amount of charge transferred to the water molecule.

A related observation from Table II is the weaker hydrogen bonding for the ions with second-row elements than the analogous first-row species. Ionic radius and polarization are obvious factors in this case. A useful rule-of-thumb for the halide, oxide, and thiolate ions is that the second-row species have hydrogen bonds 10–12 kcal/mol weaker than for their first-row counterparts. Furthermore, the maximal hydrogen bond energies are fairly constant at 26–27 kcal/mol for the first-row anions and near 15 kcal/mol for the second-row species. This discrepancy is the source of the pronounced leveling effect on, for example, the acidity of alcohols and thiols in going to aqueous solution. The gas-phase acidity difference for methanol and methanethiol of 22 kcal/mol (Table III) is cut to 12 by one water molecule and becomes 1.3 in aqueous solution.[28] Charge delocalization as in the enolate, carboxylate, and cyanide anions also gives an 8–10-kcal/mol reduction in hydrogen bond strengths.

On the technical side, the importance of diffuse functions for the first-row anions is clear for both the hydrogen bond and protonation energies. The relatively small effect of the diffuse functions for hydrogen bonding with second-row anions is largely offset by the correlation correction which in most cases increases the interaction energy by 2–3 kcal/mol. However, the diffuse functions have greater importance in obtaining accurate proton affinities for the second-row anions. The addition of diffuse functions and the correlation energy has little effect on the energetic order for alternate geometries of the hydrogen-bonded complexes, though geometry optimization at the higher levels would be necessary for full assessment of this issue.

Some generalizations can also be noted for the geometries of the hydrogen-bonded complexes. Naturally, hydrogen bond lengths $A^-\cdots H$ tend to decrease with increasing interaction energy. The crude linear correlation has a slope of ca. 12 kcal/(mol·Å); the most deviant points are for the two forms of $CN(H_2O)^-$, **6a** and **6b**, which are again found to have weaker interactions with water than expected. In general, the $A^-\cdots H$ hydrogen bonds are 0.9–1.0 Å longer for the second-row anions than their first-row analogues. Delocalization as in CH_2CHO^- and $HCOO^-$ also leads to longer hydrogen bonds by ca. 0.2 Å. Hydrogen bond bending is likewise correlated with hydrogen bond strengths. The optimal hydrogen bonds are typically bent less than 12° for the localized first-row and sp-hybridized anions, about 20° for the second-row anions and to intermediate values for the first-row anions delocalized by resonance. The drift toward bifurcated structures for the second-row anions was discussed above and is attributable to the increased dominance of ion–dipole attraction with increasing ionic radius.

Conclusion

High-level ab initio calculations have been carried out for complexes of eleven anions with water. Inclusion of diffuse functions, the correlation energy, and zero-point corrections provide favorable comparisons with available experimental data on gas-phase acidities and single molecule hydration enthalpies. The present results also yielded detailed structural characterization of the complexes, recognition of trends for both structure and energetics, and a basis for developing intermolecular potential functions for use in fluid simulations.

Acknowledgment. Gratitude is expressed to the National Science Foundation and National Institutes of Health for support of this work. Discussions with Dr. J. Chandrasekhar were also valuable.

Registry No. F^-, 16984-48-8; Cl^-, 16887-00-6; OH^-, 14280-30-9; HO_2^-, 14691-59-9; SH^-, 15035-72-0; CN^-, 57-12-5; HC_2^-, 29075-95-4; CH_3O^-, 3315-60-4; CH_3S^-, 17302-63-5; HCO_2^-, 71-47-6; CH_2CHO^-, 35731-40-9; H_2O, 7732-18-5.

Supplementary Material Available: Full geometrical details for the separated species and complexes in *Z*-matrix format (18 pages). Ordering information is given on any current masthead page.

Radical Chain Mechanism for Alkyl Rearrangement in Organocobalt Complexes

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Contribution from the Department of Chemistry, University of Houston, University Park, Houston, Texas 77004. *Received January 17, 1986*

Abstract: The molecular rearrangement of a series of 5-hexenylcobalt(III) complexes of various Schiff bases is demonstrated to proceed via an unusual radical chain process. Thus the facility with which the 5-hexenyl → cyclopentylmethyl rearrangement occurs is highly dependent on the presence of trace impurities which can vary from the age of a highly purified sample to the presence of air. We find that the rearrangement of (5-hexenyl)Co^{III}(salen) I can be deliberately controlled by inhibiting it completely or by promoting it rapidly. For example, the addition of cobalt(II), nitroxide (TEMPO), dioxygen, or dihydroanthracene as well as an electrochemical prereduction procedure can effectively squelch the 5-hexenyl rearrangement. Conversely, chemical and electrochemical oxidations with a ferrocenium salt and a platinum anode at 0.4 V, respectively, trigger the rearrangement. In each case, the limited molar amounts of additives (or faradays of charge) are sufficiently small to ensure high kinetic chain lengths. Inhibition and initiation of the chain process by these techniques relate directly to the destruction and generation, respectively, of alkyl radicals as the prime reactive intermediates. Accordingly, a homolytic displacement (S_H2) of the alkylcobalt(III) complex is proposed, in conjunction with the well-known rearrangement of the hexenyl radical, to constitute the two-step propagation cycle in Scheme III. Such a mechanism accounts for the intermolecular character of the hexenyl rearrangement as established by crossover experiments and the observation of a concurrent alkyl exchange which would otherwise be difficult to explain. The spontaneous rearrangement of a freshly prepared sample of (hexenyl)Co^{III}(salen) and the dichotomous effect of pyridine as a donor ligand are both readily accommodated within the content of the mechanism in Scheme III.

