Cobalt-Catalyzed Epoxidation of Olefins. Dual Pathways for Oxygen Atom Transfer

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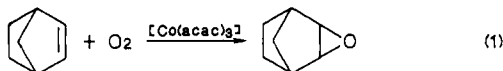*Department of Chemistry, University of Houston, University Park, Houston, Texas 77004*

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Cobalt catalysis of olefin oxidation with *tert*-butyl hydroperoxide and iodosylbenzene as terminal oxidants is examined with $Co^{II}(Ia)$, where the ligand Ia is the bis-salicylamide dianion 2,3-bis(3,5-dichloro-2-oxybenzamido)-2,3-dimethylbutane. The catalytic epoxidation of norbornene with *tert*-butyl hydroperoxide and with iodosylbenzene proceeds via different pathways, since the former is effectively inhibited by ionol (2,6-di-*tert*-butyl-*p*-cresol) whereas the latter is not. A radical chain mechanism is proposed for *tert*-butyl hydroperoxide in which the homolytic addition of *tert*-butylperoxy radicals to the double bond leads to epoxidation. Cobalt catalysis is associated with the Co^{II}/Co^{III} interconversion in the one-electron redox processes mediating the formation of the critical *tert*-butylperoxy radical. By contrast, there is no evidence for radical intermediates in the cobalt catalysis with iodosylbenzene which occurs readily with various types of olefins including 2-hexene, cyclooctene, β-methylstyrene, and even cyclohexene. A two-electron mechanism is proposed to account for the high reactivity, selectivity, and stereochemical retention in the catalytic epoxidation, despite the low solubility of $Co^{II}(Ia)$ in the reaction medium. The postulation of an active oxo–cobalt(IV) species provides a consistent explanation of the diverse aspects of the cobalt-catalyzed epoxidations with iodosylbenzene.
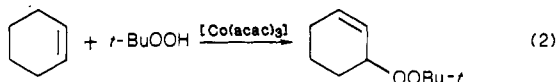
Introduction

Cobalt complexes are included among the most widely employed catalysts for the oxidation of different types of organic substrates.[1-5] Despite extensive use in industrial oxidations, little is known about the catalytically active cobalt species and how they carry out their function. Particularly germane is the nature of the oxygen-carrying cobalt intermediate(s) involved in the utilization of such terminal oxidants as dioxygen, peroxides, iodosylbenzene, etc.

Among organic compounds, olefins are especially useful substrates for catalytic oxidations since at least two important reaction pathways are available. For example, in an earlier study we showed that cobalt(III) acetylacetonate can be effectively utilized for olefin epoxidation with dioxygen as the terminal oxidant, e.g.[6] eq 1. On the other

hand, allylic substitution is the important oxidative reaction when alkyl hydroperoxides are used as the terminal oxidant, e.g.[7] eq 2. Epoxidation and allylic substitution

as described in eq 1 and 2, respectively, show an induction period.[6,7] Coupled with other characteristics of free radical chain processes, it is generally acknowledged that the cobalt catalysts function by one-electron oscillations between Co^{II} and Co^{III} oxidation states.[1]

Recently some simple binary salts of cobalt(II) have been found to catalyze the epoxidation of olefins when iodosylbenzene is used as the terminal oxidant,[8] e.g. eq 3. Such
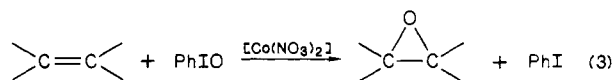
an oxidative utilization of iodosylbenzene is reminiscent of catalytic epoxidations induced by metalloporphyrins.[9-12] In the latter cases, the metal catalyst serves as a relay for oxygen atom transfer from iodosylbenzene via the intermediacy of an oxo–metal species,[13] i.e. Scheme I. The shuttling of the metal complex between the two metal states in Scheme I corresponds to a sequence of successive two-electron steps for oxidative additions and reductive eliminations. As such, there is no evidence for the chain process of the type observed for the oxidative processes in eq 1 and 2.

The cobalt species in these catalytic systems are poorly defined since they are rarely, if ever, recovered intact. Thus the rigorous definition of the multiple pathways for cobalt catalysis of olefin oxidation requires a ligand that is sufficiently robust to withstand oxidative conditions. Among the various possibilities, we chose the tetradentate amide ligands of the general structure I^{14} for this study of olefin oxidation. Accordingly, the cobalt complexes of ligand I were used for olefin oxidations with *tert*-butyl hydroperoxide and iodosylbenzene as prototypical terminal oxidants.[1]

I	R_2, R_2
a	$(CH_3)_2, (CH_3)_2$
b	1,2-trans-cyclohexylidene
c	H_2, H_2
d	o-phenylene
e	3,4-dichloro-o-phenylene

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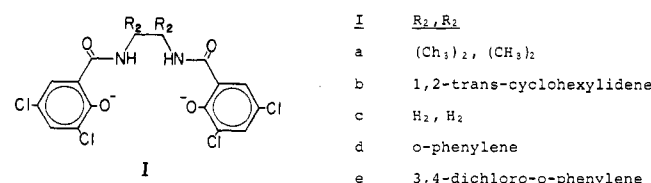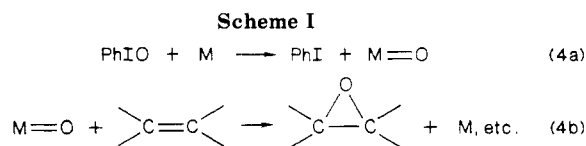
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Scheme I

$$PhIO + M \longrightarrow PhI + M{=}O \qquad (4a)$$

$$M{=}O + \diagdown C{=}C\diagdown \longrightarrow \diagdown \overset{O}{\overset{\triangle}{C{-}C}}\diagdown + M, etc. \qquad (4b)$$

Results

Synthesis of Cobalt(II) Complexes of Bis-Salicylamide Derivatives.

The class of bis-salicylamide ligands I hereafter referred to as salam were prepared generally from the condensation of salicylic acid derivatives with vicinal diamines.[14] Of particular interest to us was the 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethyl derivative Ia which was prepared in 80% yield from acetyl-3,5-dichlorosalicyloyl chloride[15] and 2,3-diamino-2,3-dimethylbutane,[16] followed by de-acetylation with aqueous alkali. Complexation of cobalt(II) acetate with Cl_4Me_4salamH_2 was carried out in refluxing methanol under an argon atmosphere. Co^{II}(Ia) was isolated in 90% yield as the purple sesquihydrate, which upon desiccation in vacuo over phosphorus pentoxide yielded the pale blue monohydrate.[17] Since the catalytic properties of these materials could not be distinguished, they will be referred to hereafter generically as Co^{II}(Ia)H_2O. The cobalt(II) complexes of the other salam derivatives Ib–e were prepared by similar procedures described in the Experimental Section.

Cobalt Catalysis of Olefin Oxidation with Hydroperoxide and Iodosylbenzene.

The efficacy of cobalt catalysis with Co(Ia)H_2O was initially examined for *tert*-butyl hydroperoxide and iodosylbenzene as representative terminal oxidants to effect oxygen atom transfer. The olefinic substrates of choice were norbornene owing to its relatively reactive (strained)double bond and cyclohexene which is particularly prone to allylic oxidation.[1]

A. *tert*-Butyl hydroperoxide (TBHP) employed as a standard 0.2 M solution in dichloromethane was treated with 1 M norbornene and catalytic amounts of the cobalt catalyst Co(Ia), as indicated in Table I. After stirring the mixture for 6 h at 25 °C, a 30% yield of norbornene oxide was obtained on the basis of the stoichiometry in eq 5.

$$\text{(norbornene)} + t\text{-BuOOH} \xrightarrow{[Co]} \text{(norbornene oxide)}{-}O + t\text{-BuOH} \qquad (5)$$
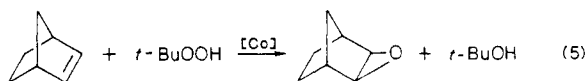
Exposure of norbornene to *tert*-butyl hydroperoxide in the absence of Co(Ia) led to less than 5% norbornene oxide (NBO).

