], has been employed in conjunction with radical initiator[6] or alkyl hydroperoxide[7] to oxidize hydrocarbon substrates to the corresponding alcohols and ketones. In the later report, the relevance of [Co(acac)$_2$(py)(OOR)] species in the oxidation of hydrocarbons in reaction mixtures consisting of [Co(acac)$_2$]/PhCMe$_2$OOH/pyridine has been discussed.[7] A close scrutiny of the literature, however, reveals that, to date, no systematic study has been carried out to assess the ability of [Co(β-diketonate)$_2$(L)OOR] complexes to catalyze oxidation of hydrocarbons. Furthermore, no [Co(β-diketonate)$_2$(L)OOR] species has been characterized by X-ray crystallography. We herein report the syntheses and characterization of four [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes. They are [Co(acac)$_2$(L)(OO^{t}Bu)] (acacH = acetylacetone; L = pyridine (py) (**1**), 4-methylpyridine (4-Mepy) (**2**), 1-methylimidazole (1-MeIm) (**3**)) and [Co(dbm)$_2$(py)(OO^{t}Bu)] (**4**, dbmH = dibenzoylmethane). The structures of **1**, **3**, and **4** have been determined by X-ray crystallography, and their metric parameters have been compared. The capacities of these complexes to induce hydrocarbon oxidation and olefin epoxidation have been determined. Analysis of products of these reactions indicates that, unlike our previous [LCo^{III}−OOR] complexes,[4,5] the present [Co(β-diketonate)$_2$(L)OOR] complexes decompose in the reaction mixture via homolysis of both the Co−O and O−O bonds of the Co−OO^{t}Bu moiety. Oxidation of hydrocarbons and epoxidation of olefins by these complexes are carried out by the resulting ^{t}BuOO$^\bullet$ and ^{t}BuO$^\bullet$ radicals.

Experimental Section

Materials. Cobalt(II) acetylacetonate, 4-methylpyridine, 1-methylimidazole, dibenzoylmethane, cyclohexene, and propionaldehyde were purchased from Aldrich Chemical Co. *tert*-Butyl hydroperoxide (TBHP, 70%), also procured from Aldrich, was dried over anhydrous MgSO$_4$. All solvents were dried and distilled following standard methods. Cyclohexene and propionaldehyde were freshly distilled before use. [Co(dbm)$_2$] was synthesized by following a procedure for the preparation of [Co(acac)$_2$].[8]

General Procedure for the Syntheses of [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] Complexes. The [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes were synthesized by following the method of Talzi and co-workers[7] with some modifications. In a typical sythesis, 1 g of [Co(acac)$_2$] (3.9 mmol) or [Co(dbm)$_2$] (2.0 mmol) was dissolved in 5 mL of benzene, and to this was added 2 equiv of the N-donor ligand L. To this solution was then added 3 equiv of dry TBHP, and the mixture was stirred at room temperature. After 1 h, pentane was added to the reaction mixture until a small amount of precipitate formed (approximately 60 mL for the [Co(acac)$_2$(L)(OO^{t}Bu)] complexes and 10 mL for [Co(dbm)$_2$(py)(OO^{t}Bu)]), and the mixture was filtered. The filtrate was then stored at 4 °C. Dark blocks were deposited after 14 h. The crystals were collected and washed with water and pentane. All [Co(β-diketonate)$_2$(L)OO^{t}Bu] complexes were isolated in analytically pure and crystalline form in 40−50% yield based on [Co(β-diketonate)$_2$].

Spectral Data. [Co(acac)$_2$(py)(OO^{t}Bu)] (1). ^{1}H NMR (C$_6$D$_6$, 250 MHz), δ (from TMS): 1.51 (9H, s, ^{t}Bu), 1.84 (3H, s), 1.89 (3H, s), 1.96 (3H, s), 2.05 (3H, s), 5.15 (1H, s), 5.38 (1H, s), 6.69 (2H, t), 6.91 (1H, t), 8.87 (2H, d). Selected IR bands (KBr pellet, cm^{-1}): 3422 (m, br), 3084 (w), 2969 (m), 2921 (m), 1581 (s), 1520 (vs), 1395 (s), 1353 (m), 1279 (m), 1192 (m), 1070 (w), 1020 (m), 934 (w), 875 (w), 832 (w), 762 (m), 693 (m), 662 (w), 620 (w), 615 (w), 585 (w), 509 (w). Electronic absorption spectrum, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): in benzene, 662 (sh, 140), 587 (159), 335 (sh, 4 950).