Molecular rearrangements are known in a wide variety of compounds, and their mechanisms are among the most difficult to delineate.[1,2] This is especially true of organometallic compounds in which the energetics of various pathways are often not strongly

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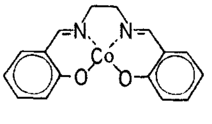
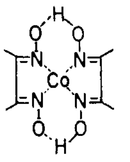
differentiated.[3] Moreover, the problems can be compounded by the substitutional lability of many of these metal complexes. An exception is the class of organocobalt(III) derivatives of which a wide variety are extant, especially those in which a (more or less) square-planar array of nitrogen and oxygen atoms are coordinated to the metal center.[4-6]

Molecular rearrangements of the carbon-centered ligands in organocobalt(III) derivatives fall essentially into two classes. On one hand, alkyl ligands of both cobalamine[7] and cobaloxime[8] complexes bearing the cyclopropylcarbinyl ligand spontaneously rearrange to their respective homoallyl isomers. In the latter case, the rearrangement was shown to be inhibited by added pyridine and accelerated by trifluoroacetic acid.[8] Similarly 1-methyl-3-butenylcobaloxime has been shown to equilibrate to its 2-methyl isomer via a cyclopropylcarbinyl intermediate.[9,10] This molecular rearrangement is also affected by pyridine and acid and is thought to be intramolecular in nature.[9] Conceptually, the rearrangement of these alkylcobalt(III) complexes relates to the biologically relevant cobalamine-dependent enzymatic rearrangement of methylmalonic acid, propanediol, ethanolamine, and other substrates.[12-15]

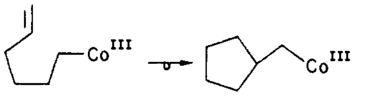


I. salen



III. dmgH

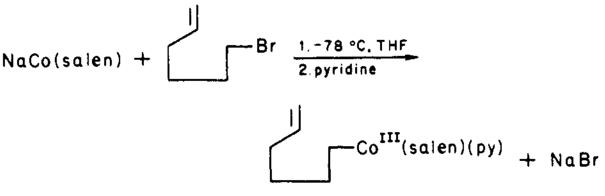
Our interest in the molecular rearrangement of organocobalt(III) derivatives derives from the novel oxidative alkylation with organic hydrazines of cobalt(II) complexes derived from various Schiff bases related to salen [*N*,*N*-ethylenebis(salicylideneaminato)].[16] In particular, we found the hexenyl rearrangement



to occur readily under certain conditions, but not others, for apparently inexplicable reasons. Accordingly we have closely examined the 5-hexenyl rearrangement in this study, with the expectation that the mechanistic conclusions derived here may lend insight into the more general problems.

Results

I. Synthesis of Alkylcobalt(III) Complexes. The alkylation of cobalt(II) complexes was carried out by initially reducing them with either sodium amalgam or borohydride to the corresponding cobaltate(I) followed by treatment with the appropriate alkyl bromide or chloride at −78 °C.[17] The addition of pyridine to the reaction mixture and chromatography through a short column of low-activity alumina to remove cobalt(II) and other impurities led to the pure alkylcobalt(III) complexes in good yields. For example, the 5-hexenyl derivative of Co^{III}(salen) was prepared in this way from 5-hexenyl bromide as a crystalline solid in 80% yield.

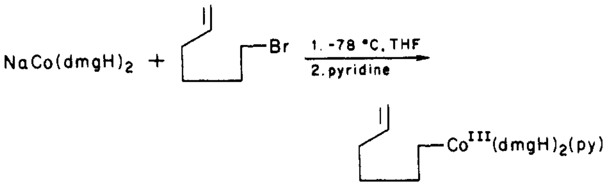


(1)

I

The isomeric cyclopentylmethyl analogue II was synthesized from bromomethylcyclopentane by the same procedure in 54% yield. The 5-hexenyl and cyclopentylmethyl derivatives I and II of Co^{III}(salen) were distinguished by their characteristic chemical shifts at δ 3.55 and 3.49, respectively, for the α-methylene protons in the ^{1}H NMR spectra. However, in order to detect minor amounts of one isomer in the presence of the other, we developed a quantitative method of analysis based on iodinolysis. Thus we could show that the treatment of (*n*-butyl)Co^{III}(salen)(py) with diiodine in methylene chloride at 25 °C afforded *n*-butyl iodide in essentially quantitative yields, as measured by gas chromatography using the internal standard method. (See the Experimental Section for details.) The application of this analytical procedure to (5-hexenyl)Co^{III}(salen)(py) led to quantitative yields of 5-hexenyl iodide without admixture of the cyclopentylmethyl isomer. Such a result indicates that (5-hexenyl)Co^{III}(salen)(py) can be synthesized in eq 1 without rearrangement. Furthermore, the subsequent iodinolysis of (5-hexenyl)Co^{III}(salen)(py) must also occur without isomerization of the 5-hexenyl moiety.

The dimethylglyoximato complex of cobalt(I) was alkylated by a similar procedure to produce the 5-hexenyl derivative III, i.e.,

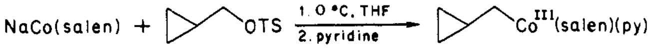


(2)

III

Quantitative analysis by iodinolysis indicated the 5-hexenyl derivative in eq 2 to be formed without contamination by the cyclopentylmethyl isomer.

The cyclopropylcarbinyl derivative of Co^{III}(salen) was prepared from Na (salen)Co[1] and cyclopropylcarbinyl tosylate, i.e.,



IV

(3)

However, even under carefully controlled conditions (see Experimental Section), we were unable to prepare the (cyclopropylcarbinyl)Co^{III}(salen)(py)(IV) without some contamination from discrete amounts (~15%) of the isomeric 3-butenyl analogue. The presence of the latter is readily determined by an inspection of the ^{1}H NMR spectrum of IV which showed the characteristic vinyl resonances at δ 4.8 (2 H) and 5.5 (1 H) in addition to the cyclopropyl resonances at δ 0.2 (4 H) and 0.5 (1 H). The analysis was confirmed by iodinolysis followed by the GC–MS determination of cyclopropylmethyl and 3-butenyl iodides in 77% and 18% yields, respectively.

II. Ligand Rearrangements of Alkylcobalt(III) Complexes. A solution of (5-hexenyl)Co^{III}(salen)(py) (I) was stable for prolonged

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(1) de Mayo, P., Ed. *Rearrangements in Ground and Excited States*; Academic: New York, 1980; Vols. 1–3.

(2) See, e.g.: Eliel, E., Wilen, S. H., Allinger, N. L., Eds. *Top. Stereochem.* **1967–1984**, *1–14*.