The catalytic oxidation of cyclohexene under the same conditions afforded 1-(*tert*-butylperoxy)-2-cyclohexene as the principal product in 22% yield but only small amounts of cyclohexene oxide. Control experiments demonstrated that cyclohexene oxide was not destroyed under the catalytic conditions employed in cyclohexene oxidation.

$$\text{(cyclohexene)} + t\text{-BuOOH} \xrightarrow{[Co]} \text{(cyclohexenyl)}{-}OOBu\text{-}t, etc. \qquad (6)$$
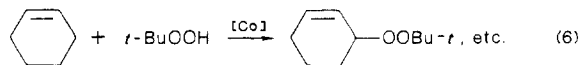
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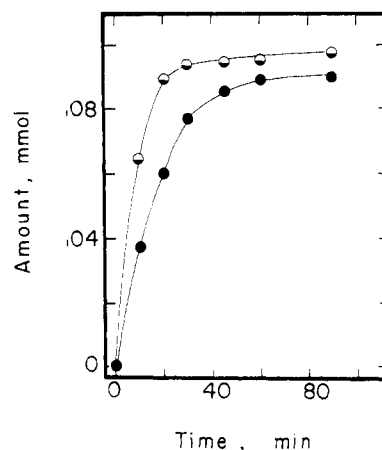(17) Koola, J. D.; Kochi, J. K. *Inorg. Chim. Acta* 1987, *133*, 119.

Figure 1. Simultaneous formation of norbornene oxide (●) and iodobenzene (○) from the reaction of 5 mmol of norbornene with 0.10 mmol of iodosylbenzene and 10^{-2} mmol of Co^{II}(Ia)H_2O in 5 mL of dichloromethane at 25 °C.

The catalytic epoxidation and allylic oxidation as expressed in eq 5 and 6, respectively, were both strongly inhibited in the presence of the phenolic inhibitor ionol (2,6-di-*tert*-butyl-*p*-cresol).[18] The results in Table I show that ionol in concentrations as low as 0.01 M was sufficient to prevent the epoxidation of norbornene. Control experiments established that any complication from a side reaction of TBHP with ionol was too slow to interfere with the olefin oxidation (vide infra). Furthermore, norbornene oxide was not destroyed by TBHP and ionol in the presence of Co^{II}(Ia)H_2O under the reaction conditions.

Cobalt catalysis of olefin oxidation with *tert*-butyl hydroperoxide could be carried out to high turnover numbers since Co^{II}(Ia)H_2O was recovered intact. Most commonly, the crude reaction mixture upon filtration yielded the catalyst as the unchanged purple Co^{II}(Ia)H_2O, together with a colorless filtrate containing the oxidation products.

B. Iodosylbenzene was employed as a slurry for the catalytic oxidation of norbornene and cyclohexene owing to its low solubility in dichloromethane.[19] Nonetheless the presence of 0.01 mmol of Co^{II}(Ia)H_2O was sufficient to convert >20 equiv of iodosylbenzene within an hour at 25 °C. Under these conditions, norbornene oxide was formed in 90% yield according to the stoichiometry in eq 7.[20] The quantitative analysis of iodobenzene indicated

$$\text{(norbornene)} + PhIO \xrightarrow{[Co]} \text{(norbornene oxide)}{-}O + PhI \qquad (7)$$
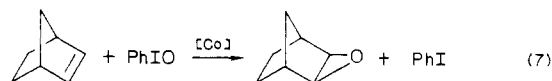
it to be the sole reduction product of iodosylbenzene. The concomitant production of norbornene oxide and iodobenzene is illustrated in Figure 1 under typical catalytic conditions.

When cyclohexene was the olefin, it was converted by iodosylbenzene with the aid of Co^{II}(Ia)H_2O to cyclohexene oxide in 60–65% yields, i.e. eq 8, together with minor

$$\text{(cyclohexene)} + PhIO \xrightarrow{[Co]} \text{(cyclohexene oxide)}O + PhI \qquad (8)$$
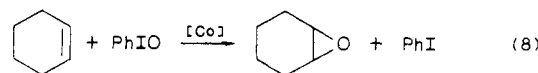
amounts of cyclohexenol (19%) and cyclohexenone (9%). It is noteworthy that the amounts of cyclohexenol formed relative to cyclohexene oxide in Table II are more or less

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(20) A small amount (0.7%) of *endo*-norbornene oxide was also found.

Table I. Cobalt Catalysis of Olefin Oxidation with *tert*-Butyl Hydroperoxide[a]

Co^{II}(Ia)H$_2$O (mmol)	olefin[b] (mmol)	TBHP (mmol)	add.[c] (mmol)	epoxide[d] (%)	allylic oxid
0.01	NB (5)	1.0	none	31	0
0.01	NB (5)	0.1	none	14	
none	NB (5)	1.0	none	5	
0.01	NB (5)	0.1	0.05	<0.5	0
0.01	NB (5)	1.0	1.0	<0.5	
0.01	NB (5)	1.0	2.0	<0.5	
0.01	CH (3)	1.0	none	<1	22[e,f]
0.01	CH (3)	1.0	1.0	0	~1[e]
none	CH (3)	1.0	0	0	3[e]

[a] In 5 mL of dichloromethane at 25 °C for 60 min. [b] NB = norbornene, CH = cyclohexane. [c] Ionol = 2,6-di-*tert*-butyl-*p*-cresol. [d] Based on stoichiometry in eq 5. [e] *tert*-Butylperoxy-2-cyclohexene. [f] Small amounts (<1%) of cyclohexenol and cyclohexenone also formed.

Table II. Cobalt Catalysis of Olefin Oxidation with Iodosylbenzene[a]

Co^{II}(Ia)H$_2$O (mmol)	olefin[b] (mmol)	PhIO (mmol)	Add.[c] (mmol)	Epoxide[d] mmol (%)	PhI (mmol)
0.01	NB (5)	0.16	none	0.14 (90)	0.15
0.01	NB (5)	0.10	0.05	0.066 (85)	0.078
0.01	NB (5)	0.10	0.10	0.054 (69)	0.078
0	0	0.10	0.10		0.078
0.01	CH (3)	0.16	none	0.11 (60)[e]	0.18
0.01	CH (3)	0.10	none	0.066 (65)[f]	0.10
0.01	CH (3)	0.10	0.05	0.043 (41)[g]	0.11
0.01	CH (3)	0.10	0.10	0.033 (32)[h]	0.10
0.01	CH (3)	0.10	0.20	0.024 (24)[j]	0.10

[a] In 5 mL of dichloromethane at 25 °C for 120 min. [b] NB = norbornene, CH = cyclohexane. [c] Ionol. [d] Based on iodobenzene formed in column 6. [e] In addition to 0.034 mmol of cyclohexenol and 0.016 mmol of cyclohexenone. In addition to [f] 0.017, [g] 0.011, [h] 0.008, [j] 0.006 mmol cyclohexenol.
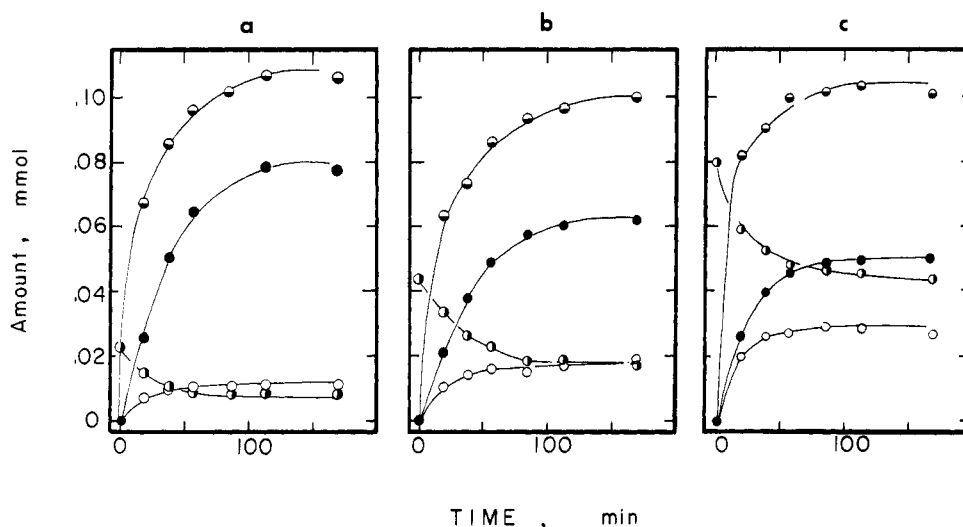

Figure 2. Effect of the ionol inhibitor on the catalytic epoxidation of norbornene (5 mmol) with iodosylbenzene (0.10 mmol) and 10^{-2} mmol of Co(Ia) in 5 mL of dichloromethane. Variation of ionol (◑) from left to right: (a) 0.025, (b) 0.49, and (c) 0.98 mmol and the formation of norbornene oxide (●), iodobenzene (◒), and ionol oxidation products (O).

unaffected by the presence of ionol. Control experiments showed that cyclohexenol did not arise from the further reaction of cyclohexene oxide since the latter was stable under reaction conditions. However cyclohexenone could have arisen from cyclohexenol owing to the facile catalytic oxidation of secondary alcohols by iodosylbenzene with Co(Ia)H$_2$O.

