as those described here are to find applications in the design of low-dimensional conductors, this detrimental feature must be overcome.

Summary

In contrast to the behavior of binary sulfur–nitrogen ring systems, the six-membered 1,2,4,6-thiatriazine unit is stable to both oxidation and reduction. Examples of the three oxidation states—cation, neutral radical, and anion (in its protonated form)—have been structurally characterized. The structural and energetic differences between the different oxidation states can be understood in terms of the degree of occupation of the π manifold of the C_2N_3S ring.

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Registry No. **2**, 94405-47-7; **3a**, 102420-46-2; **3b**, 102420-47-3; **5**, 102420-48-4; $Ph_2C_2N_3SH{\cdot}CH_2Cl_2$, 102420-49-5; $Ph_2C_2N_3SCl$, 94426-38-7; $Ph_2C_2N_3SNMe_2$, 102420-50-8; Me_2NSiMe_3, 2083-91-2; $H_2C_2N_3S^+$, 102420-51-9; $H_2C_2N_3S^{\bullet}$, 102535-02-4; $H_2C_2N_3S^-$, 102420-52-0; $H_2C_2N_3SH$, 290-94-8.

Supplementary Material Available: Anisotropic thermal parameters (Tables S1 and S2) for structures **3b** and **5** (2 pages). Ordering information is available on any current masthead page.

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Oxidative Alkylation of Cobalt Complexes with Hydrazines

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Cobalt complexes related to the salen ligand [*N,N'*-ethylenebis(salicylideneaminato)] are efficiently converted to the corresponding organocobalt(III) derivative such as RCo^{III}(salen) by various hydrazines ($RNHNH_2$) under oxidative conditions with either dioxygen or *tert*-butyl hydroperoxide. Optimum conditions are developed for the oxidative alkylation of various cobalt complexes with structurally diverse hydrazines. The limitations of the hydrazine method are delineated and accounted for by a study of the stoichiometry and reactive intermediates. Foremost among the latter are the superoxo and *tert*-butylperoxo complexes of cobalt(III) derived by oxidation, ligand exchange, or ligand-induced homolysis of different cobalt(II) and cobalt(III) precursors. Such cobalt(III) oxidants are responsible for the two-electron conversion of alkylhydrazines to their diazene derivatives. The subsequent extrusion of dinitrogen affords the organic radical (R·) as the key intermediate responsible for the alkylation of the cobalt(II) center. The primacy of alkyl radicals in the hydrazine procedure is established with the chemical clock utilizing the unimolecular homolytic rearrangement of 5-hexenyl to cyclopentylmethyl.

Introduction

A variety of synthetic methodologies is now available for the preparation of different metal–alkyl complexes.[1,2] However, those procedures that utilize oxidizing conditions are rare—a notable exception being the alkylation of chromium(II) complexes with organic hydroperoxides.[3] Thus the reports that various macrocyclic complexes of cobalt, iron, chromium, and manganese can be converted by organic hydrazines to the corresponding alkyl and aryl derivatives with air as a reagent are especially intriguing.[4-8] Accordingly, we have examined the oxidative synthesis of a variety of organocobalt complexes with different types of hydrazines. Our primary focus in this study is to delineate the reaction conditions, the stoichiometry, and the intermediates in the oxidative alkylation.

Table I. Oxidative Methylation of Co^{II}(salen) with Methylhydrazine[a]

$[CH_3NHNH_2]$, mM	oxidant (concn, mM)	temp, °C	[MeCo(salen)], mM (%)[b]
21	O_2[c]	22	14.0 (57)
42	O_2[c]	22	15.3 (73)
105	O_2[c]	22	17.8 (85)
210	O_2[c]	22	16.6 (79)
105	O_2[c]	0	17.7 (84)
105	O_2[c]	45	18.6 (89)
105	O_2[c,d]	22	17.8 (85)
105	*t*-BuOOH (52)[e]	22	18.4 (88)
105	PhIO (52)[e]	22	11.6 (55)
105	3-$ClC_6H_4CO_3H$ (46)[e]	22	0 (0)

[a] In 5 mL CH_2Cl_2 containing 2.1×10^{-2} M Co(salen) (I). [b] Based on I charged; isolated as the pyridine complex. [c] 1 atm of pure dioxygen. [d] Reverse addition of CH_3NHNH_2 to I and O_2. [e] Oxidant added to I and CH_3NHNH_2 under an argon atmosphere.

We selected the cobalt complexes that are derived mainly from salen [I, *N,N'*-ethylenebis(salicylideneaminato)] in view of the extensive preparative chemistry extant for (alkyl)- and (aryl)-Co^{III}(salen) complexes.[9] In order to provide some scope, the alkylations of the related Schiff base complexes of cobalt(II) with the ligands saloph (II), dmgH (III), and acacen (IV) are also reported. The formation of organic radicals as the reactive in-

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(3) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**; *1*, 1–63.
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(7) Battioni, P.; Mahy, J. P.; Gillet, G.; Mansuy, D. *J. Am. Chem. Soc.* **1983**, *105*, 1399.
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(9) For reviews see: (a) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, G. F. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 5, p 1. (b) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1. (c) Pratt, J. M.; Craig, P. J. *Adv. Organomet. Chem.* **1973**, *11*, 331.

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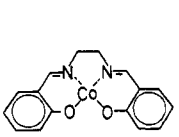
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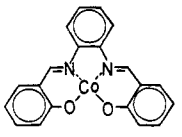
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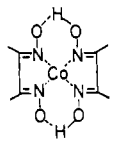
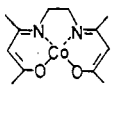

Co(dmgH)$_2$ (III)


Co(acacen) (IV)

termediates leading to the organocobalt products is described.

Results

I. Oxidative Methylation of Co^{II}(salen) with Methylhydrazine. The formation of alkylation products such as MeCo^{III}(salen) can be readily monitored by the appearance of the characteristic sharp singlet resonance at δ 2.70 in the ^{1}H NMR spectrum. More commonly this complex was isolated as the pyridine adduct V (δ 2.68). In a typical procedure, a solution of Co^{II}(salen) (I) in dichloromethane under an atmosphere of pure dioxygen was treated with excess methylhydrazine at room temperature. The oxidative methylation was accompanied by a rapid change in color from red to brown, and the reaction was complete within 10 min. The addition of pyridine to the reaction mixture, followed by chromatography through a short column of low-activity alumina to remove cobalt(II) and other impurities, led to 75–89% yields of MeCo^{III}(salen) (V). Spectroscopic analysis showed that the

$$\underset{\text{I}}{\text{Co}^{II}(\text{salen})} + CH_3NHNH_2 \xrightarrow[(2)\ \text{py}]{(1)\ O_2} \underset{\text{V}}{CH_3\text{Co}^{III}(\text{salen})\text{py}} \quad (1)$$

methyl derivative V formed under these conditions was the same as that prepared by a standard procedure involving the treatment of Na[Co^{I}(salen)] with methyl iodide in tetrahydrofuran (THF), followed by the addition of pyridine.[10]

We also found *tert*-butyl hydroperoxide to be an effective replacement for dioxygen in the methylation of Co^{II}(salen), as shown by a comparison of the results in Table I. With this oxidant, the vigorous evolution of gas (which upon GC–MS analysis was found to be mainly dinitrogen[11]), was readily apparent:

$$\text{Co}^{II}(\text{salen}) + CH_3NHNH_2 \xrightarrow[(2)\ \text{py}]{(1)\ t\text{-BuOOH}} CH_3\text{Co}^{III}(\text{salen})\text{py} + N_2 \quad (2)$$

The effects of the methylhydrazine concentration and the temperature on the yields of V are summarized in Table I. From these results, we conclude that the presence of 5 equiv of methylhydrazine is optimum for the formation of V from each mole of Co^{II}(salen). The yield of MeCo^{III}(salen) (V) is insensitive to temperatures between 0 and 45 °C and to the order of addition of methylhydrazine and dioxygen. Although *tert*-butyl hydroperoxide is equally as effective as dioxygen, the oxygen atom donor iodosylbenzene gave an inferior yield of V. Curiously, the readily available peroxyacid *m*-chloroperbenzoic acid produced no detectable amounts of V, despite an apparently vigorous reaction with Co^{II}(salen).

II. Oxidative Alkylation, Acylation, and Arylation of Co^{II}(salen). The ability of different organic hydrazines to alkylate Co^{II}(salen) (I) was investigated with *tert*-butyl hydroperoxide as the oxidant. The purified (alkyl)Co^{III}(salen) complexes in Table II were isolated whenever possible, and the identity of each cobalt(III) product was established by comparing its ^{1}H NMR spectrum with that synthesized from Na[Co^{I}(salen)] and the appropriate alkyl halide[10] after workup with pyridine.