[Co(acac)$_2$(4-Mepy)(OO^{t}Bu)] (2). ^{1}H NMR (C$_6$D$_6$, 250 MHz), δ (from TMS): 1.52 (9H, s, ^{t}Bu), 1.67 (3H, s, 4-Mepy), 1.87 (3H, s), 1.91 (3H, s), 2.00 (3H, s), 2.06 (3H, s), 5.17 (1H, s), 5.40 (1H, s), 6.53 (2H, d), 8.71 (2H, d). Selected IR bands (KBr pellet, cm^{-1}): 3448 (m, br), 3049 (w), 2970 (m), 2923 (m), 1584 (s), 1520 (vs), 1390 (s), 1353 (m), 1334 (m), 1278 (m), 1231 (w), 1215 m), 1194 (s), 1075 (w), 1019 m), 935 (m), 884 (m), 823 (m), 776 (m), 756 (m), 720 (w), 688 (w), 662 (m), 647 (m), 628 (m), 509 (m). Electronic absorption spectrum, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): in benzene, 655 (sh, 150), 573 (sh, 162), 335 (sh, 5800).

[Co(acac)$_2$(1-MeIm)(OO^{t}Bu)] (3). ^{1}H NMR (C$_6$D$_6$, 250 MHz), δ (from TMS): 1.55 (9H, s, ^{t}Bu), 1.86 (3H, s), 1.95 (6H, s), 2.03 (3H, s), 2.70 (3H, s, 1-MeIm), 5.27 (1H, s), 5.36 (1H, s), 6.17 (1H, s), 7.23 (1H, s), 8.11 (1H, s). Selected IR bands (KBr pellet, cm^{-1}): 3422 (m, br), 3144 (w), 2960 (m), 2922 (m), 1585 (s), 1519 (vs), 1396 (s), 1355 (m), 1276 (m), 1233 (m), 1192 (m), 1104 (m), 1026 (m), 934 (w), 885 (w), 753 (w), 721 (w), 662 (m), 631 (w). Electronic absorption spectrum, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): in benzene, 653 (150), 585 (sh, 153), 335 (sh, 5800).

[Co(dbm)$_2$(py)(OO^{t}Bu)]·1.5C$_6$H$_6$ (4·1.5C$_6$H$_6$). ^{1}H NMR (CDCl$_3$, 250 MHz), δ (from TMS): 1.15 (9H, s, ^{t}Bu), 6.69 (1H, s), 6.82 (1H, s), 7.36 (14H, m), 7.72 (1H, t), 7.90 (4H, m), 7.99 (2H, d), 8.11 (2H, d), 8.81 (2H, d). Selected IR bands (KBr pellet, cm^{-1}): 3633 (m), 2968 (m), 1591 (s), 1525 (vs), 1482 (s), 1452 (s), 1390 (s), 1354 (s), 1317 (s), 1228 (m), 1192 (m), 1159 (m), 1070 (m), 1025 (m), 948 (w), 879 (m), 841 (w), 796 (w), 752 (m), 721 (m), 676 (s), 611 (w), 561 (m), 542 (w). Electronic absorption spectrum, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): in benzene, 585 (sh, 197), 675 (sh, 170), 330 (22 000), 290 (sh, 25 000).

Other 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 Bruker 250 MHz Instrument. 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 μm) capillary column (Alltech).

Oxidation of Hydrocarbon Substrates. In a typical stoichiometric oxidation experiment, 60 μmol of [Co(β-diketonate)$_2$(L)OO^{t}Bu] complex was dissolved in 1 mL of substrate/solvent in a 2 dram screw cap vial fitted with a Teflon seal and was kept at ambient temperature for a certain number of hours. The reaction was then quenched by addition of a 6-fold excess (based on the cobalt complex) of triphenylphosphine, and the products were analyzed by gas chromatography. An internal standard was added to the products before GC analyses. Products were identified and quantitated by comparison with authentic samples.

X-ray Data Collection and Structure Solution and Refinement. Dark brown plates of **1**, black needles of **3**, and black plates of **4**·1.5C$_6$H$_6$, suitable for X-ray analysis, were obtained by slow cooling (4 °C) of the reaction mixtures in benzene/pentane which also contained small amounts of TBHP. Structures of complexes **1** and **3** are well ordered, and their unit cells are devoid of any solvent molecule. Complex **4**·1.5C$_6$H$_6$, however, contains a disordered peroxide group which was sucessfully modeled as two sets of atoms, excluding O1 and C1, which are shared. Disordered atoms of the same type were refined with common thermal parameters. Set A has 59.4(6)% occupancy, while set B has 40.6(6)% occupancy. In addition, the unit cell contains 1.5 benzene molecules.