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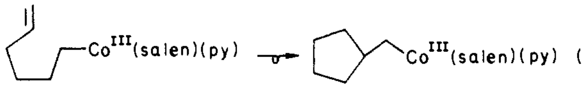
Table I. Experimental Variables for the Alkyl Rearrangement of (5-Hexenyl)Co^{III}(salen)(py)[a]

entry	RCo(salen)(py),[b] mM	Fc$^+$BF$_4^-$,[c] mM (equiv)	charge,[d] mF/mmol of I	additive,[e] mM (equiv)	time,[f] min	recovery of I,[g] %	rearrangement to II,[g] %
1	21				120[h]	16 (76)	5.0 (24)
2	20				0[i]	18 (90)	0.8 (4)
3	20				120	17 (85)	1.3 (6)
4	20			Co^{III}(salen)(py)$_2$$^+PF_6^-$, 0.20 (0.010)	120	17 (85)	1.2 (6)
5	20			Co^{II}(salen) py, 0.10 (0.005)	120	17 (85)	1.2 (6)
6	20	0.85 (0.04)			120	8.3 (42)	9.3 (46)
7	20	1.9 (0.10)			120	6.8 (34)	11 (55)
8	20	4.0 (0.20)			120	2.1 (10)	12 (60)
9	20	2.0 (0.10)		py, 2 × 10^3 (100)	120	13 (65)	3.9 (20)
10	20	2.0 (0.10)		DHA, 100 (5.0)	120	13 (65)	3.9 (20)
11	20	2.0 (0.10)		TEMPO, 200 (10)	120	14 (70)	1.1 (6)
12	22		0.05		120	10 (45)	10 (45)
13	22		0.05		0[j]	16 (73)	4.0 (18)
14	22		0.05	O$_2$[k]	120	16 (73)	3.7 (17)
15	22		0.05	Co^{II}(salen), 2.0 (0.091)	120	16 (73)	3.5 (16)
16	22		0.05	py, 1 × 10^3 (45)	120	9.4 (43)	7.1 (32)

[a] In methylene chloride containing 0.2 M TBAP under dinitrogen after prereduction at −0.8 V vs. SCE. [b] Initial concentration of (5-hexenyl)-Co^{III}(salen)(py) (I). [c] Initial concentration. [d] Charge passed at a constant potential of +0.40 V during anodic oxidation. [e] py = pyridine, DHA = 9,10-dihydroanthracene, TEMPO = 2,2,6,6-tetramethylpiperidinyloxy radical. [f] Elapsed time between initiation and iodinolysis. [g] Final concentration from iodinolysis determination. [h] The sample not prereduced. [i] The sample quenched immediately after prereduction. [j] The sample quenched immediately after oxidation. [k] 1 atm.

periods provided it was left open to the atmosphere. However, if the air was removed, the same solution underwent a spontaneous change in which the 5-hexenyl ligand of I rearranged to the cyclopentylmethyl group, i.e.,



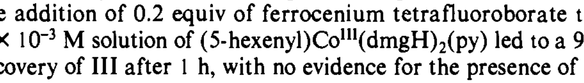
(4)

I II

(Cyclopentylmethyl)Co^{III}(salen)(py) can be observed in 20–60% yields within a few hours at 25 °C. Analysis by iodinolysis and/or inspection of the ^{1}H NMR spectrum indicated that the (cyclopentylmethyl)Co^{III}(salen)(py) derived in this manner was the same as that synthesized independently (cf. eq 1[17]).

Our initial observations of the 5-hexenyl rearrangement gave highly erratic and irreproducible results until we discovered that it was extremely sensitive to a number of experimental variables. First, we found that more rearrangement of (5-hexenyl)Co^{III}(salen)(py) occurred within a given time span the more scrupulously the methylene chloride solution was freed of air. Second, the rate of rearrangement of (5-hexenyl)Co^{III}(salen)(py) was found to vary markedly with the age of the sample. For example under an argon atmosphere, a freshly purified sample of I afforded 55–60% yields of the rearranged (cyclopentylmethyl)Co^{III}(salen)(py) **II** within 2 h. Under the same conditions, a sample of I stored for a while in air (even at −20 °C in the dark) prior to its use would lead to substantially less rearrangement. The spontaneous rearrangement of freshly prepared I under an argon atmosphere could be deliberately *retarded* by exposing the solutions to a slight negative electrode potential, which we refer to hereafter as *prereduction*.[18] As shown by the results in Table I, a solution of (5-hexenyl)Co^{III}(salen)(py) prereduced at −0.8 V afforded less than 4% rearrangement in 2 h.[19] A prereduced solution of I could be made to undergo spontaneous rearrangement by the addition of small amounts of ferrocenium (Fc$^+$) salt (compare entries 3 and 6, Table I). As efficient as ferrocenium ion was in promoting the 5-hexenyl rearrangement, its effect could be nullified by the nitroxide radical trap TEMPO,[20,21] as shown by a drop in the amount of rearrangement from 50% to 1% when 10 equiv were present (compare entries 7 and 11). Dihydroanthracene was a slightly less effective retarder of 5-hexenyl rearrangement (compare entries 7 and 10).[23] The rearrangement of a prereduced solution of (5-hexenyl)Co^{III}(salen)(py) was also initiated when a small anodic current was passed through the solution at a positive potential of +0.40 V. In summarizing these preliminary observations, we conclude that the 5-hexenyl rearrangement of I is a chain process which is strongly inhibited by dioxygen, TEMPO, as well as cobalt(II) and slightly less so by dihydroanthracene.

Contrariwise, the ligand rearrangement was not observed under comparable conditions when the 5-hexenyl group was coordinated to the dimethylglyoximato derivative of cobalt(III). Thus freshly prepared samples of (5-hexenyl)Co^{III}(dmgH)$_2$(py) (III) in either

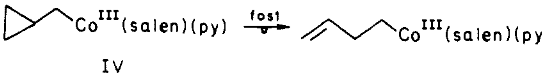


(5)

III

methylene chloride or chloroform remained intact for prolonged periods (weeks). Deliberate attempts to initiate the rearrangement by procedures which were found to be effective with I led to no evidence for rearrangement to cyclopentylmethyl. For example, the passage of anodic current at +0.75 V through a methylene chloride solution of 5 × 10^{-3} M III after several hours led to a 72% recovery of the unrearranged starting material. Similarly the addition of 0.2 equiv of ferrocenium tetrafluoroborate to a 5 × 10^{-3} M solution of (5-hexenyl)Co^{III}(dmgH)$_2$(py) led to a 92% recovery of III after 1 h, with no evidence for the presence of the cyclopentylmethyl isomer.