Table II. Alkylation, Arylation, and Acylation of Co^{II}(salen)[a]

hydrazine deriv	Co(III) product[b]	yield,[c] mmol (%)
methyl	CH_3Co(salen)py	1.37 (89)
n-butyl	$CH_3CH_2CH_2CH_2$Co(salen)py	1.35 (88)
isobutyl	$(CH_3)_2CHCH_2$Co(salen)py	1.16 (75)
acetyl	CH_3COCo(salen)py	1.23 (80)
phenyl	C_6H_5Co(salen)py	1.09 (71)
isopropyl	$(CH_3)_2CHCo$(salen)py	*d* (35)[e]
sec-butyl	$CH_3CH_2CH(CH_3)$Co(salen)py	*d* (14)[e]

[a] In methylene chloride (70 mL) containing 1.54 mmol (2.2×10^{-2} M) of Co^{II}(salen), 3.85 mmol of *t*-BuOOH, and 7.7 mmol of organic hydrazine. [b] Following chromatography and addition of pyridine. [c] Isolated after recrystallization, unless stated otherwise. Yields based on Co^{II}(salen) charged. [d] Too unstable to isolate. [e] Estimated from ^{1}H NMR spectrum of crude product (see Experimental Section).

The results in Table II indicate that primary alkylhydrazines generally afford high yields (75–90%) of the corresponding (alkyl)Co^{III}(salen). Acetyl- and phenylhydrazines are also converted to their cobalt(III) products in similar high yields of 80 and 71%, respectively:

$$CH_3C(O)NHNH_2 + \text{Co}^{II}(\text{salen}) \xrightarrow[(2)\ \text{py}]{(1)\ t\text{-BuOOH}} CH_3C(O)\text{Co}^{III}(\text{salen})\text{py} \quad (3)$$

Somewhat unexpectedly, we were not able to prepare AcCo^{III}(salen) from the cobalt(II) salen and acetylhydrazine in the presence of dioxygen. With the secondary alkylcobalt(III) derivatives from isopropyl- and *sec*-butylhydrazines, the products could not be isolated by the usual procedures without extensive degradation.[12] The poor yields (14–35%) are partly accounted for by what appears to be the alkylperoxo derivative. For example, in addition to the characteristic doublet resonance (δ = −0.14, J = 6.8 Hz) of the methyl groups in the ^{1}H NMR spectrum of *i*-PrCo^{III}(salen), a downfield doublet (δ = 0.58, J = 6.0 Hz) was observed as an impurity. A similar downfield shift of 0.4 ppm has been observed in the methyl resonance of *i*-PrCo^{III}(dmgH)$_2$ upon the photoinduced insertion of O_2.[13] Treatment of *tert*-butylhydrazine with Co^{II}(salen) and *t*-BuOOH produced no product that could be identified as the *t*-BuCo^{III}(salen) complex.[14]

III. Methylation of Cobalt(II) and Cobalt(III) Schiff Base Complexes. Upon the optimization of the reaction conditions for Co^{II}(salen), we then examined the synthetic scope of the methylation procedure with a variety of analogous Schiff base complexes of both cobalt(II) and cobalt(III). The results in Table III show that those cobalt(II) complexes I and II, which contain Schiff base ligands with aromatic rings, consistently afforded good (75–87%) yields of methylation products. However, the dmgH and acacen complexes III and IV gave 50% or less of the corresponding methylcobalt(III) derivatives, despite extensive attempts to optimize their yields beyond this limiting value. We thus conclude that a yield of 50% is the maximum that can be achieved with complexes III and IV.

Co^{III}(salen) salts such as those with pyridine and phosphine ligands and ICo^{III}(salen) are not suitable starting materials for the oxidative methylation procedure. However, those Co^{III}(salen) complexes bearing ligands derived from O_2 or *t*-BuOOH react directly with methylhydrazine under anaerobic conditions to afford MeCo^{III}(salen) in good yields (Table II). For example, the highly insoluble black (μ-peroxo)dicobalt(III) complex[15] [(salen)Co]$_2O_2$

(10) Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *11*, 333.
(11) The presence of methane was indicated from its ^{1}H NMR spectrum and by GC–MS analysis.
(12) (a) The yields in Table II are based on ^{1}H NMR analysis of the crude reaction mixture with minimal workup. (b) *i*-Pr- and *s*-BuCo^{III}(salen) from the alkylation of the cobaltate[10] do not suffer a similar rapid degradation.
(13) Giannotti, C.; Gaudemer, A.; Fontaine, C. *Tetrahedron Lett.* **1970**, 3209.
(14) The possibility of a reductive elimination of isobutylene to afford a hydridocobalt(III) derivative was not examined.
(15) Bailes, R. H.; Calvin, M. *J. Am. Chem. Soc.* **1947**, *69*, 1886.

Table III. Oxidative Methylation of Various Schiff Base Complexes of Cobalt(II) and Cobalt(III)[a]

Co complex[b]	concn, 10^3 M	oxidant[c]	product	yield,[d] 10^3 M (%)
(py)(salen)Co^{II}	21.0	O_2	CH_3Co(salen)(py)	15.8 (75)
(7,7′-Me_2salen)Co^{II}	20.2	P (50)	CH_3Co(7,7′-Me_2salen)(py)	16.2 (80)
(saloph)Co^{II}	20.6	P (50)	CH_3Co(saloph)(py)	17.9 (87)
(acacen)Co^{II}	20.0	P (50)	CH_3Co(acacen)(py)	9.3 (47)
$(dmgH)_2Co^{II}$[e]	20.7	O_2	$CH_3Co(dmgH)_2$(py)	9.5 (46)
$(dmgH)_2Co^{II}$	31.1	P (78)	$CH_3Co(dmgH)_2$(py)	14.5 (47)
$(H_2O)_2(dmgH)_2Co^{II}$	20.7	P (50)	$CH_3Co(dmgH)_2$(py)	10.2 (51)
$[(py)_2$(salen)$Co^{III}]PF_6$	21.0	O_2	CH_3Co(salen)(py)	10.8 (51)
$[(Ph_3P)$(salen)$Co^{III}]ClO_4$	21.0	O_2	CH_3Co(salen)(py)	7.8 (37)
I(salen)Co^{III}	21.0	O_2	CH_3Co(salen)(py)	9.1 (43)
$[$(salen)$Co]_2O_2$	21.0	O_2	CH_3Co(salen)(py)	17.7 (84)
(salen)(*t*-BuOO)Co^{III}	20.5	none[f]	CH_3Co(salen)(py)	15.0 (73)
(py)(salen)(*t*-BuOO)Co^{III}	20.2	none[f]	CH_3Co(salen)(py)	15.1 (75)

[a] In methylene chloride with 1×10^{-1} M CH_3NHNH_2 at 25 °C, unless stated otherwise. [b] Abbreviations: saloph, bis(salicylaldehyde) *o*-phenylenediaminato; acacen, bis(acetylacetone) ethylenediaminato; dmgH, dimethylglyoximato. Position 7 refers to the imine carbon of salen. [c] O_2 at 1 atm. P is *tert*-butyl hydroperoxide (stated in mM) in the reactions carried out under argon. [d] Based on cobalt complex charged. [e] Conducted with 2×10^{-1} M CH_3NHNH_2 in acetonitrile at 60 °C. [f] Under 1 atm of argon.

reacts spontaneously with a solution of methylhydrazine under an argon atmosphere to produce a red solution. Addition of dioxygen, followed by column chromatography, afforded V in 84% yield. Moreover, the *t*-BuOOCo^{III}(salen) complex[16] VI and its pyridine adduct[17] *t*-BuOOCo^{III}(salen)py (VII) react with methylhydrazine under argon without the aid of an added oxidant to afford V in 73 and 75% yields, respectively:

$$\underset{\text{VII}}{t\text{-BuOOCo}^{III}\text{(salen)py}} + CH_3NHNH_2 \rightarrow \underset{\text{V}}{CH_3Co^{III}\text{(salen)py}} \quad (4)$$

In both cases, the methylation is complete within a few minutes as indicated by the vigorous evolution of gas (nitrogen).[18]

IV. Stoichiometry for Oxidative Methylations. The stoichiometry for the oxidative methylation of Co^{II}(salen) was determined by quantitative analysis of the amount of methylhydrazine consumed in the reaction and by manometric determination of the nitrogen evolved. First, the analysis of methylhydrazine was carried out by complete conversion to acetone methylhydrazone, which was determined by quantitative gas chromatography.[19] When a solution of 0.02 M Co^{II}(salen) containing 5 equiv of methylhydrazine was assayed before and after exposure to an atmosphere of O_2, it was found that 1.06 ± 0.05 equiv of methylhydrazine was consumed. In a separate experiment, a solution of Co^{II}(salen) under an atmosphere of O_2 was treated with 5 equiv of methylhydrazine and the measurement of the volume of gas at constant pressure showed the absorption of 0.52 mol of gas/mol of I. Since the head gas was found by GC–MS analysis to consist of mostly dinitrogen, we deduce the stoichiometry to be[20]

$$Co^{II}\text{(salen)} + CH_3NHNH_2 + 1.5O_2 \xrightarrow[py]{} CH_3Co^{III}\text{(salen)py} + N_2 + 1.5H_2O_2 \quad (5)$$