Diffraction data was collected at 140(2) K on a Siemens R3m/V diffractometer equipped with a normal-focus sealed tube and Enraf Nonius low-temperature apparatus. Mo Kα radiation (λ = 0.710 73

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Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for [Co(acac)$_2$(py)(OO^{t}Bu)] (**1**), [Co(acac)$_2$(1-MeIm)(OO^{t}Bu)] (**3**) and [Co(dbm)$_2$(py)(OO^{t}Bu)]·1.5C$_6$H$_6$ (**4**·1.5C$_6$H$_6$)

	1	**3**	**4**·1.5C$_6$H$_6$
formula	$C_{19}H_{28}NO_6Co$	$C_{18}H_{29}N_2O_6Co$	$C_{48}H_{45}NO_6Co$
mol wt	425.35	428.36	790.78
cryst color, habit	brown plate	black needle	black plate
T, K	140(2)	140(2)	140(2)
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	9.149(2)	11.341(2)	14.907(5)
b, Å	9.741(2)	10.485(2)	18.701(5)
c, Å	13.067(2)	18.863(4)	15.207(4)
α, deg	84.22(2)	90	90
β, deg	77.89(2)	106.230(15)	103.52(2)
γ, deg	67.83(2)	90	90
V, Å^3	2634.3(9)	2153.6(8)	4122(2)
Z	2	4	4
d_{calcd}, g cm^{-1}	1.340	1.321	1.274
abs coeff, μ, mm^{-1}	0.846	0.830	0.466
GOF^a on F^2	1.012	1.018	1.003
R1,^{b} %	4.83	4.03	6.21
wR2,^{c} %	11.04	8.43	11.94

^{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 $= [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Å) was employed. Only random fluctuations of <1% in the intensities of two standard reflections were observed during data collection. The structure of **1** was solved in $P\bar{1}$, the structure of **3** was solved in $P2_1/n$, and the structure of **4**·1.5C$_6$H$_6$ was solved in $P2_1/c$ using direct methods (SHELXTL 5, Sheldrick 1990). All calculations were carried out on a 486/DX50 computer using the SHELXTL version 5.03 program.[9] The data were corrected for absorption effects by the use of the program XABS2.[10] 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 have been submitted as Supporting Information.

Results and Discussion

The synthetic strategy for the synthesis of [Co(β-diketonate)-(L)(OO^{t}Bu)] complexes involves addition of excess dry TBHP to a mixture of [Co(β-diketonate)$_2$] and N-donor ligand L in benzene. Stirring of this mixture for 1 h under ambient conditions affords a deep green solution. Subsequent addition of pentane to this mixture followed by filtration and cooling at 4 °C affords a crystalline product in each case. The [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes are relatively stable in the solid state and can be stored for months at 4 °C in a desiccator. However, when these complexes are redissolved in benzene or halogenated solvents, they begin to decompose slowly. Their decomposition is slightly accelerated in halogenated solvents such as chloroform and dichloromethane. In contrast, [LCo$^{\mathrm{III}}$−OOR] complexes with L = strong field pentadentate ligands such as Py$_3$PH$_2$ and PyPz$_2$PH$_2$ are stable for days in halogenated solvents.[4,5] The [Co(acac)$_2$(L)(OO^{t}Bu)] complexes with L = py (**1**) or 4-Mepy (**2**) are somewhat less stable than the 1-MeIm derivative (**3**) and [Co(dbm)$_2$(py)(OO^{t}Bu)] (**4**). Interestingly, when [Co(acac)$_2$(py)(OO^{t}Bu)] is dissolved in a 1:1 mixture of CH$_2$Cl$_2$:c-C$_6$H$_{12}$, its stability is enhanced to a noticeable extent. The solubility of **1**−**4** in saturated alkanes such as cyclohexane is low. Much higher solubility is noted for all complexes in olefins such as cyclohexene and aromatics such as benzene and toluene.

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

[Co(acac)$_2$(py)(OO^{t}Bu)](**1**)

Bond Distances

Co−N	1.956(2)	O5−O6	1.451(3)
Co−O1	1.902(2)	O1−C1	1.270(3)
Co−O2	1.8989(19)	O2−C3	1.273(3)
Co−O3	1.8906(19)	O3−O6	1.277(4)
Co−O4	1.937(2)	O4−C8	1.272(3)
Co−O5	1.879(2)	O6−C11	1.453(4)

Bond Angles

Co−N−C19	120.08(18)	O1−Co−O2	95.79(8)
Co−O1−C1	124.24(19)	O1−Co−O3	87.78(9)
Co−O2−C3	124.19(19)	O1−Co−O4	88.70(9)
Co−O3−C6	124.85(19)	O1−Co−O5	89.03(9)
Co−O4−C8	124.04(19)	O2−Co−O3	176.22(8)
Co−O5−O6	115.54(15)	O2−Co−O4	86.47(8)
N−Co−O1	176.77(9)	O2−Co−O5	85.15(9)
N−Co−O2	87.16(9)	O3−Co−O4	94.87(9)
N−Co−O3	89.30(9)	O3−Co−O5	93.68(9)
N−Co−O4	90.17(9)	O4−Co−O5	171.05(8)
N−Co−O5	92.54(9)	O5−O6−C11	111.1(2)

[Co(acac)$_2$(1−MeIm)(OO^{t}Bu)](**3**)