At the other extreme, we could find no procedure by which to inhibit completely the spontaneous rearrangement of (cyclopropylmethyl)Co^{III}(salen)(py) to the 3-butenyl isomer, i.e.,



(6)

IV

Indeed, (cyclopropylmethyl)Co^{III}(salen)(py) (IV) rearranged so rapidly in either methylene chloride or chloroform that it was most conveniently followed by the transformation of the characteristic ^{1}H NMR spectrum of the cyclopropyl resonances at δ 0.2 and 0.5 to the vinyl resonances at δ 4.8 and 5.5. By this technique, we could show that (cyclopropylmethyl)Co^{III}(salen)(py) rearranges

---

(18) Prereduction was carried out at a platinum cathode in methylene chloride containing 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte at a constant potential for generally 15–30 min.

(19) The presence of 0.2 M TBAP as supporting electrolyte did not affect the hexenyl rearrangement. See Experimental Section for details.

(20) TEMPO = 2,2,6,6-tetramethylpiperidinyloxy radical.

(21) TEMPO displays little or no affinity toward the related cobalt(II) macrocyclic complexes.[22]

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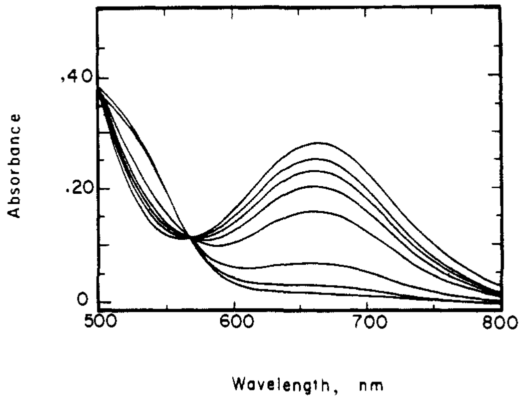

Figure 1. Spectral changes accompanying the formation of the pyridine adduct VIII from 2.0×10^{-3} M solutions of the coordinatively unsaturated (n-butyl)Co^{III}(salen) (VII) in methylene chloride containing 0.2 M TBAP. [py] from top to bottom: 0, 5×10^{-3}, 1×10^{-2}, 2×10^{-2}, 5×10^{-2}, 0.2, 0.5, 1.0 M.

Table II. Formation Constants for Adduct Formation from n-BuCo^{III}(salen) with Various Nitrogen Donor Ligands L[a]

L	K, M^{-1}
imidazole	71
n-butylamine	50
pyridine	22
quinuclidine	2.8

[a] In methylene chloride containing 2.0×10^{-3} M VII and 0.2 M TBAP at 22 °C.

in eq 6 by first-order kinetics with a half-life of 17 min at 25 °C in chloroform. This facile rearrangement differs significantly from that of the hexenyl analogue I in being only slightly retarded by the presence of either air ($\tau_{1/2} = 40$ min), TEMPO ($\tau_{1/2} = 120$ min), or Co^{II}(salen)(py) ($\tau_{1/2} \cong 60$ min).[24] The addition of large amounts of pyridine (2 M) retards the rearrangement somewhat ($\tau_{1/2} = 40$ min). Indeed the use of massive amounts of pyridine as the solvent itself were required to inhibit the rearrangement of (cyclopropylcarbinyl)Co^{III}(salen)(py) ($\tau_{1/2} > 1$ week).

III. Promotion and Inhibition of the Rearrangement of (5-Hexenyl)Co^{III}(salen)(py). Owing to the interesting and somewhat disparate observations for the ligand rearrangement of (5-hexenyl)Co^{III}(salen)(py), we decided to focus our attention on the principal experimental variables noted above with this alkylcobalt(III) complex, namely, (A) the effect of pyridine, (B) the role of oxidation and reduction in the promotion and retardation, (C) the influence of added inhibitors, and (D) self-inhibition. We also examined whether (E) the rearrangement I → II occurred by an intra- or intermolecular process.

A. Effect of Pyridine on the 5-Hexenyl Rearrangement. (Alkyl)Co^{III}(salen)(py) and related complexes undergo extensive dissociation of the axially coordinated pyridine in solution,[25,26] i.e.,

$$\underset{\text{I, II}}{\text{RCo}^{\text{III}}\text{(salen)(py)}} \underset{\text{CH}_2\text{Cl}_2}{\rightleftharpoons} \underset{\text{V, VI}}{\text{RCo}^{\text{III}}\text{(salen)}} + \text{py} \tag{7}$$

Thus methylene chloride solutions of the 5-hexenyl and cyclopentylmethyl complexes I and II in the presence of excess pyridine are red, a color characteristic of the hexacoordinate species.[27] However, either upon dilution or upon extraction with dilute aqueous acid, the solution becomes bright green ($\lambda_{max} = 655$ nm), a color characteristic of the pentacoordinate complexes (Figure 1). The coordinatively unsaturated species V from (5-hexenyl)Co^{III}(salen)(py) was isolated as a crystalline bronze solid in 89% yield by extraction of a methylene chloride solution of I with cold, dilute fluoroboric or sulfuric acid, washing, and precipitation with hexane, i.e.,

Table III. Effect of Pyridine on the Hexenyl Rearrangement of the Coordinatively Unsaturated V[a]

HexCo^{III}(salen),[b] 10 mM	py,[c] equiv	recovery of V,[d] 10 mM (%)	rearrangement to II,[d] 10 mM (%)	material balance,[e] %
1.98	0	1.57 (79)	0	79
2.01	0.20	1.54 (77)	0.192 (10)	87
2.05	0.50	0.501 (24)	1.24 (60)	84
2.01	0.75	0.331 (16)	1.47 (73)	90
2.03	1.0	0.315 (15)	1.46 (72)	82
2.01	3.0	0.428 (21)	1.43 (71)	92
1.99	6.0[f]	0.712 (36)	1.04 (52)	87
2.03	50[f]	0.703 (35)	0.918 (45)	80

[a] In 2.0 mL of methylene chloride containing 0.10 equiv of Fc$^+$BF$_4^-$ (relative to V) at 25 °C under nitrogen. [b] Initial concentration of (5-hexenyl)Co^{III}(salen) (V). [c] Pyridine. [d] As the organic iodide following iodinolysis by quenching the reaction after 120 min. [e] Material balance as sum of columns 3 and 4. [f] Inverse addition of pyridine to a mixture of V and Fc$^+$BF$_4^-$.