The determination of the stoichiometry for oxidative methylation with *tert*-butyl hydroperoxide as the oxidant was somewhat more complicated. Thus the treatment of Co^{II}(salen) and 5 equiv of methylhydrazine with 2.4 equiv of *tert*-butyl hydroperoxide resulted in the disappearance of 1.5 equiv of methylhydrazine. The overall consumption of slightly more than 1 equiv of methylhydrazine is accounted for by its decomposition by the oxidant, since the presence of more *tert*-butyl hydroperoxide (5 equiv) led to increased amounts (2.3 equiv) of methylhydrazine consumed.[21] The consumption of the extra methylhydrazine is associated with its catalytic decomposition to methane. For example, volumetric gas measurements made during the methylation of Co^{II}(salen) and 5 equiv of methylhydrazine indicated that 1.7 and 1.9 mol of gas were evolved when 2.4 and 5.0 mol, respectively, of *tert*-butyl hydroperoxide were employed. GC–MS analysis of the head gas showed that it consisted of both nitrogen and methane. We tentatively ascribe the catalytic decomposition of methylhydrazine by *tert*-butyl hydroperoxide to a side reaction with the stoichiometry

$$CH_3NHNH_2 + t\text{-BuOOH} \xrightarrow{[Co(salen)]} CH_4 + N_2 + t\text{-BuOH} + H_2O \quad (6)$$

The principal reaction that leads to the oxidative methylation of Co^{II}(salen) with *tert*-butyl hydroperoxide is then ascribed to[22]

$$Co^{II}\text{(salen)} + CH_3NHNH_2 + t\text{-BuOOH} \rightarrow CH_3Co^{III}\text{(salen)} + N_2 + t\text{-BuOH} + H_2O$$

This formulation is supported by the observation that the preformed *tert*-butylperoxo complex VII reacts directly with methylhydrazine in the absence of any added oxidant (see eq 4). Thus the changes in the ^1H NMR spectra following the addition of 1.5 equiv of CH_3NHNH_2 to a 0.02 M solution of *t*-BuOOCo^{III}(salen)py in chloroform-d_1 indicate that the *tert*-butylperoxy group (δ = 0.92) was completely converted to *tert*-butyl alcohol (δ = 1.27) with the concomitant formation of CH_3Co^{III}(salen) as shown by the appearance of its characteristic resonance at δ = 2.70. Unreacted methylhydrazine (δ = 2.5) was also present, together with a broad envelope (δ = ca. 3) believed to be due to water and other products with exchangeable protons. However, methane was absent under these conditions. We thus associate the direct reaction of the peroxo complex VII and methylhydrazine to the process with the stoichiometry given in eq 7.

$$t\text{-BuOOCo}^{III}\text{(salen)py} + CH_3NHNH_2 \rightarrow CH_3Co^{III}\text{(salen)py} + N_2 + t\text{-BuOH} + H_2O \quad (7)$$

(16) Nishinaga, A.; Tomita, A. *Chem. Lett.* **1983**, 1751.
(17) Saussine, L.; Brazi, E.; Robine, A.; Mimoun, H.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1985**, *107*, 3534.
(18) In addition to the Schiff base complexes of cobalt, we also briefly screened some more common inorganic and organometallic complexes for reaction with methylhydrazine and *tert*-butyl hydroperoxide. In each case, the anticipated methyl or dimethyl derivatives were available from different preparative methods and are known not to be highly air sensitive. Although a reaction was visible in most cases, we could find no evidence for the methylation of $Mn_2(CO)_{10}$, $Mn(CO)_5Cl$, $Mn(CO)_5$(NCMe)BF_4, $[CpFe(CO)_2]_2$ (Cp = cyclopentyl), $CpFe(CO)_2I$, Cp_2TiCl_2, (1,5-COD)$Pt(CH_3)Cl$ (1,5-COD = 1,5-cyclooctadiene), or *trans*-$(Ph_3P)_2Pt(Cl)H$.
(19) Veal, J. T. *Air Force Syst. Command, Civ. Environ. Eng. Serv. Off., [Tech. Rep.] CEEDO-TR (U.S.)* **1978**, *CEEDO-TR-78-14*; *Chem. Abstr.* **1979**, *90*, 145350g.
(20) (a) The hydrogen peroxide was not analyzed. (b) The alternative process leading to water rather than H_2O_2 predicts the net evolution of 0.25 mol of gas/mol of I. (c) Hydrogen peroxide may also be further reduced to water by the hydrazine.
(21) The consumption of the additional methylhydrazine by *tert*-butyl hydroperoxide under these conditions is metal catalyzed, since no reaction occurs in the same time span (<10 min) in the absence of Co(salen).
(22) The balanced equation is as follows: $2Co^{II}$(salen) + $2CH_3NHNH_2$ + 3*t*-BuOOH → $2CH_3Co^{III}$(salen) + $2N_2$ + 3*t*-BuOH + $3H_2O$.

V. Catalytic Oxidation of Hydrazines with Co(salen). A variety of metal salts, including cobaltous chloride, $CoCl_2$, are known to catalyze the autoxidation of aqueous hydrazine and substituted hydrazines to afford initially hydrogen peroxide.[23] In order to ascertain whether Co^{II}(salen) is capable of a similar catalysis under nonaqueous conditions, we examined the oxidation of hydrazobenzene to the stable azobenzene in methylene chloride at 25 °C. Indeed, complex I catalyzed the complete conversion of a 10-fold excess of hydrazobenzene to azobenzene (96% yield) under 1 atm of dioxygen in less than 15 min, which is equivalent to the conditions employed in oxidative alkylations. The autoxidation of hydrazobenzene is given by eq 8.[20c] A control experiment carried out without added Co^{II}(salen) showed only a 9% conversion of hydrazobenzene.

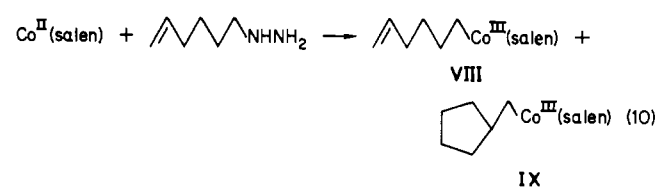
$$PhNHNHPh + O_2 \xrightarrow{[Co(salen)]} PhN{=}NPh + H_2O_2 \quad (8)$$

Similarly, the ability of the *tert*-butoxy complex VII to effect the stoichiometric oxidation of hydrazobenzene was examined in methylene chloride solutions under an atmosphere of argon. The treatment of 0.02 M VII with 3 molar equiv of hydrazobenzene afforded 1.46 molar equiv of azobenzene in ~10 min. Since this organic oxidation corresponds to a two-electron change, the reduction of the cobalt complex VII is consistent with a three-electron transformation according to the stoichiometry in eq 9.

$$2t\text{-}BuOOCo^{III}(salen)py + 3PhNHNHPh \rightarrow 2Co^{II}(salen)py + 3PhN{=}NPh + 2t\text{-}BuOH + 2H_2O \quad (9)$$

VI. Oxidative Alkylation of Co^{II}(salen) with 5-Hexenylhydrazine. Owing to the facile rearrangement of the 5-hexenyl moiety,[24] we examined the oxidative alkylation of Co^{II}(salen) with 5-hexenylhydrazine as a probe for the formation of alkyl radicals as intermediates. Authentic samples of the relevant alkylcobalt complexes VIII and IX were prepared from Na[Co^{I}(salen)] and 5-hexenyl and cyclopentylmethyl bromides, respectively. Isomers VIII and IX are distinguished in their ^1H NMR spectra by the chemical shifts of the α-methylene protons at δ 3.55 and 3.49, respectively. (See the Experimental Section for full details.) However, in order to detect minor amounts of the rearranged cyclopentylmethyl derivative IX,[25] we found that iodinolysis[26] followed by gas chromatographic analysis of the cleaved alkyl iodide is a rapid and highly sensitive method for the quantitative assay of (alkyl)Co(salen) complexes. Thus the exposure of the 5-hexenylcobalt complex VIII to a 5–10-fold excess of iodine in methylene chloride at 25 °C afforded 5-hexenyl iodide in quantitative yields without admixture of the cyclopentylmethyl isomer. Similarly the complex IX and its *n*-butyl analogue were found to be quantitatively cleaved to cyclopentylmethyl and *n*-butyl iodides, respectively, under these conditions.

Treatment of Co^{II}(salen) with 5-hexenylhydrazine and dioxygen led to complete reaction within 10 min at 25 °C. Analysis indicated the formation of the rearranged (cyclopentylmethyl)cobalt complex IX together with the 5-hexenyl isomer VIII, i.e.