Bond Distances

Co−N1	1.934(2)	O5−O6	1.466(3)
Co−O1	1.9281(19)	O1−C1	1.269(3)
Co−O2	1.8955(19)	O2−C3	1.271(3)
Co−O3	1.8842(19)	O3−O6	1.272(3)
Co−O4	1.8899(19)	O4−C8	1.267(3)
Co−O5	1.8670(19)	O6−C11	1.442(4)

Bond Angles

Co−N1−C17	127.01(19)	O1−Co−O2	94.68(8)
Co−O1−C1	124.12(18)	O1−Co−O3	87.28(8)
Co−O2−C3	124.98(18)	O1−Co−O4	87.92(8)
Co−O3−C6	124.27(19)	O1−Co−O5	179.58(8)
Co−O4−C8	123.64(19)	O2−Co−O3	176.28(9)
Co−O5−O6	109.56(14)	O2−Co−O4	86.76(8)
N1−Co−O1	91.60(9)	O2−Co−O5	85.38(9)
N1−Co−O2	89.58(9)	O3−Co−O4	96.48(8)
N1−Co−O3	87.20(9)	O3−Co−O5	92.64(8)
N1−Co−O4	176.26(9)	O4−Co−O5	92.49(8)
N1−Co−O5	87.99(9)	O5−O6−C11	108.18(19)

[Co(dbm)$_2$(py)(OO^{t}Bu)]·1.5C$_6$H$_6$(**4**·1.5C$_6$H$_6$)

Bond Distances

Co−N	1.940(3)	O1−O2B	1.465(8)
Co−O1	1.860(3)	O2A−C1	1.468(7)
Co−O3	1.884(3)	O2B−C1	1.387(8)
Co−O4	1.899(3)	O3−C5	1.282(5)
Co−O5	1.898(3)	O4−C13	1.278(5)
Co−O6	1.927(3)	O5−C20	1.267(5)
O1−O2A	1.454(6)	O6−C28	1.269(5)

Bond Angles

Co−N−C39	120.8(3)	O1−Co−O3	96.20(12)
Co−O1−O2A	111.4(3)	O1−Co−O4	92.25(12)
Co−O1−O2B	112.1(3)	O1−Co−O5	83.19(12)
Co−O3−C5	123.5(3)	O1−Co−O6	177.12(12)
Co−O4−C13	123.6(3)	O3−Co−O4	95.65(11)
Co−O5−C20	124.1(2)	O3−Co−O5	177.08(12)
Co−O6−C28	123.5(2)	O3−Co−O6	86.68(12)
N−Co−O1	89.50(14)	O4−Co−O5	87.23(11)
N−Co−O3	87.37(13)	O4−Co−O6	87.44(12)
N−Co−O4	176.32(13)	O5−Co−O6	93.93(12)
N−Co−O5	89.77(13)	O1−O2A−C1	107.2(4)
N−Co−O6	90.64(13)	O1−O2B−C1	111.1(5)

One interesting feature of the [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes has emerged from the present study: all of the

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[9] 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 the following: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer: Dordrecht, The Netherlands, 1992; Vol. C.

[10] Parkins, S.; Moezzi, B.; Hope, H. XABS2: An empirical absorption corrections program. *J. Appl. Crystallogr.* **1995**, 53−56.

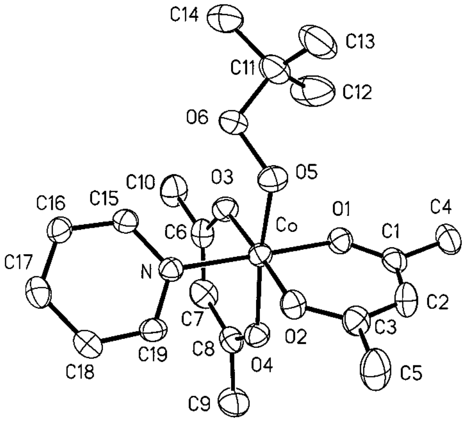

Figure 1. Thermal ellipsoid (probability level 50%) plot of [Co(acac)$_2$(py)(OO^{t}Bu)] (**1**) with atom-labeling scheme. H atoms are omitted for the sake of clarity.

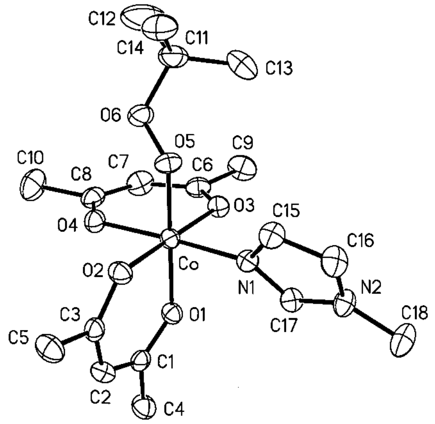

Figure 2. Thermal ellipsoid (probability level 50%) plot of [Co(acac)$_2$(1-MeIm)(OO^{t}Bu)] (**3**) with atom-labeling scheme. H atoms are omitted for the sake of clarity.