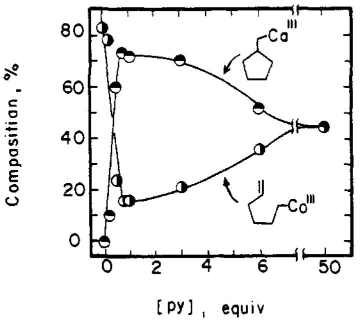

Figure 2. Dual effect of pyridine in promoting the hexenyl rearrangement of the coordinatively unsaturated (hexenyl)Co^{III}(salen) (V) (4.0×10^{-2} M) and in retarding the rearrangement of its hexacoordinate adduct (hexenyl)Co^{III}(salen)(py) (I). All reactions were induced by the addition of 0.1 equiv of Fc$^+$BF$_4^-$.

$$\underset{\text{I}}{\text{RCo}^{\text{III}}\text{(salen)(py)}} + \text{HBF}_4 \rightleftharpoons \underset{\text{V}}{\text{RCo}^{\text{III}}\text{(salen)}} + \text{Hpy}^+\text{BF}_4^- \tag{8}$$

The n-butyl analogue VII was isolated by a similar procedure and the formation constant K in eq 9 was measured by spectral

$$\underset{\text{VII}}{\text{BuCo}^{\text{III}}\text{(salen)}} + \text{L} \overset{K}{\rightleftharpoons} \underset{\text{VIII}}{\text{BuCo}^{\text{III}}\text{(salen)L}} \tag{9}$$

titration with pyridine and other nitrogen ligands L. We take the values of K listed in Table II to be representative for ligand dissociation of the 5-hexenyl complex I, since its ^{1}H NMR spectrum did not show any perturbation of the vinyl resonances or any evidence of vinyl coordination (see Experimental Section). The value of K allows the equilibrium population of (5-hexenyl)Co^{III}(salen)(py) I and of the coordinatively unsaturated species V to be calculated at various concentrations of added donor ligand L = py. Thus at a typical concentration of 2.0×10^{-2} M, the solutions were ruddy green and we expect more than 75% of I to exist as the coordinatively unsaturated species V. In the presence of added pyridine (1.0 M), the solutions were red, and we calculate that less than 4% of the complex to be present as the pentacoordinate (5-hexenyl)Co^{III}(salen) (V).

It is noteworthy that the pentacoordinate species V was inert to 5-hexenyl rearrangement. This conclusion was reached in the following way. Methylene chloride solutions of the unsaturated V were treated with increasing amounts of pyridine from 0 to 50 equiv. Each of the resulting solutions was treated with small amounts (10 mol %) of ferrocenium, and the yield of the rearranged II, as well as the amounts of recovered I, was determined after iodinolysis. In the absence of added pyridine, no rearranged (cyclopentylmethyl)Co^{III}(salen)(py) was observed after 2 h (Table III). However, the presence of as little as 0.5 equiv of pyridine per mol of V led to 60% rearrangement, as shown in Figure 2.

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(24) Paramagnetic linebroadening with TEMPO and cobalt(II) led to inaccurate measurements with these additives.

(25) Dodd, D.; Johnson, M. D. *J. Organomet. Chem.* **1973**, *52*, 1.

(26) Graddon, D. P.; Siddiqi *J. Organomet. Chem.* **1977**, *133*, 87.

(27) Costa, G.; Mestroni, G.; Stefani, L. *J. Organomet. Chem.* **1967**, *7*, 493.

Table IV. Inhibition and Promotion of the Alkyl Rearrangement of (Hexenyl)Co^{III}(salen)(py)[a]

HexCo^{III}(salen)(py),[b] 10^2 mM	Fc^+,[c] mol %	Co^{II},[d] mol %	recovery of I[e] 10^2 mM (%)	rearrangement to H,[e] 10^2 mM (%)	material balance,[f] %
2.08	0	0	1.33 (64)	0.646 (31)	95
2.11	2.4	0	0.80 (38)	1.29 (61)	99
2.11	4.7	0	0.54 (26)	1.56 (74)	100
2.09	9.8	0	0.27 (13)	1.69 (83)	96
2.09	19.1	0	0.42 (20)	1.39 (64)	84
2.10	0	0.476	1.995 (95)	0.09 (4)	99
2.06	2.4	0.485	0.890 (43)	1.13 (55)	98
2.09	4.78	0.478	0.721 (34)	1.33 (64)	98
2.00	10.1	0.501	0.355 (18)	1.55 (77)	95
2.11	19.0	0.474	0.71 (34)	1.22 (58)	91
2.11	0	0.948	2.03 (96)	0.067 (3)	99
2.13	2.35	0.939	1.07 (50)	0.98 (46)	96
2.07	4.83	0.966	0.477 (23)	1.31 (63)	86
2.07	9.66	0.966	0.379 (18)	1.57 (76)	94
2.10	19.1	0.952	0.737 (35)	1.08 (51)	86

[a] In methylene chloride at 22 °C under nitrogen. [b] Initial concentration of (5-hexenyl)Co^{III}(salen)(py). [c] Initial concentration of ferrocenium tetrafluoroborate. [d] Initial concentration of Co^{II}(salen)(py). [e] As organic iodide following iodinolysis by quenching the reaction after 60 min. [f] Material balance as sum of columns 4 and 5.

Beyond about 0.75 equiv of added py, the amount of rearrangement did not increase. Indeed larger amounts of pyridine suppressed the rearrangement somewhat, although in the presence of 50 equiv of pyridine, 45% rearrangement was still observed.