(10)

The extent of rearrangement of the 5-hexenyl moiety in eq 10 varies with the concentration of Co^{II}(salen) and the sequence with which the reagents are mixed. For example, when a 0.02 M solution of Co^{II}(salen) in methylene chloride saturated with O_2 was treated with a 5-fold molar excess of 5-hexenylhydrazine, the rearranged cyclopentylmethyl derivative IX was formed in 54% yield together with 36% of VIII. When a 0.01 M solution of Co^{II}(salen) was treated under the same conditions, less rearrangement (22% of IX) was observed, as listed in Table IV. Furthermore, when a mixture of 0.02 M Co^{II}(salen) and 5-hexenylhydrazine was treated with O_2, a diminished yield of IX (16%) was found. Inverse mixing of a more dilute (0.01 M) solution of Co^{II}(salen) gave only a 1% yield of IX. We conclude from these experiments that the 5-hexenyl radical is an important intermediate in the alkylation of Co^{II}(salen). Its lifetime is strongly dependent on the concentration of Co^{II}(salen) and the order of mixing the hydrazine and O_2. In order to establish that 5-HxnCo^{III}(salen) (5-Hxn = 5-hexenyl) does not undergo subsequent rearrangement under reaction conditions, we carried out the following control experiments. An equimolar mixture of 0.02 M Co^{II}(salen) and 5-HxnCo^{III}(salen) (VIII) in O_2-saturated methylene chloride was treated with excess *n*-butylhydrazine at 25 °C. Upon completion of the reaction (10 min), quantitative analysis of the reaction mixture by the iodinolysis procedure indicated that more than 65% of VIII remained intact, and less than 6% of the rearranged IX was found together with major amounts (>80%) of *n*-BuCo^{III}(salen). We thus conclude that the rearrangement during oxidative alkylation with 5-hexenylhydrazine by and large does not result from the subsequent rearrangement of VIII.[27]

Table IV. Rearrangement of the 5-Hexenyl Group during the Oxidative Alkylation of Co^{II}(salen)[a]

amt of Co^{II}(salen), 10^2 mmol	O_2 addition[b]	Co(III) product[c] amt of 5-Hxn, 10^2 mmol (%)	Co(III) product[c] amt of $CpCH_2$, 10^2 mmol (%)	mass balance,[d] %
4.98	normal	2.5 (51)	1.1 (22)	73
4.98	inverse	3.2 (63)	0.06 (1)	64
10.0	normal	3.6 (36)	5.4 (54)	90
10.5	inverse	6.3 (60)	2.3 (21)	81
14.9	inverse	11.8 (79)	2.6 (18)	97

[a] In methylene chloride (5 mL) containing 5 equiv of 5-hexenylhydrazine/equiv of Co(II) at 25 °C. [b] Legend: normal, addition of hydrazine to cobalt(II) and O_2. Inverse, addition of O_2 to cobalt(II) and hydrazine. [c] Analyzed as alkyl iodide after iodinolysis. [d] Based on Co^{II}(salen) charged.

Discussion

The oxidative alkylation of the Schiff base complexes of cobalt(II) proceeds in high yields with a variety of organic hydrazines, $RNHNH_2$, especially those with R = primary alkyl, acyl, and aryl groups. The organocobalt(III) products are most conveniently isolated in 80–90% yields as the pyridine adducts. The stoichiometric requirements for the oxidant, which can be either dioxygen or *tert*-butyl hydroperoxide, are consistent with a three-electron change to effect alkylation according to eq 11.[29]

$$Co^{II} + RNHNH_2 \rightarrow RCo^{III} + N_2 + 3H^+ + 3e^- \quad (11)$$

The principal advantages of the hydrazine procedure over the more traditional preparative methods lie in its compatibility with aerobic conditions as well as its speed of reaction and ease of workup. Since primary alkylhydrazines are readily available or are easily synthesized,[30] this method offers a convenient route to

(23) von Aebi, H.; Dewald, B.; Suter, H. *Helv. Chim. Acta* **1965**, *48*, 656.
(24) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 8.
(25) The partial overlapping of the resonances due to the α-methylene protons (even in the 360-MHz NMR spectra) made the quantitative spectral analysis less accurate.
(26) (a) Dreos, R.; Tauzher, G.; Marsich, N.; Costa, G. *J. Organomet. Chem.* **1975**, *92*, 227. (b) Magnuson, V. E.; Weber, J. H. *Ibid.* **1975**, *92*, 233.
(27) The small amount of 5-hexenyl rearrangement arises from VIII by a slow spontaneous process that is inhibited by O_2. Since *tert*-butyl hydroperoxide is not an inhibitor of this process, it could not be used in this series of control experiments.[28]
(28) Samsel, E. G.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.
(29) Hereinafter when the ligand is not included, the transformation is intended to be general.
(30) Jensen, K. A.; Bacccaro, H. R.; Buchardt, O.; Olsen, G. E.; Pedersen, C.; Toft, J. *Acta Chem. Scand.* **1961**, *15*, 1109. Stroh, H. H.; Scharnow, H. G. *Chem. Ber.* **1965**, *98*, 1588. Amundsen, L. H.; Nelson, L. S. *J. Am. Chem. Soc.* **1951**, *73*, 242. Eslager, E. F.; Weinstein, E. A.; Worth, D. F. *J. Med. Chem.* **1964**, *7*, 493. Karabatsos, G. J.; Osborne, C. E. *Tetrahedron* **1968**, *24*, 3361.

alkylcobalt(III) complexes. The major disadvantage of the hydrazine method is the rather narrow scope of applicability, since it does not include various cobalt complexes (Table III) and most secondary or tertiary alkyl groups (Table II). This latter fact may not be surprising in view of the generally reduced kinetic and thermodynamic stability of such branched alkylcobalt(III) derivatives.[31] For example, the alkyl thermolysis of *i*-$PrCo^{III}$(saloph)py occurs at least 100 times faster than that of the *n*-propyl analogue—the bond dissociation energy being ~5 kcal mol^{-1} lower.[32,33]

The nature of the oxidative alkylations with organic hydrazines can best be understood by considering prior studies of the interaction of cobalt(II) complexes with oxidants such as dioxygen[35] and *tert*-butyl hydroperoxide.[36] For example, Co^{II}(salen) is known to rapidly form a 1:1 adduct with O_2 in nonpolar solvents such as methylene chloride, toluene, and chloroform, as indicated by its low-temperature EPR spectrum:

$$Co^{II}(salen) + O_2 \rightleftharpoons \underset{X}{\cdot OOCo^{III}(salen)} \qquad (12)$$

The superoxo complex X can be converted in a slow subsequent step to the insoluble 2:1 μ-peroxo adduct XI:

$$\underset{X}{\cdot OOCo^{III}(salen)} + Co^{II}(salen) \rightarrow (salen)Co^{III}\underset{XI}{OOCo^{III}}(salen) \qquad (13)$$

The oxygen uptake in eq 12 is reversible, and when the solutions above are warmed to ~0 °C, the equilibrium is shifted entirely toward the cobalt(II) complex. However, in coordinating solvents such as pyridine, dimethyl sulfoxide, and *N*,*N*-dimethylformamide the thermodynamics favor the paramagnetic dioxygen adduct even at room temperature. The latter implies that coordination of the sixth site in X by donor ligands L stabilizes the dioxygen adduct; i.e.[37]

$$LCo^{II}(salen) + O_2 \rightleftharpoons \underset{X'}{LCo^{III}(salen)OO\cdot} \qquad (14)$$

Thus we interpret the instantaneous color change from red to brown attendant upon the addition of dioxygen to a mixture of Co^{II}(salen) and methylhydrazine as such a stabilization of the dioxygen complex by the nitrogen-centered donor ligand (L = alkylhydrazine).

In an analogous manner, the rapid color change from red to brown observed upon the addition of *tert*-butyl hydroperoxide to Co^{II}(salen) is due to the formation of the (*tert*-butylperoxo)cobalt(III) complex. Indeed, the sparingly soluble complex VI precipitates rapidly from solution when *tert*-butyl hydroperoxide is added in the absence of a hydrazine to Co^{II}(salen) at room temperature:[16]

$$\underset{II}{2Co^{II}(salen)} + 3t\text{-BuOOH} \rightarrow \underset{VI}{2t\text{-BuOOCo}^{III}(salen)} + t\text{-BuOH} + H_2O \qquad (15)$$

The corresponding pyridine derivative is more soluble, and the rapid color change from red to brown attendant upon the mixing of $pyCo^{II}$(salen) and *tert*-butyl hydroperoxide is characteristic of the *tert*-butylperoxo complex VII, which has been isolated in good yields:[17]

$$\underset{II}{2pyCo^{II}(salen)} + 3t\text{-BuOOH} \rightarrow \underset{VII}{2t\text{-BuOOCo}(salen)(py)} + t\text{-BuOH} + H_2O \qquad (16)$$

Such a ready formation of the *tert*-butylperoxo complexes VI and VII coupled with their ability to effect alkylation directly with the hydrazines (see eq 4 and 6) suggests that they are the reactive intermediates in the procedure employing *tert*-butyl hydroperoxide as the oxidant. Similarly, we propose that the 1:1 dioxygen adduct in eq 14 (where L = alkylhydrazine) is the reactive intermediate in the reaction when O_2 is the oxidant. Accordingly, the stoichiometry for the oxidative alkylation with *tert*-butyl hydroperoxide can be deduced from eq 4, 6, and 7 as consisting basically of two parts, which are included in the generalized formulation given in Scheme I.[29]

Scheme I

$$A:\ 2Co^{II} + 3t\text{-BuOOH} \rightarrow 2t\text{-BuOOCo}^{III} + t\text{-BuOH} + H_2O \qquad (17)$$

$$B:\ t\text{-BuOOCo}^{III} + RNHNH_2 \rightarrow RCo^{III} + N_2 + t\text{-BuOH} + H_2O \qquad (18)$$

When the alkylation is considered in this light, the diverse reactivities of the various cobalt(II) and cobalt(III) complexes described in Table III are understandable. Thus we now consider how each of these processes occurs.