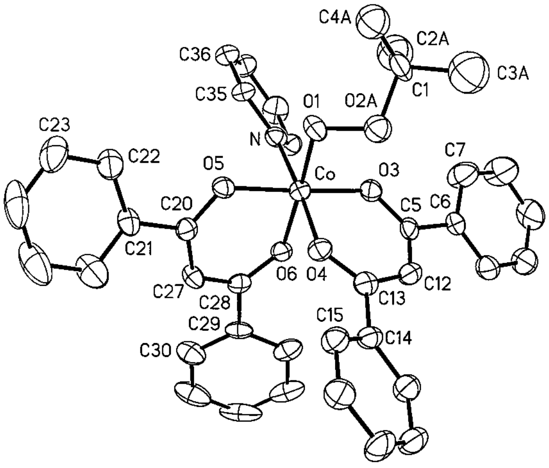

Figure 3. Thermal ellipsoid (probability level 50%) plot of [Co(dbm)$_2$(py)(OO^{t}Bu)] (**4**) with atom-labeling scheme. H atoms are omitted for the sake of clarity.

isolated complexes have the cis configuration. Attempts to synthesize and isolate the trans species were unsuccessful even when starting materials such as *trans*-[Co^{II}(acac)$_2$(2-aminopyridine)],[11] *trans*-[Co^{II}(acac)$_2$(py)],[12] and *trans*-[Co^{II}(acac)$_2$(py)$_2$][13] were employed. Results of studies on the stereochemistry of [Co^{III}(acac)$_2$(X)(Y)] complexes (where X and Y are monodentate ligands) by Herrington and Boucher suggest that (a) the cis configuration of these complexes is more stable than the trans configuration and (b) although both may form initially, the trans species tends to isomerize to the cis species within hours.[14] Isolation of the cis forms of **1**−**4** is therefore not surprising.

Structures of [Co(acac)$_2$(py)(OO^{t}Bu)] (1) and [Co(acac)$_2$(1-MeIm)(OO^{t}Bu)] (3). The molecular structures of **1** and **3** are shown in Figures 1 and 2, respectively. Selected bond distances and bond angles for these two complexes are listed in Table 2. In both **1** and **3**, the cobalt atom is coordinated to five oxygen atoms (four from the acac$^-$ ligands and one from the OO^{t}Bu group) and one nitrogen (pyridine nitrogen in **1** and 3-imidazole nitrogen in **3**) in an octahedral fashion. The Co−O5 bond length in **1** (1.879(2) Å) is slightly longer than the corresponding bond distance in **3** (1.867(2) Å); both, however, are longer than the same corresponding distance in [Co(BPI)(OBz)(OO^{t}Bu)][15] (1.838(5) Å), which is the only other structurally characterized Co(III)−alkylperoxide complex possessing an oxygen donor trans to a OO^{t}Bu group. The O−O bond distance in **1** (1.451(3) Å) is slightly shorter than the corresponding bond in **3** (1.466(3) Å). Both, however, are well within the range of O−O bond distances of other Co(III)−alkylperoxide complexes (1.40−1.50 Å).[4,5,15,16] The O6−C11 bond distances in **1** (1.453(4) Å) and **3** (1.442(4) Å) also fall within the range of such distances for other structurally characterized [LCo^{III}−OO^{t}Bu] complexes.[4,5] In the basal plane of **1**, the Co−O bond trans to the pyridine is elongated (1.9281(2) Å) compared to the other equatorial Co−O bonds (1.899(2) and 1.891(2) Å). Complex **3**, however, has very similar equatorial Co−O distances (see Figure 2). The Co−N bond distance in **1** (1.956(2) Å) is also noticeably longer than the Co−N bond distance in **3** (1.934(2) Å).

Structure of [Co(dbm)$_2$(py)(OO^{t}Bu)]·1.5C$_6$H$_6$ (4·1.5C$_6$H$_6$). The molecular structure of **4** is displayed in Figure 3, and selected bond distances and bond angles are listed in Table 2. As in **1** and **3**, the geometry around the cobalt(III) center of **4** is distorted octahedral with five oxygen atoms (four from the dbm$^-$ ligands and one from the OO^{t}Bu group) and one pyridine nitrogen serving as the donors. The Co−O1 bond length (1.860(3) Å) is shorter than the same bond distance in **1**, presumably due to greater electron delocalization in the ligand framework of dbm$^-$ with phenyl groups. The Co−N bond distance in **4** (1.940(2) Å) is also shorter than the Co−N bond distance in **1** (1.956(2) Å). Although the O−O bond in **4** is disordered, the weighted average O−O bond distance (1.458 Å) is very similar to the O−O bond distance in **1** (1.451(3) Å).