The catalytic epoxidation carried out with iodosylbenzene was not materially affected by the presence of ionol, certainly in comparison with the concentrations found to be highly effective with *tert*-butyl hydroperoxide in Table I. The somewhat reduced yield of norbornene oxide in Table II (entry 2) was readily attributed to the partial destruction of iodosylbenzene by ionol (compare with entries 3 and 4).[21] This competition is graphically illustrated in Figure 2 which was carried out at various levels of the inhibitor. In every case, the rate of ionol oxidation by iodosylbenzene was not fast enough to elim-

inate it from circulation. Thus sufficient amounts of ionol were always present to inhibit the radical chain process for olefin epoxidation.

Cobalt catalysis of olefin epoxidation with iodosylbenzene could be carried out to high turnover numbers (>100) by the repeated additions of the terminal oxidant. Finally, the catalyst was recovered intact by simple filtration to yield the unchanged purple Co^{II}(Ia)H$_2$O. No reaction occurred between iodosylbenzene and norbornene or cyclohexene in the absence of Co^{II}(Ia)H$_2$O.

Owing to the highly selective catalytic epoxidation with iodosylbenzene and Co(Ia)H$_2$O in Table II, we examined the efficacy of this system with some representative olefins.

(21) GC-MS analysis indicated the oxidation products of ionol to consist of a complex mixture, the predominant component of which was assigned to 2,6-di-*tert*-butylquinone methide (see Experimental Section).

Table III. Olefin Epoxidation with Iodosylbenzene and Co(Ia)[a]

olefin	epoxide (%)
(1-hexene)	(65) (2)
(cyclooctene)	(56)
(norbornene)	(90) [69]
(cyclohexene)	(60) [47] (19)[b] [12][c]
(2-hexene)	(25)
(Ph, (Z)-β-methylstyrene)	(76) [76] (0)
(Ph, (E)-β-methylstyrene)	(68) [54] (0)

[a] Under standard conditions with 2–5 mmol of olefin, 0.16 mmol of iodosylbenzene, and 10^{-2} mmol of Co(Ia)H$_2$O in 5 mL of dichloromethane stirred at room temperature for 3–5 h. Yields in dichloromethane and acetonitrile indicated in parentheses and brackets, respectively. In addition to [b] 9% and [c] 2% cyclohexenone.

Catalytic Epoxidation of Olefins with Iodosylbenzene and Co^{II}(Ia)H$_2$O.

Cobalt catalysis of epoxidation was carried out at room temperature under standard conditions with Co^{II}(Ia)H$_2$O and the various olefins listed in Table III. The epoxide yields generally exceeded 70%, except with terminal alkenes such as 1-hexene. The selectivity in epoxide formation was also high, and the competition from allylic oxidation was only observed in significant amounts with cyclohexene.

The stereochemistry of the oxygen atom transfer with Co(Ia)H$_2$O and iodosylbenzene is shown in Table III with (Z)- and (E)-β-methylstyrene, from which only the stereochemically retained epoxides were formed. Furthermore the high degree of retention observed with 2(Z)-hexene was a particularly useful probe since oxygen atom transfer to this cis olefin often results in significant amounts of the rearranged trans epoxide.[19] Control experiments established that the small amounts of 2(E)-hexene oxide did not arise from the rearrangement of the first-formed Z isomer under the catalytic conditions.

Rearrangement and cleavage products from olefins were also scrutinized with the electron-rich β-methylstyrene. Analysis of the reaction mixture revealed the formation of only traces of phenylacetone (<1%) and no α-phenylpropionaldehyde. Furthermore, less than 1% benzaldehyde was detected.[22] Similarly the GC-MS analysis of the reaction mixtures from the other olefins showed little contamination from byproducts.

Effect of Cobalt Catalyst and Reaction Conditions on Olefin Epoxidation.

Owing to the reasonable yields of the epoxides in Table III, we examined the effects of solvent, catalyst, added ligand, terminal oxidant, and concentration as variables for the optimization of the catalytic process.
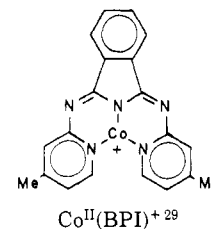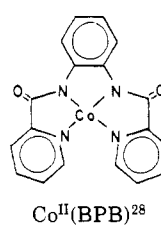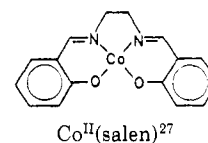
Dichloromethane and acetonitrile are representatives of aprotic media with different properties, especially as

evaluated by most measures of solvent polarity.[23] The results in Table III show that the epoxidation generally proceeded with higher efficiency in the less polar dichloromethane. Since Co^{II}(Ia)H$_2$O has limited solubility in these solvents, we also examined ethyl chloroacetate in which it formed a colloidal suspension. The reduced yields of norbornene oxide from 90% in dichloromethane to <50% in ethyl chloroacetate indicated that the heterogeneous nature of the catalyst was not a limiting factor.

This conclusion was also borne out by converting Co^{II}(Ia)H$_2$O to the more soluble N,N-dimethylformamide, pyridine, and 4-picoline adducts, which produced norbornene oxide in 65%, 53%, and 43% yields, respectively, in dichloromethane media. Moreover the addition of 2 and 10 equiv of the promotor[19] triethylphosphine oxide to Co(Ia)H$_2$O in dichloromethane successively lowered the norbornene oxide yield to 72% and 61%, respectively. The reduced yields for epoxidations carried out in ethyl chloroacetate coincided with the partial oxidation of the active catalyst from cobalt(II) to cobalt(III), as indicated by the change in color to green. The same oxidative conversion of Co^{II}(Ia)H$_2$O was noted with the more soluble catalysts Co^{II}(Ia)DMF and Co^{II}(Ia)py, as well as when triethylphosphine oxide was added to Co^{II}(Ia)H$_2$O. Indeed the deliberate oxidation of Co^{II}(Ia) by molecular bromine led to the green Co^{III}(Ia)Br, which was a significantly less effective catalyst for olefin epoxidation with iodosylbenzene.

Alteration of the salam ligand on cobalt(II) had a substantial effect on the catalytic activity. Thus the replacement of the tetramethyl groups on the ethano bridge with a 1,2-trans-cyclohexylidene[24] as in Ib (vide supra) produced a cobalt(II) catalyst which afforded a 75% yield of norbornene oxide under conditions in which Co^{II}(Ia) yielded 90% epoxide. A further reduction to 65% was obtained when all four methyl groups in Co(Ia) were replaced with hydrogen, as in Co^{II}(Ic).[25] Replacement of the ethano bridge with an o-phenylene or 3,4-dichloro-o-phenylene group as in Co^{II}(Id) and Co^{II}(Ie) led to a further diminution of epoxide yield to 44% and 48%, respectively.[26]

The catalytic activity of the salen complex Co^{II}(Ia) was also compared with that of other, somewhat related cobalt(II) complexes, the structures of which are presented below.[27-29] The salen complex of cobalt(II) together with

Co^{II}(salen)[27]

Co^{II}(BPB)[28]   Co^{II}(BPI)$^{+}$ [29]

(22) For the significance of rearrangement and cleavage of olefins during catalytic epoxidation, see discussion in ref 19.

(23) (a) Kosower, E. M. *Introduction to Physical Organic Chemistry*; Wiley: New York, 1968. (b) Reichardt, C. *Liebig Ann.* 1971, 752, 64.

(24) Compare for the salen complex. Bresciani, N.; Calligaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1974, 1606.

(25) Compare this structure with that in ref 15.

(26) Compare this ligand system with that in Anson, F. C.; Collins, T. J.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Peake, G. T. *J. Am. Chem. Soc.* 1986, 108, 6593.