Process A. For oxidative alkylation, the active form of the cobalt complex consists of the superoxo or *tert*-butylperoxo derivative, which is derived by an oxidation (eq 14–16), a ligand exchange (eq 19)[38]

$$ICo^{III}(salen) + t\text{-BuOOH} \xrightarrow{\text{base}} t\text{-BuOOCo}^{III}(salen) + I^- \qquad (19)$$

or a ligand-induced dissociation (eq 20).[39]

$$(salen)Co^{III}OOCo^{III}(salen) \xrightarrow{L} LCo^{III}(salen)OO\cdot + LCo^{II}(salen) \qquad (20)$$

The postulation of these reactive intermediates also provides a ready explanation for the otherwise puzzling observation that the oxidative methylations of Co^{II}(salen) and Co^{II}(saloph) proceed in high yields whereas the close relatives $Co^{II}(dmgH)_2$ and Co^{II}(acacen) cannot be methylated beyond 50% (see Table III). The difference arises from the influence of the Schiff base ligand in determining the maximum yield of the (*tert*-butylperoxo)cobalt(III) derivative, which is obtainable from the treatment of the relevant cobalt(II) complex with *tert*-butyl hydroperoxide. Thus Espenson and co-workers have shown that the oxidative substitution of $Co^{II}(dmgH)_2py$ by *tert*-butyl hydroperoxide in benzene leads to the corresponding *tert*-butylperoxo complex $t\text{-BuOOCo}^{III}(dmgH)_2py$ in a yield of only 50% based on the stoichiometry[40]

$$2Co^{II} + 2t\text{-BuOOH} \rightarrow t\text{-BuOOCo}^{III} + HOCo^{III} + t\text{-BuOH} \qquad (21)$$

In contrast, Nishinaga, Mimoun, and co-workers have obtained yields of 80–90% of the peroxocobalt(III) complexes from Co^{II}(salen) and $Co^{II}(BPI)O_2CPh$ according to the stoichiometry[36,41]

$$2Co^{II} + 3t\text{-BuOOH} \rightarrow 2t\text{-BuOOCo}^{III} + t\text{-BuOH} + H_2O \qquad (22)$$

(31) See ref 9.
(32) (a) Halpern, J. *Pure Appl. Chem.* **1983**, *55*, 1059; *Acc. Chem. Res.* **1982**, *15*, 238. (b) Tsou, T.-T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623.
(33) Nonetheless, *i*-$PrCo^{III}$(salen) can be synthesized in 58% yield from $Co^{I}(salen)^-$ and isopropyl chloride.[34]
(34) Floriani, C.; Puppis, M.; Calderazzo, F. *J. Organomet. Chem.* **1968**, *12*, 209.
(35) Ochiai, E.-I. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3375. Abel, E. W.; Pratt, J. M.; Whelan, R. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 151; **1971**, *7*, 901. Busetto, C.; Neri, C.; Palladino, N.; Perrotti, E. *Inorg. Chim. Acta* **1971**, *5*, 129. Cockle, S. A.; Hill, H. A. O.; Williams, R. J. P. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 161. Diemente, D.; Hoffman, B. M.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1970**, 467. Crumbliss, A. L.; Basolo, F. *J. Am. Chem. Soc.* **1970**, *92*, 55.
(36) See ref 16 and 17.
(37) Under the reaction conditions, the donor ligand L = alkylhydrazine would function in a manner similar to pyridine.
(38) In the presence of base such as a hydrazine, *tert*-butyl hydroperoxide ($pK_a \approx 10$) would be partially converted to a stronger nucleophile.
(39) As a result of the stabilization of the superoxo adduct as in eq 14.
(40) (a) Espenson, J. H.; Melton, J. T. *Inorg. Chem.* **1983**, *22*, 2779. (b) Espenson, J. H.; Martin, A. H. *J. Am. Chem. Soc.* **1977**, *99*, 5953.
(41) (a) The stoichiometry in eq 22 is the sum of those in eq 21 and 23. (b) BPI = 1,3-bis(2-pyridylimino)isoindoline.

The discrepancy between the stoichiometries in eq 21 and 22 is represented by the further exchange of the hydroxo complex formed in eq 21; i.e.

$$HOCo^{III} + t\text{-}BuOOH \rightarrow t\text{-}BuOOCo^{III} + H_2O \quad (23)$$

Indeed the detection of water in eq 22[17] is consistent with this formulation. If so, cobalt complexes are distinguished by the substitution lability of the various $HOCo^{III}$ forms as they are affected by the Schiff base ligand—the aromatic ones such as salen and BPI facilitate the ligand exchange in eq 23 whereas the aliphatic analogues such as dmgH and acacen do not.[42] Be that as it may, the methylation yields of the various cobalt(II) complexes in Table III clearly follow the trends in the yields of the (*tert*-butylperoxo)cobalt(III) complexes according to either eq 21 or 22.

For the first phase of the alkylation process, the sequence of reactions leading to the formation of the *tert*-butylperoxocobalt(III) intermediate can be summarized as shown in Scheme II.[43] Such a redox scheme in which alkoxy (*t*-BuO·) and alkylperoxy (*t*-BuOO·) radicals are key intermediates is in accord with extensive mechanistic studies previously made of the interaction of alkyl hydroperoxides with a variety of metal complexes.[44,45]

Scheme II

$$Co^{II}(salen)L + t\text{-}BuOOH \rightarrow HOCo^{III}(salen)L + t\text{-}BuO\cdot \quad (24)$$

$$t\text{-}BuO\cdot + t\text{-}BuOOH \rightarrow t\text{-}BuOH + t\text{-}BuOO\cdot \quad (25)$$

$$t\text{-}BuOO\cdot + Co^{II}(salen)L \rightarrow t\text{-}BuOOCo^{III}(salen)L \quad (26)$$

$$HOCo^{III}(salen)L + t\text{-}BuOOH \rightarrow t\text{-}BuOOCo^{III}(salen)L + H_2O \quad (27)$$

$$\text{net: } 2Co^{II}(salen)L + 3t\text{-}BuOOH \rightarrow 2t\text{-}BuOOCo^{III}(salen)L + t\text{-}BuOH + H_2O \quad (28)$$

Process B. In the second phase of Scheme I, the route by which the alkyl group is transferred from the hydrazine moiety to the cobalt center with the loss of dinitrogen in eq 18 can also be partially delineated. Thus the efficient oxidation of hydrazobenzene to azobenzene in eq 9 suggests that the alkylhydrazines are converted by an overall two-electron oxidative process to the corresponding diazenes[46]

$$RNHNH_2 \rightarrow RN{=}NH + 2H^+ + 2e^-$$

which are known to undergo further one-electron conversions to produce organic free radicals:[47]

$$RN{=}NH \rightarrow R\cdot + N_2 + H^+ + e^-$$

Indeed the observation of extensive isomerization of the 5-hexenyl group during the oxidative alkylation with 5-hexenylhydrazine in Table IV confirms the intermediacy of alkyl radicals, since the rearrangement to cyclopentylmethyl is known to occur with a first-order rate constant of 1×10^5 s^{-1}:[48]

(29)

Addition of the alkyl radical to cobalt(II) constitutes the final step of the alkylation, and it is known to be facile.[40] On this basis the sequence of transformations leading to the alkylation of cobalt(II) can be summarized as shown in Scheme III. This formulation emphasizes three aspects of the alkylation, viz., the oxidative formation of the alkyldiazine (eq 30), its homolytic scission to alkyl radicals (eq 31), and the trapping of these radicals by the cobalt(II) complex (eq 32). The transformations are not necessarily intended to represent elementary steps. For example, the oxidation of the hydrazine may be a stepwise process involving successive hydrogen atom abstractions from either a free $RNHNH_2$ or one coordinated to the cobalt center (i.e., L = $RNHNH_2$).[49] In the latter case, the alkyldiazene may exist as a ligand coordinated to cobalt.[50] The extrusion of dinitrogen from an alkyldiazene is known to proceed via an alkyldiazenyl radical ($RN{=}N\cdot$) as an intermediate in eq 31.[51] Such an intermediate may also arise by homolysis of an (alkyldiazenido)cobalt(III) complex.[52] In either case, we judge from the extensive rearrangement of the 5-hexenyl moiety that the lifetime of the alkyl radical is too long for it to be involved in a cage process (i.e., geminate combination).[53] Such a conclusion however does raise the interesting question of how the alkyl radicals survive the trapping by dioxygen when it is employed as the oxidant.[54] We surmise from the common patterns of the alkylations with dioxygen and *tert*-butyl hydroperoxide in Tables I and III that similar intermediates are involved. For example, the oxidative alkylation with the 1:1 oxygen adduct X′ can be represented as in Scheme IV. The overall stoichiometry in eq 37 is in accord with the experimental one presented in eq 5. The earlier considerations of possible elementary steps also apply to the transformations in Scheme IV. Thus it is likely that hydroperoxy radicals are involved in the oxidative transformation of the hydrazine in eq 34 and in the production of alkyl radicals in eq 35. Such paramagnetic intermediates and the analogous ones derived from *tert*-butyl hydroperoxide (viz., *t*-BuO· and *t*-BuOO·) are undoubtedly responsible for the extraneous consumption of the hydrazine (see eq 6) during the alkylation process, as well as in the catalytic oxidation of hydrazobenzene in eq 8.[56]