^{1}H NMR Spectra of [Co(*β*-diketonate)(L)(OO^{t}Bu)] Complexes. The ^{1}H NMR spectra of **1**−**4** have been monitored at 25 °C with freshly prepared solution in C$_6$D$_6$ (vide infra) with Me$_4$Si as the internal standard. All four complexes exhibit clean NMR spectra (Figures S1 and S2, Supporting Information)

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[11] Doring, M.; Gorls, H.; Uhlig, E. *Z. Anorg. Allg. Chem.* **1991**, *603*, 7.

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which confirm their integrity in solution. The ^{t}Bu group of these [Co(β-diketonate)(L)OO^{t}Bu] complexes gives rise to a sharp singlet at ~1.5 ppm. The methyl group of the 4-methylpyridine ligand of **2** resonates at 1.67 ppm while the peak for the methyl group of the 1-methylimidazole ligand of **3** is noted at 2.70 ppm. In the case of complexes **1**−**3**, retention of the cis configuration in solution is clearly indicated by (a) nonequivalence of the methine protons of the acac$^-$ ligand (two peaks around 5.3 ppm) and (b) appearance of separate resonances for the methyl groups of the acac$^-$ ligands between 1.8 and 2.2 ppm (some overlap is observed with complex **3**). The nonequivalency of the methine protons in complex **4** is not clear in C_6D_6 solution due to overlap with the aromatic resonances. However, when the spectrum is monitored in $CDCl_3$, separate peaks for the two protons are observed. This confirms the cis configuration of **4** in solution.

Role of Ligands in the Stability of the [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] Complexes. NMR spectra of all four of the [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes indicate that they lose the coordinated ^{t}BuOO$^-$ group when dissolved in benzene or chloroform. Such loss of coordinated ^{t}BuOO$^-$ groups from complexes **1**−**4** in C_6D_6 at room temperature has been monitored by following the disappearance of the peak for the coordinated ^{t}BuOO$^-$ group in their ^{1}H NMR spectra. Results of these studies indicate that the rate of loss of the coordinated ^{t}BuOO$^-$ group is slow in benzene compared to chloroform and continues over a period of 2−3 days. The rate follows the order **1** > **2** > **3** > **4** in C_6D_6. In the case of complex **1**, loss of the coordinated ^{t}BuOO$^-$ group is complete within 48 h, while complex **4** takes 96 h to completely lose the same group. It is interesting to note that the order of the rate of this loss, namely, **1** > **3** > **4**, parallels the Co−O bond distance of the Co−OO^{t}Bu moiety of these species (**1** > **3** > **4**, Table 2).

Oxidation of Hydrocarbons with [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] Complexes. When complexes **1**−**4** are dissolved in 1 mL of 2:3 C_6H_6:CyH, they initiate oxidation of cyclohexane (CyH) to cyclohexanol (CyOH), cyclohexanone (CyO), and *tert*-butyl cyclohexyl peroxide (CyOO^{t}Bu). A noticeable extent of oxidation is observed at temperatures as low as 2 °C. Results of oxidation carried out for 2 h and at different temperatures indicate that the yields of the oxidized products (yields based on the amounts of the cobalt complexes) increase with temperature up to 50 °C. Further increases in temperature result in diminished yields, presumably due to complete destruction of cobalt complex early in the reaction. Among complexes **1**−**4**, **1** appears to be the most active oxidizing agent and affords the highest yields of oxidized products at temperatures up to 50 °C. It is, however, more convenient to run the oxidation reactions at room temperature for longer periods of time. For example, when **1** is dissolved in 1 mL of 2:3 C_6H_6:CyH and allowed to stand for 2 h at room temperature, CyOH, CyO, and CyOO^{t}Bu are obtained in 23%, 8%, and 2% yield, respectively. When stored for 15 h, the same reaction mixture affords 50% CyOH, 20% CyO, and 1% CyOO^{t}Bu. Substrates with considerably weaker C−H bonds (compared to cyclohexane), such as compounds possessing allylic or benzylic groups, are oxidized at those positions at a greater rate when mixed with the [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes. For example, when 60 μmol of **1** is dissolved in neat indan and allowed to stand at room temperature, 43% 1-indanol and 19% 1-indanone are obtained after 2 h.

The product distributions of the oxidation reactions provide clues regarding the nature of the active species actually responsible for oxidation of hydrocarbons by the present [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes. In the case of oxidation of CyH by all four cobalt complexes (**1**−**4**) at 50 °C, the mixed peroxide CyOO^{t}Bu is obtained in noticeable yields. This result indicates that the [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes undergo homolysis of the Co−O bond of the Co−OO^{t}Bu moiety and afford ^{t}BuOO$^\bullet$ radicals in the reaction mixture.[17] To confirm the presence of significant amounts of ^{t}BuOO$^\bullet$ radicals in the reaction mixture at room temperature, the following trapping experiment was performed. Under anaerobic conditions, a solution of [Co(acac)$_2$(py)(OO^{t}Bu)] (**1**) in C_6D_6 was mixed with a solution of excess [Co^{II}(Py$_3$P)]^4 in CH_2Cl_2 and kept at room temperature for 48 h. Next, the reaction mixture was exposed to air to remove all paramagnetic Co(II) species, and the resulting solution was filtered. The ^{1}H NMR spectrum of the filtrate showed the presence (in 40% yield) of [Co^{III}(Py$_3$P)(OO^{t}Bu)],^{4} a stable species formed via trapping of the ^{t}BuOO$^\bullet$ radicals by [Co^{II}(Py$_3$P)] (eq 1).