B. Oxidative Initiation of the 5-Hexenyl Rearrangement. In order to clarify the manner in which oxidation triggered the 5-hexenyl rearrangement, we first examined the redox properties of the various cobalt complexes by cyclic voltammetry. For example, the initial positive-scan cyclic voltammogram of the cobalt(II) precursor Co^{II}(salen) at 500 mV s^{-1} showed a quasi-reversible anodic wave with $E_{1/2} \cong 0.59$ V vs. SCE in methylene chloride (eq 10).[28] In the presence of pyridine, the anodic wave

$$Co^{II}(salen) \overset{-e}{\rightleftharpoons} Co^{III}(salen)^+ \qquad (10)$$

was shifted to more negative potentials $E_p = 0.34$ V but became irreversible. Under the same conditions, ferrocene showed a reversible cyclic voltammetric wave at $E_{1/2} = 0.48$ V vs. SCE. Thus the driving force for the electron transfer from Co^{II}(salen)(py) to ferrocenium is expected to be exergonic, i.e.,

$$Co^{II}(salen)(py) + Cp_2Fe^+ \rightarrow Co^{III}(salen)(py)^+ + Cp_2Fe \qquad (11)$$

Accordingly, any Co^{II}(salen)(py) present in solution would be rapidly oxidized upon the addition of ferrocenium salts.[29]

The cyclic voltammogram of (hexenyl)Co^{III}(salen)(py) (I) at 500 mV s^{-1} in methylene chloride showed an irreversible 1-electron anodic wave at 0.70 V, which corresponds to the formal Co^{III}/Co^{IV} transformation,[30] i.e.,

$$(hexenyl)Co^{III}(salen)(py) \xrightarrow{-e} (hexenyl)Co^{IV}(salen)(py)^+ \qquad (12)$$

The anodic peak potential was slightly shifted to $E_p = 0.69$ V in the pentacoordinate base-off form (hexenyl)Co^{III}(salen) (V). Although the oxidation potential of I appeared to be more positive than that of ferrocene, we found that the ferrocenium ion oxidized (hexenyl)Co^{III}(salen)(py) in methylene chloride, i.e.,

$$RCo^{III}(salen)(py) + Fc^+BF_4^- \rightarrow RCo^{IV}(salen)(py)^+BF_4^- + Fc \qquad (13)$$

as judged by the appearance of ferrocene in the ^{1}H NMR and UV-vis spectra of the reaction mixture (see Experimental Section).

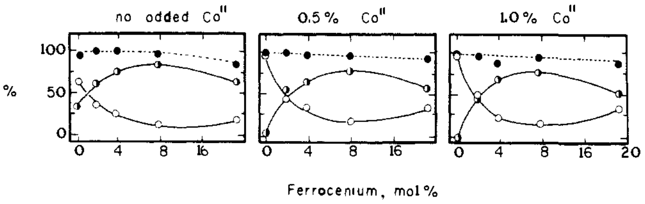

Figure 3. Effects of cobalt(II) and ferrocenium on the inhibition and promotion of the hexenyl rearrangement of 2 × 10^{-2} M I (⊙) to II (◑). Amount of Co^{II}(salen)(py) initially present is, from left to right: none, 0.5, and 1.0 mol %. Ferrocenium added as $Fc^+BF_4^-$ is varied from 0 to 0.19 equiv per mol of I. The material balance (i.e., I + II) is indicated by (●).

The effect of a ferrocenium additive on the 5-hexenyl rearrangement was established by the following set of experiments. First, the rearrangement of (5-hexenyl)Co^{III}(salen)(py) in methylene chloride was deliberately inhibited by doping it with 0–1 mol % of Co^{II}(salen)(py). Indeed the results in Table IV show that as little as 0.5 mol % Co^{II}(salen)(py) was sufficient to completely prevent the 5-hexenyl rearrangement. The inhibited solutions were then treated with ferrocenium salt which was serially varied from 0 to 20 mol %. The amount of rearrangement after a standard span of time (2 h) was determined by quenching the mixtures with iodine, followed by gas chromatographic analysis. The results in Table III show that the addition of only 2 mol % of ferrocenium ion was sufficient to overcome the strong inhibitory effect of Co(II)—the presence of the oxidant leading to 45–60% rearrangement within 2 h. Maximum rearrangement of ~80% was attained with the addition of about 10 mol % of the oxidant. When 20 mol % of ferrocenium was employed, however, there was a slight decrease in the product conversion to about 60%.[31] The trend in the 5-hexenyl conversion to cyclopentylmethyl is graphically illustrated in Figure 3. We conclude from these experiments that ferrocenium ion acted in two capacities. First, it destroyed the cobalt(II) inhibitor—present either as Co^{II}(salen)(py) or the coordinatively unsaturated Co^{II}(salen). (Note in Table I that the same initiation can be carried out electrochemically by anodic pretreatment of the solutions at +0.4 V.) Second, the ferrocenium ion oxidized (hexenyl)Co^{III}(salen)(py) to the cobalt(IV) cation at a reasonable rate to induce the hexenyl rearrangement.

C. Inhibition and Retardation of 5-Hexenyl Rearrangement. Three additives were identified in Table I as effective inhibitors of either the spontaneous or the Fc^+-induced rearrangement of I. In particular, the addition of either TEMPO, Co^{II}(salen), or Co^{II}(salen)(py) was sufficient to eliminate completely the process

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(28) The cyclic voltammogram of Co^{II}(salen) is reversible in THF containing 0.2 M TBAP with $E_{1/2} = 0.44$ V ($E_p^a - E_p^c = 81$ mV at 500 mV s^{-1}).

(29) See: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 4186.

(30) (a) Coulometric measurements during the bulk oxidiation of I in CH_2Cl_2 containing 0.2 M TBAP at a constant current of 10.0 μA showed the consumption of 1.03 electrons per Co when the potential was allowed to vary over the entire, broad, irreversible anodic CV wave from 0.45 to 0.90 V vs. SCE. (b) Compare: Costa, G. *Coord. Chem. Rev.* **1972**, *8*, 63 and vide infra.

(31) For the decreased material balance in the presence of ferrocenium ion, see the Discussion.