Scheme III

$$t\text{-}BuOOCo^{III}(salen)L + RNHNH_2 \rightarrow Co^{II}(salen)L + RN{=}NH + H_2O + t\text{-}BuO\cdot \quad (30)$$

$$RN{=}NH + t\text{-}BuO\cdot \rightarrow R\cdot + N_2 + t\text{-}BuOH \quad (31)$$

$$R\cdot + Co^{II}(salen)L \rightarrow RCo^{III}(salen)L \quad (32)$$

$$\text{net: } t\text{-}BuOOCo^{III}(salen)L + RNHNH_2 \rightarrow RCo^{III}(salen)L + N_2 + t\text{-}BuOH + H_2O \quad (33)$$

Scheme IV

$$\cdot OOCo^{III}(salen)L + RNHNH_2 \rightarrow Co^{II}(salen)L + RN{=}NH + H_2O_2 \quad (34)$$

$$RN{=}NH + 0.5O_2 \rightarrow R\cdot + N_2 + 0.5H_2O_2 \quad (35)$$

$$R\cdot + Co^{II}(salen)L \rightarrow RCo^{III}(salen)L \quad (36)$$

$$\text{net:}^{55}\ Co^{II}(salen)L + RNHNH_2 + 1.5O_2 \rightarrow RCo^{III}(salen)L + N_2 + 1.5H_2O_2 \quad (37)$$

(42) The dichotomy was pointed out by Mimoun et al.,[17] who suggested that anion exchange of $HOCo^{III}$ with *tert*-butyl hydroperoxide occurs with some complexes but those with dmgH ligands are inert to this substitution.
(43) L is an axially coordinated donor ligand, and in the alkylation procedure it is most likely the hydrazine.
(44) For a review, see: Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.
(45) In aqueous solution, the *tert*-butoxy radical formed in eq 22 undergoes rapid β scission to afford methyl radicals, which are subsequently converted to the methyl complex $CH_3Co^{III}(dmgH)_2$.[40]
(46) Kosower, E. M. *Acc. Chem. Res.* **1971**, *4*, 193.
(47) Nicholson, J.; Cohen, S. G. *J. Am. Chem. Soc.* **1966**, *88*, 2247.
(48) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.
(49) For radicals derived from various hydrazines, see for leading references: (a) Nelsen, S. F. *Acc. Chem. Res.* **1981**, *14*, 131. (b) Stanbury, D. M. *Inorg. Chem.* **1984**, *23*, 2879.
(50) For stable methyldiazene and aryldiazo complexes, see ref 7 and: Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2784. See also related papers.
(51) Compare ref 46 and 47.
(52) Compare: Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic; New York, 1978; Chapter 9.
(53) For example, the homolysis of an (alkyldiazo)cobalt(III) species to an alkyldiazenyl radical–cobalt(II) pair followed by loss of dinitrogen and collapse of the alkyl radical–cobalt(II) pair would constitute a cage process for the formation of the alkylcobalt(III) product. However, the lifetime of a geminate alkyl radical is expected to be $<10^{-10}$ s, which is much shorter (10^{-5} s) than that required for 5-hexenyl rearrangement. Thus, its presence in a chain-transfer capacity as in Scheme III is favored.
(54) The bimolecular reaction of alkyl radicals with dioxygen is diffusion-controlled. It is possible that the rapidity of the hydrazine oxidation leads to a local deficiency of dioxygen sufficient to preclude this complication.
(55) Including the preequilibrium step in eq 14.

Experimental Section

Materials. The cobalt complexes Co^{II}(salen),[58] Co^{II}(salen)py,[15] Co^{II}(acacen),[59] $Co^{II}(dmgH)_2$,[60] $Co^{II}(dmgH)(H_2O)_2$,[60] and [(salen)$Co^{III}]_2O_2$[15] were prepared by the procedures described in the literature. Co^{II}(7,7′-Me_2salen) was prepared from 7,7′-Me_2salenH_2[61] by the same procedure used for Co^{II}(salen). Similarly, $(Ph_3P)Co^{III}$(salen)ClO_4,[62] $(py)_2Co^{III}$(salen)PF_6,[63] and ICo^{III}(salen)[34] were prepared as described in the literature. The (*tert*-butylperoxy)cobalt(III) complex VI was prepared by the method of Nishinaga et al.,[16] whereas the pyridine analogue VII was synthesized by a slight modification of the method of Mimoun et al.[17] as follows. To a solution of 2.02 g (5.0 mmol) of Co^{II}(salen)py in 60 mL of methylene chloride was added 0.80 mL (7.5 mmol) of *tert*-butyl hydroperoxide. The solution was stirred under air for 30 min at room temperature. Pyridine (2 mL) was added, and the volume of the solution was reduced in vacuo to about 30 mL. Ether (200 mL) was added slowly, and the brown crystals were removed by filtration, washed with ether, and dried in vacuo overnight; yield of *t*-BuOOCo^{III}(salen)py 1.81 g (73%). ^{1}H NMR ($CDCl_3$): δ 8.1 (d, J = 5 Hz, 2 H), 7.9 (s, 2 H), 7.7–6.4 (m, 11 H), 4.1 (m, 2 H), 3.5 (m, 2 H), 0.92 (s, 9 H).

Methylhydrazine was used as received from Aldrich Chemical Co. (*Caution*! This compound is highly toxic.) Acetylhydrazine (Aldrich) was recrystallized from ethanol. Phenylhydrazine (Aldrich) was distilled in vacuo prior to use. *tert*-Butylhydrazine (Lucidol) obtained as the hydrochloride was neutralized and purified by distillation. Hydrazobenzene (K & K Labs) was recrystallized twice from petroleum ether under an argon atmosphere. *tert*-Butyl hydroperoxide (Lucidol –90) was used as received. Iodometric titration[64] indicated it to be 93.3% by weight. The other substituted hydrazines were prepared by standard procedures.[30] The synthesis of 5-hexenylhydrazine is a typical example. To 54 g (930 mmol) of 85% hydrazine hydrate (Matheson Coleman and Bell) was added a solution of 15 g (92 mmol) of 5-hexenyl bromide in 30 mL of methanol. The flask was thoroughly flushed with argon and stirred for 50 h at room temperature. The solution was then extracted three times with 100-mL portions of ether, which were combined and dried over anhydrous barium oxide. Following the removal of ether in vacuo, the residue was distilled in vacuo: bp 50–53 °C (0.05 mm); yield of 5-hexenylhydrazine 7.9 g (75%). ^{1}H NMR ($CDCl_3$): δ 5.7 (m, 1 H), 5.0 (m, 2 H), 3.2 (br s, 3 H), 2.7 (m, 2 H), 2.0 (m, 2 H), 1.6–1.3 (m, 4 H).