$$[\mathrm{Co^{II}(Py_3P)}] + {}^t\mathrm{BuOO}^\bullet \rightarrow [\mathrm{Co^{III}(Py_3P)(OO^tBu)}] \qquad (1)$$

Talzi and co-workers have studied the decomposition of [Co(acac)$_2$(py)(OOCMe$_2$Ph)] in $CDCl_3$ by EPR spectroscopy.[18] Their results demonstrate that [Co(acac)$_2$(py)(OOCMe$_2$Ph)] also undergoes homolysis of the Co−O bond in the Co−OOR fragment at room temperature. Collectively, these results show that the [Co(β-diketonate)$_2$(L)(OO^{t}Bu)] complexes afford ^{t}BuOO$^\bullet$ radicals in solution at all temperatures. Since ^{t}BuOO$^\bullet$ radical is not strong enough (radical strength = 83 kcal/mol)[19] to abstract an H atom from C−H bonds of higher molecular weight (>C_4) alkanes including CyH (bond energy = 95 kcal/mol)[20] at room temperature, it is also evident that more energetic ^{t}BuO$^\bullet$ radicals (radical strength = 105 kcal/mol)[20] are generated in the reaction mixture either via homolysis of the O−O bond of the Co−OOR fragment or via the disproportionation reaction 2.

$$2\,{}^t\mathrm{BuOO}^\bullet \rightarrow 2\,{}^t\mathrm{BuO}^\bullet + \mathrm{O_2} \qquad (2)$$

With both ^{t}BuO$^\bullet$ and ^{t}BuOO$^\bullet$ radicals in the reaction mixture, one can account for all the products of oxidation of cyclohexane by **1**−**4**. At room temperature, the ^{t}BuO$^\bullet$ radicals abstract H atoms from CyH to form cyclohexyl radicals (Cy$^\bullet$), which then initiate radical-driven autoxidation of CyH (to afford CyOH and CyO) and formation of the mixed peroxide CyOO^{t}Bu (via combination of ^{t}BuOO$^\bullet$ and Cy$^\bullet$). At elevated temperatures, the more energetic ^{t}BuOO$^\bullet$ radicals directly take part in H-atom abstraction from CyH and combine with Cy$^\bullet$ to afford more CyOO^{t}Bu in the reaction mixture. Gas chromatographic analysis indicates that free N-donor ligand (L) is always present in reaction mixtures at the end of oxidation. Whether L or the ^{t}BuOO$^\bullet$ group is lost first is not clear at this time; however, Talzi and co-workers suggest that the ^{t}BuOO$^\bullet$ unit is lost first.[18]

Epoxidation of *cis*-Stilbene and Cyclohexene by [Co(β-diketonate)$_2$(L)(OO^{t}Bu)]. Since complexes **1**−**4** readily afford ^{t}BuOO$^\bullet$ in solution and peroxyl radicals are known to add an

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(17) One reviewer has suggested that the mixed peroxide CyOO^{t}Bu could form in the reaction mixture via attack of Cy$^\bullet$ radical on intact complex [Co(acac)$_2$(L)(OO^{t}Bu)]. Since we do not obtain any CyOO^{t}Bu in oxidation of cyclohexane with other Co(III) complexes like [Co(Py$_3$P)(OO^{t}Bu)], this pathway appears unlikely.

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(20) *Handbook of Chemistry and Physics*, 67th ed; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1987; pp F178−F179.