Table V. Effect of 9,10-Dihydroanthracene on the Fc$^+$-Induced Rearrangement of (Hexenyl)Co^{III}(salen)(py)[a]

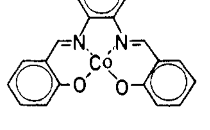
Fc$^+$,[b] mol %	DHA,[c] mM (equiv)	recovery of I[d] mM (%)	rearrangement to II,[d] mM (%)	material[e] balance, %
10.1	0	2.09 (10.4)	14.4 (71.8)	82
10.2	1.01 (.050)	2.82 (14.1)	14.4 (71.8)	86
10.2	1.91 (.096)	3.93 (19.6)	12.7 (63.4)	83
10.1	4.10 (.205)	4.59 (23.0)	12.4 (62.0)	85
9.70	7.04 (.352)	8.00 (40.0)	8.16 (40.8)	81
10.0	19.9 (.998)	10.6 (53.2)	6.43 (32.1)	85
10.4	39.9 (2.00)	12.8 (63.8)	4.03 (20.2)	84
9.52	80.0 (4.00)	13.0 (64.8)	2.99 (15.0)	80
10.0	101 (5.03)	12.6 (63)	3.87 (19.4)	80
0[f]	0	16.8 (89)	0.86 (4.3)	88
0	0	17.3 (87)	1.34 (6.7)	93

[a] In methylene chloride solutions of 2.0×10^{-2} M I containing 0.2 M TBAP prereduced at -0.80 V. [b] Initial concentration of Fc$^+$BF$_4^-$. [c] Initial concentration of 9,10-dihydroanthracene. [d] As organic iodide by iodinolysis following the reaction for 120 min, unless stated otherwise. [e] As sum of columns 3 and 4. [f] Reaction quenched immediately after prereduction.

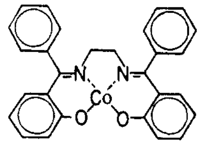
leading to 5-hexenyl rearrangement for prolonged periods (see Table IV). All of these inhibitors are potent traps for alkyl radicals. Since the other additive 9,10-dihydroanthracene (DHA) is a hydrogen atom donor and is the most innocuous toward Fc$^+$ and various cobalt complexes, we examined its effect in greater detail.

Under a standard set of conditions, the extent the Fc$^+$-induced rearrangement of I was measured at varying concentrations of dihydroanthracene. Initially a 2.0×10^{-2} M solution of I in methylene chloride was prereduced at -0.5 V. Measured aliquots of this solution were added to a mixture consisting of 0.10 equiv of Fc$^+$BF$_4^-$ and various amounts of dihydroanthracene under an argon atmosphere. After 2 h, the reaction was quenched with iodine and analyzed by gas chromatography. The results in Table V indicate that the extent of hexenyl rearrangement decreased from 70% to 30% in the presence of 1 equiv of dihydroanthracene. Increasingly larger amounts of dihydroanthracene (up to 5 equiv) decreased the conversion to a limiting value of ca. 20%. Control experiments demonstrate that only ~5% conversion occurred during the period of prereduction and a further 2–3% in the following 2 h without any additive (i.e., Fc$^+$ or DHA). Control experiments also showed that the presence of 5 equiv of dihydroanthracene in the absence of ferrocenium did not initiate hexenyl rearrangement. We thus conclude that dihydroanthracene retards the conversion I → II, but it cannot inhibit the rearrangement completely.

D. Self-Inhibition of 5-Hexenyl Rearrangement. Effect of the Schiff Base Structure. The behavior of (5-hexenyl)cobalt(III) complexes is strongly influenced by the equatorial Schiff base. Let us consider as examples the differences between the alkylcobalt(III) complexes with saloph and 7,7′-diphenylsalen.



IX. saloph



X. 7,7′-Ph$_2$salen

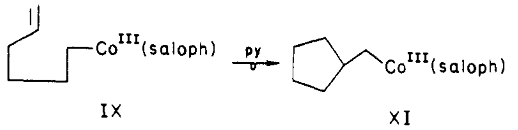
(5-Hexenyl)Co^{III}(saloph) (IX) crystallized as black microcrystals from a 1:1 mixture of pyridine and methylene chloride. Analysis indicated, however, that IX is a pentacoordinate complex which contains no coordinated pyridine (see experimental section). On the other hand, (5-hexenyl)Co^{III}(7,7-Ph$_2$salen)(py) (X) prepared by the same procedure as IX crystallized with one coordinated pyridine when treated similarly. Since the saloph derivative IX apparently has little affinity for pyridine coordination, we added 3 equiv of pyridine in all subsequent studies of 5-hexenyl rearrangement.

Table VI. Self-Inhibition of the Alkyl Rearrangement of (5-Hexenyl)Co^{III}(saloph). Effect of Ferrocenium Salt[a]

HexCo^{III}(saloph),[b] 10^2 mmol	Fc$^+$,[c] mol %	recovery of IX,[d] 10^2 mmol (%)	rearrangement to XI,[e] 10^2 mmol (%)
1.66	0	1.37 (83)	trace
1.73	4.3	0.735 (42)	0.743 (43)
1.61	10.9	0.606 (42)	0.547 (38)
1.49	14.3	0.526 (35)	0.624 (42)
1.53	23.7	0.554 (36)	0.612 (40)

[a] In 0.5 mL of methylene chloride containing 3 equiv of pyridine relative to IX for 2 h at 22 °C. [b] Initial concentration of (5-hexenyl)-Co^{III}(saloph) (IX). [c] Initial amount of Fc$^+$BF$_4^-$. [d] Analyzed as 5-hexenyl iodide following iodinolysis. [e] As cyclopentylmethyl iodide.

Freshly prepared solutions of (5-hexenyl)Co^{III}(saloph), unlike the salen analogue, could not be made to undergo spontaneous rearrangement. Only upon the addition of ferrocenium salt could rearrangement be observed to the cyclopentylmethyl isomer XI—and then to an extent of only ~50%, i.e.,

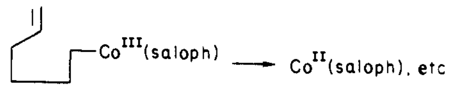


IX XI (14)

The presence of ferrocenium ion in concentrations greater than 4 mol % did not materially effect the amount of rearrangement, as shown by the results in Table VI. The ligand rearrangement of IX could be readily monitored by the rather large shift in the ^{1}H resonances of the α-methylene group from δ 3.53 in (5-hexenyl)Co^{III}(saloph) to δ 3.45 in the cyclopentylmethyl isomer. The latter was confirmed by iodinolysis followed by GC–MS analysis of the cyclopentylmethyl iodide. Control experiments again established that iodine did not induce the 5-hexenyl rearrangement of IX.

In contrast to (5-hexenyl)Co^{III}(saloph), the 7,7′-Ph$_2$salen analogue X in chloroform was converted spontaneously upon standing in chloroform overnight. It rearranged more quickly in the presence of 1 mol % ferrocenium ion, giving complete conversion to the cyclopentylmethyl isomer within 2 h. The identity of (cyclopentylmethyl)Co^{III}(7,7′-Ph$_2$salen) was confirmed by iodinolysis followed with GC–MS analysis or by ^{1}H NMR spectroscopy.