(27) (a) Callifaris, M.; Nardin, G.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* 1974, 1903. (b) Calligaris, M.; Minichelli, D.; Nardin, G.; Randaccio, L. *J. Chem. Soc. A* 1970, 2411. See also ref 24.
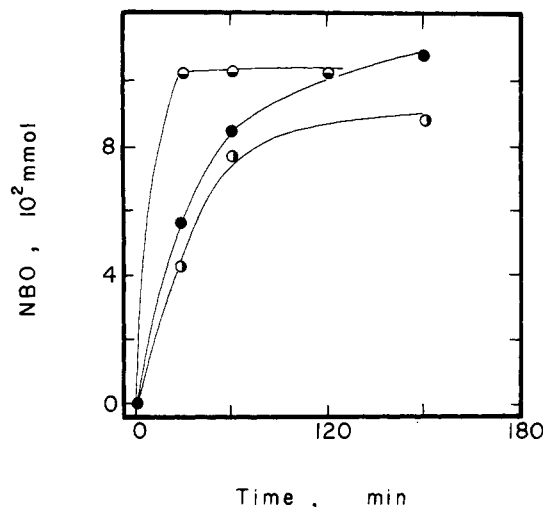
Figure 3. Evolution of epoxide from norbornene (5 mmol) and 10^{-2} mmol of Co(Ia) in 5 mL of dichloromethane containing 0.15 mmol of iodosylbenzene (●), 0.15 mmol of pentafluoroiodosylbenzene (◐), and 0.15 mmol of PhIO plus 0.02 mmol of triethylphosphine oxide (◑) at 25 °C.
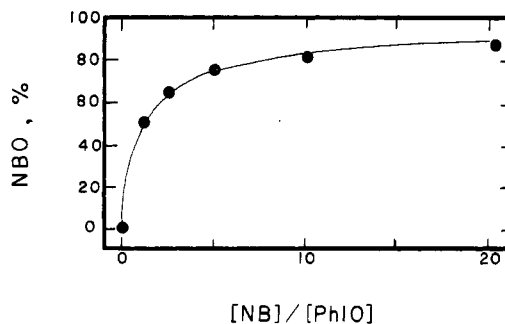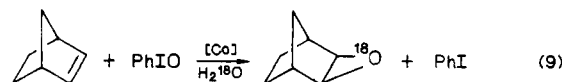

Figure 4. Effect of olefin concentration on the efficiency of the catalytic epoxidation of norbornene with 0.10 mmol of iodosylbenzene and 10^{-2} mmol of Co(Ia) in 5 mL of dichloromethane at 25 °C. Yield of norbornene oxide based on iodobenzene produced.

its pyridine adduct was partially soluble in dichloromethane. However under the standard conditions described above, Co^{II}(salen) and Co^{II}(salen)py led to only 16% and 18%, respectively, of norbornene oxide. Moreover the isonicotinamide derivative Co^{II}(BPB)[28] and the iminoisoindoline analogue Co^{II}(BPI)OAc[29] produced only 15% and 25% yields of norbornene oxide under the conditions in which Co^{II}(Ia) afforded a 90% yield of the epoxide.

Reactivity and Selectivity of the Catalytic System with Co^{II}(Ia)H_2O. The foregoing studies have shown that the catalytic system comprised simply of iodosylbenzene and Co^{II}(Ia) in a nonpolar solvent such as dichloromethane was the most effective for olefin epoxidation. Despite the insolubility of both iodosylbenzene and Co^{II}(Ia)H_2O in this medium, olefin epoxidation proceeded remarkably smoothly to produce essentially no byproducts. For example, from norbornene and (Z)-β-methylstyrene as representative olefins, we could detect only the epoxides by GC-MS analysis. By way of contrast, the catalytic reactions of these olefins with either Co^{II}(salen), Co^{II}(BPB), Co^{II}(BPI)OAc, and Co^{II}(OAc)$_2$ produced low yields of epoxides and numerous (>10) oxidation byproducts which comprised a significant fraction of the iodosylbenzene utilization (see Experimental Section). Furthermore, the replacement of the aquo ligand in Co^{II}(Ia)H_2O by dimethylformamide, pyridine, or triethylphosphine oxide afforded catalysts which were less effective, as judged by the reduced yields of epoxide and the increased amounts of oxidation byproducts.

The kinetics of olefin epoxidation with Co^{II}(Ia)H_2O were not measured owing to the heterogeneous nature of the catalytic system. However the rate of oxidation could be evaluated qualitatively under a standard set of reaction conditions by measuring the evolution of epoxide and iodobenzene by GC-MS analysis. The results in Figure 3 show that the epoxidation of norbornene occurs quite readily with iodosylbenzene and Co^{II}(Ia)H_2O. The rate profile under standard conditions has an apparent half-life

of approximately 30 min at room temperature. When the more active pentafluoroiodosylbenzene[30] was used as the terminal oxidant, the apparent half-life was decreased to less than 10 min. The slightly reduced yields of norbornene oxide with pentafluoroiodosylbenzene may be due to the partial oxidation of the cobalt catalyst to cobalt(III) species (green) by the more active terminal oxidant. The retarding effect of triethylphosphine oxide on Co^{II}(Ia)H_2O is also shown in the figure.

The yield of norbornene oxide was relatively insensitive to the amount of Co^{II}(Ia) charged, in accord with the largely heterogeneous nature of the catalysis. Furthermore the utilization of olefin was rather high, as seen in Figure 4 by the reasonable yields of norbornene oxide obtained even at a molar ratio of norbornene/iodosylbenzene of unity.

Owing to its insolubility in the reaction medium, Co^{II}(Ia) could always be readily recovered by filtration. The clear colorless filtrate contained only the epoxide and unreacted olefin together with the reduced iodobenzene. When the recovered catalyst was recycled repeatedly, turnover numbers in excess of 100 were easily achieved.

The course of oxygen atom transfer via cobalt catalysis was examined by the incorporation of isotopic oxygen-18 into the epoxide from labeled water. In a typical experiment, 1 mmol of norbornene was treated with 0.1 mmol of iodosylbenzene and 10^{-2} mmol of Co^{II}(Ia)H_2O in acetonitrile (1 mL) containing 2 mmol of labeled water which was 90% enriched with oxygen-18. The mixture was stirred at room temperature for approximately 2 h and filtered to remove the catalyst. Direct GC-MS analysis of the colorless filtrate for the isotopic norbornene oxides by their principal mass ion peaks at m/z 110 and 112 indicated a 80% oxygen-18 incorporation, i.e. eq 9. Control

$$\text{(structure)} + \text{PhIO} \xrightarrow[\text{H}_2{}^{18}\text{O}]{\text{[Co]}} \text{(structure)}{}^{18}\text{O} + \text{PhI} \qquad (9)$$

experiments established that iodosylbenzene did not undergo prior isotopic exchange nor did norbornene oxide suffer subsequent exchange with water under the catalytic conditions.

Catalytic Oxidation of Cyclohexane with Iodosylbenzene. The versatility of Co^{II}(Ia) as an oxidation catalyst for saturated hydrocarbons was examined with cyclohexane as the substrate. When 5 mmol of cyclohexane in dichloromethane (5 mL) was treated with 0.2 mmol of iodosylbenzene and 10^{-2} mmol of Co^{II}(Ia)H_2O, a slow conversion to cyclohexanol (1%) and cyclohexanone (20%)

(28) (a) Chapman, R. L.; Vagg, R. S. *Inorg. Chim. Acta* **1979**, *33*, 227. (b) Barnes, D. J.; Chapman, R. L.; Stephens, F. S.; Vagg, R. S. *Inorg. Chim. Acta* **1981**, *51*, 155.

(29) (a) Siegl, W. O. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 825. (b) Gagne, R. R.; Marritt, W. A.; Marks, D. N.; Siegl, W. O. *Inorg. Chem.* **1981**, *20*, 3260. See also ref 2d.

(30) Traylor, T. G.; Nakano, T.; Dunlap, B. E.; Traylor, P. S.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782.

was observed (eq 10). No cyclohexene, cyclohexene oxide,
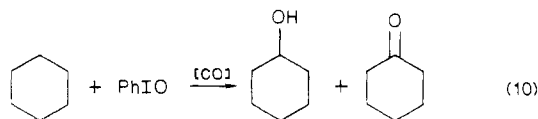
or bicyclohexyl was detected in the reaction mixture. Cyclohexanol was readily converted to cyclohexanone under the catalytic conditions.