oxygen atom across a double bond,[21] we were curious to find out whether these complexes are capable of epoxidizing olefins. Here we report that such complexes indeed promote epoxidation. When 20 μmol of **1** in 1 mL of neat *cis*-stilbene is allowed to stand at room temperature for 24 h under dinitrogen, one obtains *trans*-stilbene oxide in 16% yield. The extent of epoxidation diminishes to 4% with cyclohexene as the substrate, presumably due to competing reactions such as allylic oxidation. More epoxidation is, however, observed when the reaction is performed in air although the yields of the products of allylic oxidation also increase under this condition. For example, when 60 μmol of **1** was dissolved in 1 mL of neat cyclohexene and allowed to stand at room temperature for 15 h, cyclohexene oxide (**E**, 9%), 2-cyclohexen-1-ol (**A**, 76%), 2-cyclohexen-1-one (**K**, 81%), and *tert*-butyl-2-cyclohexenyl-1-peroxide (**P**, 31%) were obtained. Mukaiyama and co-workers have shown that, in the presence of aldehydes, [Co(β-diketonate)$_2$] complexes epoxidize olefins selectively and in good yields.[22] We therefore decided to attempt the epoxidation reaction by the present complexes in the presence of aldehydes. A dramatic increase in the yield of epoxide is indeed observed when propionaldehyde or heptaldehyde is added to the reaction mixture. For example, when 60 μmol of **1** was dissolved in 1 mL of a 3:1 (mol/mol) propionaldehyde:cyclohexene mixture and allowed to stand at room temperature for 15 h, **E** was obtained as the major (51%) product along with 4% **A** and just 1% **K**.[23] Interestingly, very similar yields and selectivity were observed when the same reaction was performed with a 1:1:1 mixture of [Co(acac)$_2$]:pyridine:TBHP (added in the sequence shown) in place of complex **1**. Since the electronic spectrum of the latter mixture closely resembles that of **1**, it is evident that complex **1** is an intermediate in these epoxidation reactions. Similar results have been obtained with the other complexes. The mechanism of aldehyde-assisted olefin epoxidation has been discussed by Valentine and co-workers.[24] In such reactions, either ^{t}BuO$^\bullet$ or ^{t}BuOO$^\bullet$ radical first abstracts an H atom from the aldehyde RCHO to generate RCO$^\bullet$, which then reacts with O$_2$ to form acylperoxyl radical RCOOO$^\bullet$, the species actually responsible for epoxidation of olefins. We believe that such reactions are operative in the present case since selective epoxidation of cyclohexene by **1**−**4** is observed only when aldehydes are present in the reaction mixtures.

Finally we wish to comment on the two distinct pathways by which alkylperoxo complexes of tervalent cobalt decompose in solution. Results of studies on alkane oxidation and olefin epoxidation by us[4,5] and others[7,15,22,25] now indicate that when the [L$_n$Co^{III}−OOR] species comprise strong-field ligand(s) L (thus stabilizing the +3 oxidation state), homolysis of the O−O bond in the Co−OOR moiety is favored. These [L$_n$Co^{III}−OOR] complexes therefore afford RO$^\bullet$ radicals in solution and promote alkane oxidation.[4,5,15] With olefins, one observes mostly allylic oxidation products with such [L$_n$Co^{III}−OOR] species. In contrast, [L$_n$Co^{III}−OOR] complexes with ligands that give rise to stable Co(II) species decompose via homolysis of both Co−O and O−O bonds and produce ROO$^\bullet$ and RO$^\bullet$ radicals in the reaction mixtures. As a result, these complexes initiate alkane oxidation *and* selective epoxidation of alkenes under different reaction conditions.[4,7,22] The ligand(s) L therefore influences the way a specific [L$_n$Co^{III}−OOR] complex decomposes in solution and promotes oxidation of hydrocarbons.

Summary and Conclusions

The following are the principal findings of this investigation.

(i) Four Co(III)−alkylperoxo complexes of the type [Co(acac)$_2$(L)(OO^{t}Bu)] (**1**, L = py); **2**, L = 4-Mepy; **3**, L = 1-MeIm) and [Co(dbm)$_2$(py)(OO^{t}Bu)] (**4**) have been synthesized. The structures of **1**, **3**, and **4** have been determined by X-ray crystallography.

(ii) Complexes **1**−**4** all possess the cis configuration with respect to the β-diketonate ligands.

(iii) The order of stability for complexes **1**−**4** in benzene at room temperature is **1** < **2** < **3** < **4**.

(iv) Complexes **1**−**4** initiate oxidation of hydrocarbon substrates beginning at a reaction temperature of 2 °C with yields increasing up to 50 °C. Among the four, complex **1** is the most effective oxidant.

(v) Product analysis under different reaction conditions indicates that, in hydrocarbon solvents, these complexes afford ^{t}BuOO$^\bullet$ radicals via homolysis of the Co−O bond of the Co−OO^{t}Bu moiety. The reaction mixtures in all cases also contain ^{t}BuO$^\bullet$ radicals which are formed either via homolysis of the O−O bond of the Co−OO^{t}Bu unit or in the disproportionation reaction 2.

(vi) In the presence of aldehydes, these complexes selectively epoxidize cyclohexene. When aldehydes are not present, considerable amounts of allylic oxidation products are also obtained.

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Supporting Information Available: ^{1}H NMR spectra of **1**−**3** in C$_6$D$_6$ (Figure S1) and **4** in CDCl$_3$ (Figure S2) and crystal structure data for **1**, **3**, and **4** including atomic coordinates and isotropic thermal parameters, bond distances and angles, anistropic thermal parameters, and H-atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Attempts to decrease the reaction time by increasing the reaction temperature resulted in loss of selectivity with more allylic oxidation. For example, the same reaction with **1** performed at 50 °C for 2 h afforded **E**, **A**, and **K**, in 28%, 47%, and 11% yield, respectively.

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