1-Bromo-5-hexene was prepared from 5-hexen-1-ol (Columbia Organic Chemicals) as follows.[65] To a solution of 30 g (0.30 mmol) of the alcohol in 100 mL of ether under argon at –78 °C was added dropwise a solution of 31 g (0.12 mol) of phosphorus tribromide (Matheson Coleman and Bell) in 50 mL of ether. The reaction mixture was slowly allowed to warm to room temperature overnight, whereupon water (7 mL) and ether (50 mL) were added. The mixture was washed with 100 mL of an aqueous solution of saturated potassium carbonate. After drying and removal of the solvents, the residue afforded 28 g (56%) of the hexenyl bromide, bp 34–36 °C (0.05 mm). ^{1}H NMR ($CDCl_3$): δ 5.8 (m, 1 H), 5.1–4.9 (m, 2 H), 3.40 (t, J = 7 Hz, 2 H), 2.5–0.8 (br m, 6 H). 1-Iodo-5-hexene[66] was prepared from the bromide as follows. A solution of 5.0 g (31 mmol) of 5-hexenyl bromide and 6.9 g (46 mmol) of sodium iodide in 25 mL of acetone was heated in a 4-oz Fisher-Porter pressure bottle for 18 h at 110 °C. Filtration followed by removal of the solvent afforded a residue that yielded 3.8 g (59%) of 1-iodo-5-hexene, bp 45–52 °C (0.05 mm). ^{1}H NMR ($CDCl_3$): δ 5.8 (m, 1 H), 5.0 (m, 2 H), 3.15 (approximate t, J = 7 Hz, 2 H), 2.05 (approximate q, J = 7 Hz, 2 H), 1.8 (m, 2 H), 1.5 (m, 2 H). The ^{13}C NMR spectrum agreed with the literature report.[67] Bromomethylcyclopentane[68] was prepared from cyclopentylacetic acid (Aldrich) by initial reduction to the alcohol with lithium aluminum hydride. A solution of 3.0 g (30 mmol) of cyclopentylmethanol was converted to the bromide with 8.4 g (32 mmol) of triphenylphosphine and bromine[69] to afford 3.0 g (61%) of (bromomethyl)cyclopentane, bp 44 °C (1 mm). ^{1}H NMR ($CDCl_3$): δ 3.3 (d, J = 7 Hz, 2 H), 2.3 (m, 1 H), 2.0–1.2 (br m, 8 H). The alcohol (3.0 g, 30 mmol) was also converted to (iodomethyl)cyclopentane with 6.2 g (15 mmol) of phosphorus triiodide (Alfa) by a procedure analogous to that used for the bromide; yield 1.5 g (24%) of material contaminated (20%) by unreacted alcohol. This material was used qualitatively as a standard without further purification. ^{1}H NMR ($CDCl_3$): δ 3.19 (d, J = 7 Hz, 2 H), 2.16 (m, 1 H), 1.84 (m, 2 H), 1.66 (m, 2 H), 1.59 (m, 2 H), 1.22 (m, 2 H).

Instrumentation. ^{1}H NMR spectroscopy was performed on a Nicolet NT-360, a JEOL FX-90Q, or a Varian T-60 spectrometer. Gas chromatography of organic compounds was carried out on a Hewlett-Packard 5890 chromatograph with FID detection that was fitted with a 12.5-m cross-linked dimethylsilicone capillary column (except as noted below). GC–MS was conducted by interfacing the chromatograph to a Hewlett-Packard 5970 mass spectrometer.

Synthesis of Organocobalt(III) Complexes. The organocobalt(III) complexes were prepared by a slight modification of the procedure described by Costa et al.[10] In a typical example, to a Schlenk flask containing sodium amalgam (prepared from 250 mg of Na and 13 mL of Hg) and 200 mL of tetrahydrofuran (THF) under argon was added 2.0 g (6.15 mmol) of Co^{II}(salen). A green solution was obtained after stirring the mixture overnight under an argon atmosphere. The solution was cooled to –78 °C, and the supernatant liquid was transferred with the aid of a stainless steel cannula to a Schlenk vessel containing 2.0 g (12 mmol) of 5-hexenyl bromide and 20 mL of THF held at –78 °C under argon. After the mixture was stirred for 1 h at –78 °C and for 1 h at 25 °C, pyridine (3 mL) was added. The volume of the mixture was reduced to ~50 mL in vacuo. The resulting slurry was chromatographed through a 1 in. × 5 in. column of neutral alumina (Woelm grade III) using 5 vol % py in methylene chloride as eluent. The red band was collected and concentrated to ~50 mL. The slow addition of hexane yielded 2.6 g (80%) of 5-HxnCo^{III}(salen)py (Hxn = 5-hexenyl), which was recrystallized from a mixture of pyridine, methylene chloride, and hexane. The assay by iodine cleavage followed by gas chromatographic analysis indicated 94% purity. No cyclopentylmethyl iodide was detected (<0.5%) in the products of iodine cleavage. ^{1}H NMR for 5-HxnCo^{III}(salen)py ($CDCl_3$, 360 MHz): δ 8.6 (d, J = 6 Hz, 2 H), 7.9 (s, 2 H), 7.6 (m, 1 H), 7.3–7.0 (m, 8 H), 6.5 (m, 2 H), 5.6 (m, 1 H), 4.8 (m, 2 H), 3.8 (m, 2 H), 3.6 (m, 2 H), 3.5 (~t, J = 8 Hz, 2 H), 1.9 (~q, J = 8 Hz, 2 H), 1.4 (~quin, J = 8 Hz, 2 H), 0.75 (~quin, J = 8 Hz, 2 H). The side-chain assignments were confirmed by sequential homonuclear decoupling experiments. Quantitative analysis of the ^{1}H NMR spectrum (with 2,4-dichlorotoluene as the internal standard) indicated the presence of 0.52 equiv of methylene chloride of crystallization. Anal. Calcd for $C_{27}H_{30}O_2N_3Co \cdot {}^1/_2CH_2Cl_2$: C, 62.33; H, 5.90. Found: C, 63.54; H, 6.09.[70]

CpCH_2Co^{III}(salen)py (Cp = cyclopentyl) was prepared by a similar procedure from 2.24 mmol of Co^{II}(salen) in 53% (1.19 mmol) yield. Iodinolysis and ^{1}H NMR analysis indicated 93 and 95% purity, respectively. ^{1}H NMR ($CDCl_3$, 360 MHz): δ 8.6 (s, 2 H), 7.9 (s, 2 H), 7.6 (t, J = 7 Hz, 1 H), 7.3–7.0 (m, 8 H), 6.5 (m, 2 H), 3.8 (m, 2 H), 3.6 (m, 2 H), 3.5 (d, J = 6 Hz, 2 H), 1.6 (m, 2 H), 1.4 (m, 2 H), 1.27 (m, 2 H), 1.14 (m, 3 H). Anal. Calcd for $C_{27}H_{30}N_3O_2Co$: C, 66.52; H, 6.20. Found: C, 66.34; H, 6.25.

i-BuCo^{III}(salen)py was prepared similarly from Co^{II}(salen) (1.54 mmol) in 76% (1.16 mmol) yield. ^{1}H NMR (Me_2SO-d_6, 360 MHz): δ 9.0 (br s, 2 H), 8.03 (s, 2 H), 7.75 (br m, 1 H), 7.6 (br m, 2 H), 7.14–6.4 (m, 8 H), 3.75 (m, 2 H), 3.51 (m, 2 H), 3.02 (d, J = 5.5 Hz, 2 H), 0.85 (m, 1 H), 0.72 (d, J = 6.4 Hz, 6 H).

s-BuCo^{III}(salen)py was prepared by a modified procedure since the chromatography as described above resulted in the rapid and complete decomposition of the product, accompanied by gas evolution. Amalgam reduction of Co^{II}(salen) and treatment with *sec*-butyl chloride followed

(56) (a) For eq 6, the radical chain process would be

$$t\text{-BuO}\cdot + RNHNH_2 \rightarrow t\text{-BuOH} + R\dot{N}NH_2$$

$$R\dot{N}NH_2 + t\text{-BuOOH} \rightarrow RN{=}NH + H_2O + t\text{-BuO}\cdot, \text{ etc.}$$

(b) A similar chain process can be formulated for the autoxidation in eq 8 with hydroperoxy radicals as the chain carrier.[57] (c) Alkoxy and alkylperoxy radicals may also be responsible for the enhanced rate of degradation of the alkylcobalt(III) products, especially those derived from (secondary and tertiary alkyl)hydrazines.

(57) For a discussion see ref 44, Chapters 2 and 3.
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(70) The variable amounts of CH_2Cl_2 occluded (vide infra) undoubtedly account for this mediocre analysis.

by pyridine gave a slurry that was filtered through a bed of Celite. The solution upon workup gave 0.42 g of impure material. Nonetheless, the resonances in the ^1H NMR spectrum could be assigned and confirmed by selective homonuclear decoupling experiments. ^1H NMR (Me_2SO-d_6, 360 MHz): δ 11.4 and 8.4 (v br m), 4.34 (m, 1 H), 3.8 and 3.6 (m, 4 H), 0.77 (t, J = 6.7 Hz, 3 H), 0.65 (m, 2 H), −0.38 (d, J = 6.3 Hz, 2 H).

Analysis by Iodinolysis of Organocobalt(III) Complexes. The procedure is exemplified by the cleavage of *n*-$BuCo^{III}$(salen)py, which was previously assayed from its ^1H NMR spectrum to be 93%. To a solution of 101 mg (0.219 mmol) of *n*-$BuCo^{III}$(salen)py in 10 mL of CH_2Cl_2 was added 140 mg (0.56 mmol) of diiodine. After the mixture was stirred for 5 min, it was transferred to a separatory funnel and extracted with aqueous sodium thiosulfite. Analysis of the methylene chloride layer by gas chromatography after the addition of mesitylene (0.136 mmol) as internal standard showed the presence of 0.203 mmol (93%) of *n*-butyl iodide. Similar assays of the 5-hexenyl and cyclopentylmethyl analogues showed a good agreement with the NMR assays.