The oxidative substitution into saturated carbon–hydrogen groups was also indicated during the exposure of dichloromethane and acetonitrile to iodosylbenzene and catalytic amounts of $Co^{II}(Ia)$ in the absence of an olefin substrate. The slow disappearance of iodosylbenzene was accompanied by the simultaneous production of the reduced iodobenzene. Although all the products have not yet been characterized thoroughly, it was clear that the catalytic system was capable of the oxidative degradation of the solvent.[31] In the absence of Co(Ia), no reaction occurred between iodosylbenzene and either dichloromethane or acetonitrile, even upon prolonged stirring.
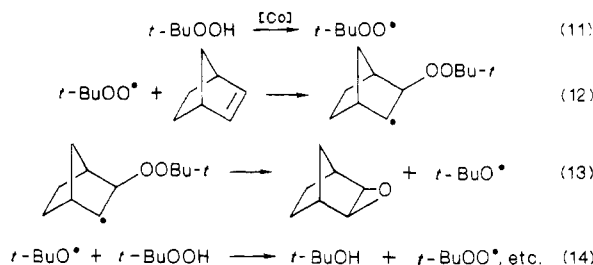
Discussion

Cobalt catalysis of the epoxidation of norbornene can be carried out with both *tert*-butyl hydroperoxide and iodosylbenzene as the terminal oxidants, as described in eq 5 and 7, respectively. However the catalytic pathways for oxygen atom transfer from the terminal oxidant to the alkene must differ in these two systems. Thus the results in Table I demonstrates that norbornene epoxidation by *tert*-butyl hydroperoxide is effectively inhibited by ionol. Contrariwise, the catalytic epoxidation of norbornene with iodosylbenzene is singularly unaffected by ionol (Table II).

Since ionol is known to be a potent scavenger of free radicals,[18] norbornene epoxidation with *tert*-butyl hydroperoxide follows the traditional route for homolytic cobalt catalysis,[1] as summarized below: The efficiency of epoxidation in Scheme II depends on the facility of the homolytic addition step (eq 12) which is known to be facile for norbornene.[33] The subsequent β-elimination[34] of the adduct in eq 12 leads to norbornene oxide with preponderant exo stereochemistry. The homolytic mechanism in Scheme II accords with the absence of epoxidation when the substrate is cyclohexene, which is less prone to undergo addition of peroxy radicals.[35] Indeed the predominance of peroxy substitution according to eq 6 follows from the facility with which hydrogen atom abstraction occurs from the allylic position of cyclohexene, i.e. eq 15. The effective inhibition of norbornene epoxidation (eq 5) and cyclohexene substitution (eq 6) by ionol is achieved by the interception of the oxy free radicals,[18,36] e.g. eq 16.

Since ionol has minimal effect on norbornene epoxidation with iodosylbenzene, oxy radicals of the type described above cannot be involved in this cobalt catalysis. Such a conclusion is strongly supported by the 60% yields of epoxide which can be obtained from cyclohexene. These yields are all the more remarkable when considered in the light of previous studies of cyclohexene epoxidation with

(31) (a) Iodobenzene (>90%) was formed in ~10 h in the absence of olefin. (b) For attack on solvent, see ref 32.

(32) Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.

(33) Nonhebel, D. C.; Walton, J. C. *Free Radical Chemistry*; Cambridge University Press: London, 1974. See also: Traylor, T. G. *Acc. Chem. Res.* **1969**, *2*, 152.

(34) van Sickle, D. E.; Mayo, F. R.; Arluck, R. M. *J. Am. Chem. Soc.* **1965**, *87*, 4824. van Sickle, D. E.; Mayo, F. R.; Gould, E. S.; Arluck, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 977.
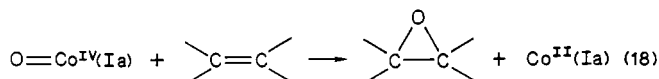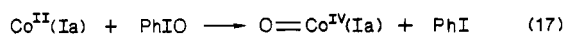
(35) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193.

(36) See also: Srinivasan, K.; Perrier, S.; Kochi, J. K. *J. Mol. Catal.* **1986**, *36*, 297.

Scheme II

iodosylbenzene and other metal catalysts.[9–13] In the latter, the catalytic utilization of iodosylbenzene proceeds via the relay mechanism presented in Scheme I. The analogous formulation as applied to the results in this study is given below.
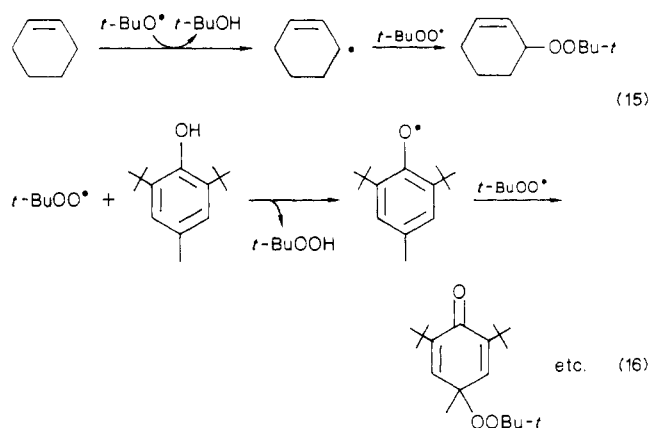
According to Scheme III, the active carrier is an oxo-cobalt(IV) species[37] formed by a two-electron oxidation of $Co^{II}(Ia)$ by iodosylbenzene. The insensitivity to ionol is understandable since free radicals as such are not the viable intermediates in the catalytic cycle. However, the attack of cyclohexane (eq 10) and on solvents such as dichloromethane suggests that an oxo–cobalt(IV) species is capable of oxygen transfer into a carbon–hydrogen bond.[32] With olefins, the process is not competitive with oxygen atom transfer to the double bond, except in unusual cases like cyclohexene, as indicated by the formation of minor amounts of cyclohexenol and cyclohexenone.

Oxygen atom transfer to olefin occurs with very high but not exclusive stereospecificity. Thus the conversion of (E)-β-methylstyrene to the trans epoxide occurs without contamination of the cis epoxide. Furthermore the conversion of (Z)-β-methylstyrene to only the cis epoxide is more unusual owing to driving forces for the rearrangement of cisoid configurations in olefins and epoxides which are greater than their transoid counterparts. Under more testing conditions with aliphatic olefins such as 2(Z)-hexene, small amounts (~2%) of the more stable trans epoxide are formed. These results suggest that oxygen atom transfer to olefin occurs synchronously or by successive steps in which the second is sufficiently rapid to largely preclude bond rotation about the olefinic center.[38] A reactive oxo–cobalt species such as that in Scheme III

(37) For other examples of cobalt(IV) species, see: (a) Levitin, I.; Sigan, A. L.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1975**, 469. (b) Topich, J.; Halpern, J. *Inorg. Chem.* **1979**, *18*, 1339. (c) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 5037. (d) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512. (e) See also: Lee, W. A.; Bruice, T. C. *Inorg. Chem.* **1986**, *25*, 131. Bryne, E. K.; Richeson, D. S.; Theopold, K. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1491.

(38) For a discussion of this point, see ref 19.

Scheme III

$$Co^{II}(Ia) + PhIO \longrightarrow O=Co^{IV}(Ia) + PhI \qquad (17)$$

$$O=Co^{IV}(Ia) + \underset{}{\overset{}{>}}C=C\underset{}{\overset{}{<}} \longrightarrow \underset{}{\overset{}{>}}C\overset{O}{-}C\underset{}{\overset{}{<}} + Co^{II}(Ia) \qquad (18)$$

would be consistent with the stereochemical results. Furthermore the small but discrete amounts (~1%) of endo norbornene oxide point to an early transition state for oxygen atom transfer.[39] By comparison, the epoxidation of norbornene via the homolytic process in Scheme II produces less endo isomer (<0.1%).

Cobalt catalysis of olefin epoxidation occurs too readily to obtain direct information of the putative oxo–cobalt(IV) intermediate. However the postulation of such an active species does help to explain a unique facet of the catalytic epoxidation with $Co^{II}(Ia)$. The unusual position of this catalyst among other close relatives lies in its selectivity and reactivity despite its limited solubility[40] in the reaction medium. Such a property would maintain low levels of cobalt in solution and minimize deactivation of the active species by its *bimolecular* reaction with cobalt(II) to form μ-oxo–cobalt(III) dimers, i.e. eq 19. Since the latter are

$$O=CO^{IV} + Co^{II} \rightarrow Co^{III}OCo^{III} \qquad (19)$$

notoriously stable,[41] they are expected to be unavailable for further catalytic action. Viewed in this way, the low solubility actually represents a beneficial feature for effective catalysis by cobalt(II) complexes and is uniquely exemplified in $Co^{II}(Ia)H_2O$.[42] The postulation of an active oxo–cobalt(IV) species also accounts for the ready incorporation of isotopic oxygen-18 into the epoxide from labeled water in eq 9. Thus it has been established in a related oxo–chromium(V) complex that oxygen exchange with water is a facile process,[43] i.e. eq 20. An analogous

$$O=Cr^V(salen)^+ + H_2{}^{18}O \underset{}{\overset{fast}{\rightleftharpoons}} {}^{18}O=Cr^V(salen)^+ + H_2O \qquad (20)$$
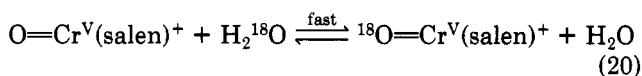
exchange with an oxo–cobalt intermediate would lead to the isotopically labeled epoxide in eq 9.

Cobalt catalysis of olefin epoxidation with $Co^{II}(Ia)$ is compared in Table IV with that obtained earlier with $Cr^{III}(salen)^+$ and $Mn^{III}(salen)^+$ under similar conditions.[19,32] Oxygen atom transfer during chromium catalysis is known to occur via the oxo–chromium(V) intermediate $O=Cr^V$-$(salen)^+$, and it is strongly indicated to occur during manganese catalysis via an analogous oxo–manganese species. Thus the parallel behavior shown in Table IV supports a similar species as a reactive intermediate in cobalt catalysis. If so, the slight differences in the relative amounts of byproducts accord with an oxo–cobalt species which is not only more selective but also more reactive than its chromium and manganese counterparts.

We hasten to add however that there are other mechanistic possibilities for cobalt catalysis which do not include

Table IV. Comparative Behavior of Oxo–Metal Intermediates in the Catalytic Epoxidation of Olefins

olefin	product	$Co^{II}(Ia)^a$	$Cr^{III}(salen)^{+\,b}$	$Mn^{III}(O_2Nsalen)^{+\,c}$
		65	10	69
		2	4	<1
		76	58	39
		0	0.5	1
		68	44	31
		0	3	4
PhCHO		<1	5	
PhCH₂COCH₃		1	16	7

^{a}This work. ^{b}From ref 19. ^{c}From ref 32.

oxo–cobalt species as oxygen carriers. Such formulations would include the direct transfer of an oxygen atom from iodosylbenzene to the olefin by mediation of the cobalt catalyst in a more or less Lewis acid capacity.[44] Why $Co^{II}(Ia)$ is unusually suited to effect olefin epoxidation is not clear from this formulation.

We infer from the spectroscopic and elemental analyses (see Experimental Section) and from the basic structure of the ligand Ia that the catalyst consists of the core structure A. In the solid, the coordination number of

A
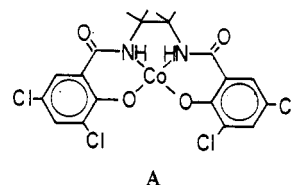
cobalt is probably expanded by intermolecular interactions leading to an overall polymeric structure with low solubility.[17] Thus our varied attempts to crystallize $Co^{II}(Ia)$ has been uniformly unsuccessful, and we cannot establish the structure of $Co^{II}(Ia)$ by X-ray crystallography. The effective catalyst in our studies is largely amorphous, as indicated by an X-ray powder diffraction pattern. Accordingly we are pursuing other analogues to elucidate those intriguing mechanistic aspects of cobalt catalysis which have eluded us. We wish to emphasize that from an operational viewpoint, $Co^{II}(Ia)$ is a remarkably efficient and selective cobalt catalyst for epoxidation. Its distinctive action with iodosylbenzene as the terminal oxidant is to be differentiated from the more common Co^{II}/Co^{III} redox processes presented in Scheme II for *tert*-butyl hydroperoxide. As such, it emphasizes the dual pathways which are available in cobalt catalysis of organic oxidations.

Experimental Section

Materials. Cobaltous acetate $(Co(O_2CCH_3)_2 \cdot 4H_2O)$ from Matheson, Coleman and Bell was used as supplied. Salicylic acid (Fisher), 1,2-dicyanobenzene, α-picolinic acid, *trans*-(±)-1,2-diaminocyclohexane, ethylenediamine from Aldrich, 2-amino-4-

(39) For example, the oxygen transfer in eq 18 from the endo face of norbornene must overcome steric hindrance from the 5- and 6-endo hydrogens.

(40) Gravimetric analysis indicates the concentration of $Co(Ia)H_2O$ in dichloromethane to be less than 10^{-4} M. At this juncture we are unable to state unequivocally whether catalysis occurs at the surface or arises from small amounts of $Co(Ia)$ dissolved in solution.

(41) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980. (b) Sykes, A. G.; Weil, J. A. *Prog. Inorg. Chem.* **1970**, *13*, 1. (c) Sykes, A. G. *Chem. Brit.* **1974**, 170. Herein no distinction is made between μ-oxo and μ-hydro complexes.

(42) For a similar effect of solubility on the catalytic activity of nickel complexes, see: Koola, J. D.; Kochi, J. K. *Inorg. Chem.* **1987**, *26*, 908.

(43) Srinivasan, K.; Kochi, J. K. *Inorg. Chem.* **1985**, *24*, 4671.

(44) See, e.g.: Tai, A. F.; Margerum, L. D.; Valentine, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 5006.

methylpyridine (Eastman), ionol (Shell Chemical), and oxygen-18-labeled water (90% isotopic purity, Aldrich) were also used as received. Pyridine and γ-picoline from Aldrich were distilled from CaH_2 under an argon atmosphere prior to use. *o*-Phenylenediamine (Matheson, Coleman and Bell) and 1,2-diamino-4,5-dichlorobenzene (Aldrich) were purified by refluxing with activated charcoal in dichloromethane followed by recrystallization. Thionyl chloride was distilled from triphenyl phosphite. Triethylphosphine oxide,[19] cobalt(II) salen,[45] cobalt(II) salen(py),[45] and cobaltic acetate[46] were obtained from previous studies. The hydrocarbon substrates obtained from previous studies[19,32] were distilled from $LiAlH_4$ and stored in Schlenk flasks under an argon atmosphere. Iodosylbenzene,[47] pentafluoroiodosylbenzene,[48] $Co^{II}(BPB)H_2O$,[28a] $Co^{II}(4$-methyl-BPI)OAc,[29b] and 2,3-dimethyl-2,3-diaminobutane[16] were prepared by the procedures described in the literature. The ligands IcH_2 and IeH_2 were prepared as described by Collins et al.[15] *tert*-Butyl hydroperoxide (90%, Wallace and Tiernan) was converted to the sodium salt with 30% aqueous sodium hydroxide. It was separated from the aqueous solution by vacuum filtration and was washed with benzene repeatedly until apparently dry. The salt was suspended in water and the mixture neutralized with carbon dioxide. The separated oil was extracted with hexane, and the organic solution was dried. Removal of the solvent followed by distillation in vacuo (*Caution*: explosion!) afforded *tert*-butyl hydroperoxide of >99% by iodometric titration.