Oxidative Alkylations with Hydrazines. General Procedure. To a Schlenk flask containing 0.50 g (1.54 mmol) of Co^{II}(salen) under an argon atmosphere was added 70 mL of CH_2Cl_2 and 5 equiv (7.7 mmol) of the appropriate hydrazine with the aid of a hypodermic syringe. After the mixture was stirred for 10 min at 25 °C, 0.41 mL of *tert*-butyl hydroperoxide was added. (*Caution*! This causes vigorous gas evolution.) Pyridine (3 mL) was added after 10 min and the mixture concentrated in vacuo. Chromatography was carried out through a 2 in. × 1 in. plug of neutral alumina (Woelm grade V) with 5% pyridine in CH_2Cl_2 as eluent. [Alternatively, the products could be flash chromatographed through a 5 in. × 1 in. jacketed column of silica gel (Aldrich grade 62) at −78 °C without appreciable decomposition.] The eluent was reduced in volume in vacuo, and hexane (200–300 mL) was slowly stirred in. Cooling at −15 °C for several hours yielded crystals of products as reported in Tables I–III. Material crystallized in this manner often occluded nonstoichiometric amounts of CH_2Cl_2 which varied from none to 1 mol/mol of organocobalt product. Heating the complexes in vacuo often liberated pyridine rather than the CH_2Cl_2 solvate.

The yields of alkylcobalt product could also be determined by ^1H NMR analysis. In a typical procedure 40.9 mg (0.126 mmol) of Co^{II}(salen) was added to a Schlenk flask, which was then flushed with argon. Methylene chloride (6 mL) and methylhydrazine (34 μL, 0.63 mmol) were added with the aid of hypodermic syringes, and the mixture was stirred until Co^{II}(salen) was completely dissolved. The contents of the flask were frozen and evacuated. After the contents were thawed in vacuo, 1 atm of dry dioxygen (dried over anhydrous $CaSO_4$) was admitted. After the mixture was stirred for 10 min, the solvent was removed in vacuo and the residue taken up in 5 vol % pyridine in CH_2Cl_2. Chromatography through neutral alumina yielded a clear solution, which was concentrated in vacuo. A measured amount of internal standard (2,4-dichlorotoluene, *p*-dimethoxybenzene, or *p*-di-*tert*-butylbenzene) was added and the residue taken up in either $CDCl_3$ or CH_2Cl_2. Analysis of the ^1H NMR spectrum was carried out by integration of the methyl resonance at δ 2.6.

Stoichiometry of Oxidative Alkylation. The change in the volume of gas was measured in a closed system consisting of the reaction vessel and a gas buret fitted with an adjustable silicone oil reservoir to maintain constant pressure. The absorption of dioxygen was measured in a closed system in which Co^{II}(salen) (325 mg, 1.00 mmol) was contained in a small thin-walled sealed glass container separated from CH_2Cl_2 and placed under a pure dioxygen atmosphere. When the tube was broken, Co^{II}(salen) dissolved without significant O_2 absorption, as expected.[71] The addition of 266 μL (5.00 mmol) of methylhydrazine however was accompanied by oxygen absorption [11.7 mL (0.52 mmol)] within 15 min. GC–MS analysis of the head gas indicated the presence of dinitrogen.

The gas evolution with *tert*-butyl hydroperoxide was measured under argon in the same apparatus. When 330 mg (1.01 mmol) of Co^{II}(salen) was dissolved in 50 mL of CH_2Cl_2, the addition of methylhydrazine was effected without a change in volume of the gas. However, when 219 μL (2.2 mmol) of *tert*-butyl hydroperoxide was added, 38.2 mL (1.69 mmol) of gas was evolved within 30 min. GC–MS analysis of the gas indicated the presence of both dinitrogen and methane.

Gas evolution (21.7 mL, 0.97 mmol) during the reaction of 494 mg (1.00 mmol) of (*tert*-butylperoxo)cobalt(III) (VII) with 5 equiv of methylhydrazine was complete within 15 min. GC–MS analysis indicated the presence of dinitrogen, but no methane.

The disappearance of methylhydrazine was determined by GC analysis of its acetone hydrazone.[19] Typically, 40.5 mg (0.124 mmol) of Co^{II}(salen) in 6 mL of CH_2Cl_2 was treated with excess methylhydrazine as described above. A small aliquot of the reaction mixture was withdrawn and added to degassed acetone under argon. After the mixture stood for 10 min, GC analysis indicate the presence of 0.55 mmol of hydrazone. The contents were frozen, evacuated, and thawed, and 1 atm of dioxygen was admitted. Analysis after 10 min indicated that the same size aliquot contained 0.420 mmol of hydrazine, which corresponded to a net consumption of 0.126 mmol of methylhydrazine.

Catalytic Oxidation of Hydrazobenzene. A Schlenk vessel was charged with 40.7 mg (0.101 mmol) of Co^{II}(salen)py, 186 mg (1.01 mmol) of freshly recrystallized hydrazobenzene, and 5.0 mL of CH_2Cl_2. The mixture was successively frozen, evacuated, and thawed in the usual way. Introduction of 1 atm of dioxygen led to 0.60 mmol of azobenzene within 5 min and 0.972 mmol within 14 min. In a blank experiment run without added Co^{II}(salen)py, only 0.088 mmol of azobenzene was formed within a 20-min period.

Hydrazobenzene (56.4 mg, 0.306 mmol) was treated with 43.7 mg (0.089 mmol) of *t*-$BuOOCo^{III}$(salen) in 5 mL of CH_2Cl_2 under argon. Within 8 min, 0.126 mmol of azobenzene was formed at room temperature.

Oxidative Alkylation with 5-Hexenylhydrazine. A Schlenk flask containing 32.6 mg (0.100 mmol) of Co^{II}(salen) in 5 mL of CH_2Cl_2 was frozen, degassed, and filled with 1 atm of dioxygen. 5-Hexenylhydrazine (60 μL, 0.50 mmol) was added with the aid of a hypodermic syringe. After it was stirred for 10 min, the solution was extracted with a cold aqueous solution of 10% trifluoromethanesulfonic acid. Separation of the CH_2Cl_2 phase, followed by iodinolysis and washing with sodium thiosulfide, afforded a solution that was analyzed by gas chromatography. It yielded 0.036 mmol (36%) of 5-hexenyl iodide and 0.054 mmol (54%) of cyclopentylmethyl iodide. As a control experiment the treatment of 17.2 mg (0.053 mmol) of Co^{II}(salen) and 26.9 mg (0.051 mmol) of 5-$HxnCo^{III}$(salen) in 5 mL of CH_2Cl_2 with 22 mg (0.25 mmol) of *n*-butylhydrazine afforded 0.033 mmol (65%) of 5-hexenyl iodide and 0.0032 mmol (6%) of cyclopentylmethyl iodide together with large amounts (>80%) of *n*-butyl iodide.

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Registry No. I, 14167-18-1; II, 39836-45-8; III, 36451-49-7; IV, 36802-26-3; V, 52759-66-7; VI, 88231-26-9; VII, 101915-82-6; Co(salen)py, 30227-50-0; 5-hxnCo(salen)py, 101859-88-5; $CpCH_2$(salen)py, 101859-89-6; *i*-BuCo(salen)py, 97428-47-2; *s*-BuCo(salen)py, 101915-83-7; CH_3COCo(salen)py, 18346-35-5; *n*-BuCo(salen)py, 15608-77-2; C_6H_5Co(salen)py, 75730-52-8; *i*-PrCo(salen)py, 18639-64-0; CH_3Co-(7,7-Me_2salen)py, 53260-96-1; CH_3Co(saloph)py, 65885-95-2; CH_3-(acacen)py, 18115-79-2; CH_3(dmgH)py, 23642-14-0; (7,7′-Me_2salen)Co, 39729-99-2; $(H_2O)_2(dmgH)_2Co$, 37115-10-9; $[(py)_2(salen)Co]PF_6$, 97409-73-9; $[Ph_3P(salen)Co]ClO_4$, 60293-55-2; I(salen)Co, 101859-90-9; $[(salen)Co]_2O_2$, 23602-28-0; 5-hexenylhydrazine, 101859-91-0; hydrazine hydrate, 7803-57-8; 5-hexenyl bromide, 2695-47-8; 5-hexen-1-ol, 821-41-0; phosphorous tribromide, 7789-60-8; 1-iodo-5-hexene, 18922-04-8; (bromomethyl)cyclopentane, 3814-30-0; cyclopentylmethanol, 3637-61-4; (iodomethyl)cyclopentane, 27935-87-1; phosphorous triiodide, 13455-01-1; *sec*-butyl chloride, 78-86-4; methylhydrazine, 60-34-4; *n*-butylhydrazine, 3530-11-8; isobutylhydrazine, 42504-87-0; acetylhydrazine, 1068-57-1; phenylhydrazine, 100-63-0; isopropylhydrazine, 2257-52-5; *sec*-butylhydrazine, 30924-14-2; hydrazobenzene, 122-66-7; azobenzene, 103-33-3.

(71) See ref 35.