Acetyl-3,5-dichlorosalicylic acid was prepared by passing chlorine through an acetic acid solution of salicylic acid, followed by acetylation with acetic anhydride. It was converted to the acid chloride with thionyl chloride in the presence of a catalytic amount of anhydrous $AlCl_3$ at 50–60 °C which was treated with 2,3-diamino-2,3-dimethylbutane in dichloromethane and then triethylamine. Hydrolysis and workup yielded a colorless solid which was recrystallized from aqueous acetone followed by removal of acetone in vacuo, mp 198–200 °C, yield 77% of 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethylsalamH$_2$ [2,3-bis(3,5-dichloro-2-hydroxybenzamido)-2,3-dimethylbutane]. ^{1}H NMR (CDCl$_3$): δ 1.59 (s, 12 H), 7.44 (d, *J* = 2 Hz, 2 H), 7.56 (d, *J* = 2 Hz, 2 H), 7.95 (s, 2 H), 12.18 (s, 2 H). IR (KBr): 3374 (m), 3269 (m), 3086 (w), 2995 (m), 1644 (vs), 1589 (vs), 1562 (vs), 1548 (vs, br), 1450 (vs, br), 1400 (vs), 1360 (vs), 1330 (vs), 1253 (vs), 1204 (w), 1190 (w), 1144 (s), 977 (w), 930 (m), 879 (s), 859 (m), 791 (s), 772 (m), 753 (m), 736 (s), 709 (w), 687 (w), 632 (w), 610 (w), 561 (m), 520 (m), 485 (m). The ligand IbH$_2$ was prepared from 6.8 g (27.3 mmol) of acetyl-3,5-dichlorosalicylic acid and 1.2 g (10.5 mmol) of *trans*-(±)-1,2-diaminocyclohexane by a procedure analogous to that used for IaH$_2$. Crystallization for a mixture of ethanol and THF yielded 3.5 g (67%) of IbH$_2$. mp 286–288 °C. ^{1}H NMR (DMSO-d_6): δ 1.6 (br, m), 7.68 (d, *J* = 2 Hz, 2 H), 7.89 (d, *J* = 2 Hz, 2 H), 8.98 (s, 2 H). The ligand IdH$_2$ was obtained by a procedure similar to that reported by Collins et al.[15]

Synthesis of Co^{II}(Cl$_4$Me$_4$salam). A solution containing Co-(OAc)$_2$·4H$_2$O (0.125 g, 0.50 mmol) and 2,2′,4,4′-tetrachloro-8,8,8′,8′-tetramethylsalamH$_2$ (0.25 g, 0.51 mmol) in methanol was deaerated with a stream of argon and then refluxed for 3 h, during the course of which a light purple solid separated. Alternatively a solution of Cl$_4$Me$_4$salamH$_2$ (8.0 g, 16.2 mm) in 1000 mL of deoxygenated methanol was refluxed under an argon atmosphere. To this was slowly added a solution of cobaltous acetate [Co-(OAc)$_2$·4H$_2$O, 4.3 g, 17.3 mmol] in 300 mL of methanol and the mixture was stirred overnight at 25 °C. The solution was filtered to remove particulate matter and the clear filtrate carefully concentrated to yield a purple solid. Yield: 8.0 g (89%) of Co(Cl$_4$Me$_4$salam)·^{3}/$_2$H$_2$O. Anal. Calcd for C$_{20}$H$_{18}$Cl$_4$CoN$_2$O$_4$·^{3}/$_2$H$_2$O: C, 41.55; H, 3.66; N, 4.85. Found: C, 41.46; H, 3.75; N, 4.80. IR (KBr): 3230 (m, br), 3085 (m), 2995 (m), 1620 (vs, br), 1568 (vs, br), 1447 (vs, br), 1403 (s), 1379 (w), 1343 (m), 1313 (w), 1294 (w), 1250 (s), 1234 (s), 1138 (s), 1097 (w), 1026 (w), 1001 (vw),

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980 (w), 930 (w), 873 (s), 794 (s), 764 (s), 711 (m), 676 (m), 643 (w), 613 (w), 559 (w), 534 (m), 479 (w), 457 (w), 419 (m). The light purple sesquihydrate, when dried over P_2O_5 under vacuum, yielded the light blue monohydrate, Co^{II}(Ia)H$_2$O. Anal. Calcd for C$_{20}$H$_{18}$Cl$_4$CoN$_2$O$_4$·H$_2$O: C, 42.21; H, 3.54. Found: C, 42.35; H, 3.70. This cobalt(II) complex was very stable to air either in the solid state or when suspended in solvents. All attempts to crystallize it were unsuccessful owing to its insolubility in organic solvents except pyridines. Various attempts were made to obtain the complex in a crystalline form before its precipitation. The following methods were followed. The complex was prepared in solution in methanol at high dilution and carefully concentrated, taking care not to precipitate the complex. Then, solvents like ether, pentane, hexane or dichloromethane were slowly allowed to diffuse into the complex solution in methanol at room temperature or ice bath temperature. Nevertheless, a noncrystalline material precipitated. Attempts to crystallize the complex by carrying out the synthesis in a biphasic system (water and benzene) using a phase-transfer catalyst or by solvent extraction of the ligand into an aqueous methanolic solution of Co(O-Ac)$_2$·4H$_2$O were also not successful. A finely pulverized powder of Co(Ia)H$_2$O (0.5 g) was mounted on an aluminum block and rotated at 4 kHz. The X-radiation with λ = 1.54050 Å was generated at a fixed voltage of 30 kV and fixed current of 10 mA. Only a nondescript, broad diffraction pattern with a few occasional peaks was observed at low angles with a crude maximum at ∼15–30°.

Synthesis of the Pyridine Adduct of Co^{II}(Ia). Co(O-Ac)$_2$·4H$_2$O (0.125 g, 0.5 mm) dissolved in 20 mL of deaerated methanol was slowly added to a solution of Cl$_4$Me$_4$salamH$_2$ (0.25 g, 0.51 mm) in 100 mL of deaerated methanol under argon. The solution was then kept stirred at 40 °C for 2 h. Pyridine (1 mL) was then added and the mixture stirred overnight. Finally the solvents were removed to obtain a deep blue solid. It was then dissolved in pyridine and hexane was slowly diffused into this blue solution, whereupon the brown pyridine adduct separated. Yield: 0.2 g, 57%. IR (KBr): 3234 (s, br), 3072 (s, br), 2995 (m, br), 1657 (vs, br), 1573 (vs, br), 1447 (vs, br), 1379 (w), 1343 (w), 1308 (w), 1250 (m), 1220 (m), 1141 (s), 1097 (w), 1070 (m), 1040 (m), 1013 (m), 980 (w), 928 (w), 873 (s), 791 (s), 769 (s), 701 (s), 676 (m), 632 (m), 561 (m), 529 (m), 496 (w), 477 (w), 449 (w), 422 (m).

Synthesis of the DMF Adduct of Co^{II}(Ia). The DMF adduct of I was prepared by reacting Co(OAc)$_2$·4H$_2$O (0.25 g, 1 mm, dissolved in 20 mL dry DMF) with Cl$_4$Me$_4$SalamH$_2$ (0.5 g, 1.01 mm, dissolved in 60 mL dry DMF) under argon at 110–120 °C for 3 h. The resulting deep blue solution was dried in vacuum and then washed with benzene and dichloromethane to obtain a blue solid. The blue solid was readily soluble in DMF. However it could not be crystallized from DMF solution. Yield: 0.5 g, 71%. IR (KBr): 3085 (w), 2995 (w), 1622 (vs, br), 1554 (vs, br), 1442 (vs, br), 1343 (m), 1316 (w), 1250 (s), 1144 (s), 1098 (w), 1023 (w), 980 (w), 930 (w), 870 (m), 835 (w), 791 (s), 772 (m), 734 (w), 712 (w), 679 (s), 668 (s), 619 (m), 561 (w), 537 (w), 493 (w), 473 (w), 452 (w), 436 (w), 422 (w).

Synthesis of Co^{II}(Ib). The ligand IbH$_2$ (0.5 g, 1.02 mmol) was suspended in 50 mL of MeOH and the mixture was heated under an argon atmosphere. A solution of sodium methoxide prepared from 0.050 g (2.17 mmol) of sodium in 20 mL of MeOH was added slowly. This was followed by a solution of cobaltous acetate (0.25 g, 0.98 mmol) dissolved in 10 mL of MeOH. The refluxing mixture was stirred for an additional hour. The purple solid was removed by filtration, washed with methanol, and dried. Yield: 0.45 g (83%) of Co(Ib)7H$_2$O. Anal. Calcd for C$_{20}$H$_{16}$Cl$_4$CoN$_2$O$_4$·7H$_2$O: C, 35.57; H, 4.47; N, 4.14. Found: C, 35.38; H, 3.86; N, 4.13.[49]

Synthesis of Co(Ic). The ligand IcH$_2$ (0.66 g, 1.5 mmol) was treated as above with sodium methoxide (3.1 mmol) in 10 mL of MeOH and Co(OAc)$_2$·4H$_2$O (0.367 g, 1.47 mmol) to yield 0.3 g (43%) of Co(Ic)8H$_2$O. Anal. Calcd for C$_{16}$H$_{10}$Cl$_4$CoN$_2$O$_4$·8H$_2$O: C, 30.07; H, 4.10. Found: C, 29.78; H, 3.13.

Synthesis of Co(Id). The ligand IdH$_2$ (0.49 g, 1.01 mmol) in 20 mL of MeOH, sodium methoxide (2.26 mmol) in 10 mL of MeOH, and Co(OAc)$_2$·4H$_2$O (0.245 g, 0.98 mmol) in 15 mL of

(49) Elemental analyses by Atlantic Microlab, Inc., Atlanta, GA.

MeOH was treated as above to yield 0.25 g (47%) of Co(Id)7H$_2$O. Anal. Calcd for C$_{20}$H$_{20}$Cl$_4$CoN$_2$O$_4$·7H$_2$O: C, 35.90; H, 3.62. Found: C, 36.08; H, 4.29.

Synthesis of Co(Ie). The preparation of this complex with the ligand IeH$_2$ followed that given above. Anal. Calcd for C$_{20}$H$_8$Cl$_6$CoN$_2$O$_4$·3/2H$_2$O: C, 37.60; H, 1.74. Found: C, 37.69; H, 2.55.

Reactions of Co^{II}(Ia)H$_2$O. Co^{III}(Ia)Br was prepared from Co^{II}(Ia)H$_2$O by a method analogous to that used for Co^{III}(salen)I.[50] Typically, Co^{II}(Ia)H$_2$O (155 mg, 0.27 mmol) was suspended in 10 mL of dichloromethane and treated with 1 equiv of Br$_2$. After stirring the mixture overnight, the green cobalt(III) bromide was obtained. The *tert*-butylperoxy complex Co^{III}(Ia)(OOBu-*t*)(4-Mepy) was prepared by a method analogous to that described by Mimoun et al.[2d] Co^{II}(Ia)H$_2$O (0.111 g, 0.19 mmol) was suspended in 10 mL of dichloromethane to which 100 µL of γ-picoline and 0.3 mL of 90% TBHP was added. The mixture was stirred for 4 h, and the resulting green solution was dried with anhydrous Na$_2$SO$_4$. After filtration and concentration in vacuo, the green residue was treated with 20 mL of diethyl ether. The green *tert*-butylperoxocobalt(III) complex was collected. Attempts to oxidize Co^{II}(Ia)H$_2$O with NOPF$_6$ in acetonitrile led to ligand loss of Ia. However oxidation with ceric ammonium nitrate in acetonitrile yielded a chocolate brown complex.

Instrumentation. Infrared spectra were recorded on a Nicolet 10 DX FT spectrometer with the aid of KBr pellets. ^{1}H NMR spectra were obtained on a JEOL FX 90Q FT spectrometer, and all chemical shifts were reported relative to Me$_4$Si. GC-MS analyses were carried out on a Hewlett-Packard 5890 chromatograph interfaced to a HP 5970 mass spectrometer (EI, 70 eV). The X-ray powder diffraction was carried out with a Rigaku Model CN 2005 Miniflex.

Catalytic Epoxidation of Olefins. Cobalt catalysis of olefin epoxidation was carried out under an argon atmosphere with anhydrous solvents. In a typical experiment, 0.01 mmol of the cobalt(II) catalyst and 0.15–0.16 mmol of iodosylbenzene were suspended in 5 mL of the solvent containing 2–5 mmol of olefin. The reaction was stirred magnetically for 3–5 h and analyzed by GC-MS after filtration of the solids. Authentic samples of the epoxides were available from a previous study.[19,32] Chlorobenzene was generally used as the internal standard for GC analysis of epoxides and *n*-decane for the products of cyclohexene oxidation. For oxidations with TBHP, 0.01 mmol of Co^{II}(Ia)H$_2$O was treated with 1 mmol of the hydroperoxide and 5 mmol of the olefin in 5 mL of dichloromethane and the mixture stirred magnetically. After 5–6 h, excess triphenylphosphine was added to quench TBHP and the solution analyzed as described above. The conversion of TBHP was not quantitated.

The reaction mixtures obtained from the epoxidation of norbornene with various cobalt(II) catalysts differed in significant ways. This is indicated by the following: (a) yield of norbornene oxide, (b) number of byproduct components, and (c) relative percentage with respect to norbornene oxide: Co^{II}(Ia)H$_2$O, 90%,

nil, –; Co^{II}(Ia)DMF, 73%, 11, 5%; Co^{II}(Ia)py, 53%, 17, 24%; Co^{III}(Ia)Br, 71%, 8, 9%; Co^{II}(salen), 11%, 12, 175%; Co^{II}(salen)py, 18%, 17, 240%; Co^{II}(OAc)$_2$, 41%, 7, 164%; Co^{III}(OAc)$_3$, 61%, 21, 45%. With cyclohexene (cyclohexene oxide, number of byproducts, amount of byproducts): Co^{II}(Ia)H$_2$O, 60%, 3, 3%; Co^{II}(Ia)DMF, 49%, 12, 11%; Co^{II}(Ia)py, 31%, 8, 22%; Co^{II}(Ia)Br, 47%, 6, 9%; Co^{II}(salen), 8%, 9, 131%; Co^{II}(salen)py, 4%, 13, 400%; Co^{II}(OAc)$_2$, 19%, 7, 64%; Co^{III}(OAc)$_3$, 43%, 12, 21%. For (Z)-β-methylstyrene (epoxide, number of byproducts, amount of byproducts): Co^{II}(Ia)H$_2$O, 68%, nil, –; Co^{II}(Ia)DMF, 45%, 15, 8%; Co^{II}(Ia)py, 17%, 27, 35%; Co^{III}(Ia)Br, 30%, 22, 17%; Co^{II}-(OAc)$_2$, 38%, 20, 8%, Co^{III}(OAc)$_3$, 21%, 29, 45%.

The studies with ionol in Tables I and II were carried out by essentially the same procedure. (A) The thermal reaction of ionol (0.10 mmol) with iodosylbenzene (0.1 mmol) shown in Figure 2 afforded a complex mixture of products. GC-MS analysis (retention time; relative GC area, *m/z* of the parent ion) indicated the following: 5.02 min, 6%, 236; 5.07 min, 62%, 218; 5.19 min, 8%, 302, 304; 6.24 min, 13%, 253; 6.77, 11%, 302, 304. (B) The same reaction in the presence of norbornene (5 mmol) indicated the following: 1.74 min, 6%, 110; 5.02 min, 10%, 236; 5.07 min, 36%, 218; 5.91 min, 3%, 302, 304; 6.24 min, 15%, 253; 6.77 min, 4%, 302, 304. After 3 h, the additional components are 7.65 min, 6%, 330; 7.73 min, 13%, 328; 7.92 min, 3%, 328; 8.08 min, 3%, 328. (C) The additional presence of 0.01 mmol of Co^{II}(Ia)H$_2$O to B gave 1.74 min, 40%, 110 (norbornene oxide); 5.07 min, 55%, 218 (2,6-di-*tert*-butylquinone methide); 6.24 min, 5%, 253.

Isotopic Exchange with Labeled Water. The catalyst Co^{II}(Ia)H$_2$O (0.01 mmol) and norbornene (1.0 mmol) in 1 mL of acetonitrile was treated with 0.10 mmol of iodosylbenzene and 1.85 mmol H$_2$^{18}O (90% enriched). After stirring the mixture for 1 h, the solid was separated and the products were analyzed by GC-MS as described earlier.[15,17,32] A control experiment was also carried out in which norbornene oxide (0.5 mmol) was exposed to iodosylbenzene (0.10 mmol), 0.01 mmol of Co(Ia)H$_2$O, and 1.85 mmol of H$_2$^{18}O in 1 mL of acetonitrile. The recovered epoxide showed no isotopic enrichment. Moreover the treatment of iodosylbenzene (0.1 mmol) with 1.85 mmol of H$_2$^{18}O in the presence of Co^{II}(Ia)H$_2$O (0.01 mmol) was carried out until about half the terminal oxidant was consumed. The remaining iodosylbenzene was recovered, and an analysis as described earlier[15,32] showed no isotopic enrichment.

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