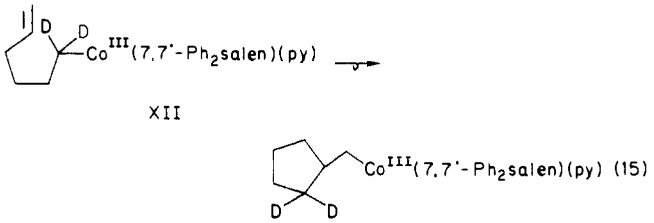
The difference in behavior between the saloph and 7,7′-Ph$_2$salen complex is directly attributable to relative ease of the homolytic decomposition. Thus crystalline (5-hexenyl)Co^{III}(saloph) (IX) produced detectable traces of cobalt(II) impurities within a few days even upon standing at −15 °C, i.e.,



IX

Such a decomposition occurred faster in either methylene chloride or chloroform solution at room temperature, since IX afforded cobalt(II) within a few hours under these conditions. The cobalt(II) impurity was readily detected by thin-layer chromatography, the R_f value and the color of the band being coincident with those of authentic Co^{II}(saloph). Indeed the self-inhibition induced by the Co^{II}(saloph) contaminant was readily demonstrated by the addition of a slightly aged sample of IX (plus 3 equiv of pyridine) to a solution of (5-hexenyl)Co^{III}(salen)(py). The otherwise spontaneous rearrangement of the latter to (cyclopentyl)Co^{III}(salen)(py) (vide supra) was completely inhibited by IX. By contrast, (5-hexenyl)Co^{III}(7,7′-Ph$_2$salen)(py) was readily obtained in purified form by the standard technique developed for the salen analogue I (vide infra). The analysis indicated no detectable amounts of Co^{II}(7,7′-Ph$_2$salen) as an impurity.

E. Chain Process for Intermolecular Alkyl Transfer in Organocobalt(III) Complexes. In order to determine whether the hexenyl ligand rearrangement occurred by an intra- or intermolecular process, we carried out a series of double-label crossover experiments. Since the rearrangement was highly sensitive to external variables, it was desirable to follow the process directly in a sealed system. Accordingly we chose the Schiff base complexes derived from saloph and 7,7′-Ph_2salen in which the α-methylene protons in the hexenyl derivatives IX and X, respectively, showed the largest differences in chemical shifts in the ^1H NMR spectra relative to those of the corresponding cyclopentylmethyl isomers. Thus the ^1H resonances at δ 3.53 and 3.72 for IX and X were readily resolved from those of the corresponding cyclopentylmethyl derivatives at δ 3.45 and 3.62, respectively, in the 300 MHz NMR spectrum. The α,α-dideuteriated analogue of (hexenyl)Co^{III}(7,7′-Ph_2salen) (XII) was prepared from 1-bromo-1,1-dideuteriohex-5-ene by reaction with Na(7,7′-Ph_2salen)Co^I. As expected, a solution of XII in methylene chloride displayed no detectable resonance at δ 3.72. However, when the solution was treated with 10 mol % ferrocenium ion, a new resonance due to the cyclopentylmethyl isomer at δ 3.62 grew in with time, i.e.,

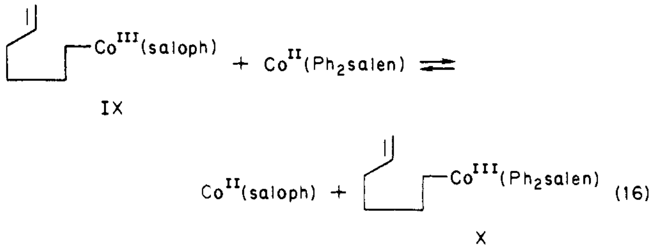


(15)

No ^1H resonance at δ 3.72 appeared during this change. Thus the integrity of the deuteriated positions remained intact during the rearrangement in eq 15. Unfortunately we were unable to examine this process directly owing to the α-deuterium resonances which were broadened beyond detection (probably due to quadrupolar effects) in the ^2H NMR spectrum of XII. The γ-deuterium resonances in the rearranged cyclopentylmethyl isomer were less broadened, but the accuracy of the integration was not sufficient for quantitative analysis.

The intermolecular exchange of hexenyl groups during the rearrangement reaction was demonstrated in the following way. An equimolar solution of (5-hexenyl)Co^{III}(saloph) (IX) (with 3 equiv of pyridine) and (hexenyl-d_2)Co^{III}(7,7′-Ph_2salen)(py) (XII) were treated with $Fc^+BF_4^-$ [32] in chloroform in vacuo. Inspection of the ^1H NMR spectrum showed the growth of cyclopentylmethyl resonances at δ 3.45 and 3.62 in accord with the rearrangements given in eq 14 and 15, respectively.[33] In addition to these, a new triplet resonance appeared at δ 3.71 which is diagnostic of (hexenyl)Co^{III}(7,7′-Ph_2salen)(py) as described above. After 1 h, the apparent ratio of (hexenyl)Co^{III}(7,7′-Ph_2salen)(py) to (hexenyl)Co^{III}(saloph) was 0.41:1.0, from which we concluded that the hexenyl group was scrambled between the cobalt centers concomitant with rearrangement. When (5-hexenyl)Co^{III}(saloph) and (hexenyl-d_2)Co^{III}(7,7′-Ph_2salen)(py) were allowed to react as described above, but without added ferrocenium salt, much less rearrangement was observed as indicated by the small amplitudes of the ^1H resonances at δ 3.45 and 3.62. Furthermore, the molar ratio of (hexenyl)Co^{III}(7,7′-Ph_2salen)(py) to (hexenyl)Co^{III}(saloph) was only 0.09. Therefore, both alkyl exchange and hexenyl rearrangement were simultaneously initiated by the added ferrocenium oxidant.

The possibility of the cobalt(II)-catalyzed alkyl exchange between alkylcobalt(III) complexes, as suggested by Johnson et al. for exchange among alkylcobaloximes,[34] was also considered. A solution of (hexenyl)Co^{III}(saloph) was treated with 20 mol % Co^{II}(7,7′-Ph_2salen). Similarly, the reverse combination consisting of a solution of (hexenyl)Co^{III}(7,7′-Ph_2salen) was treated with 18 mol % Co^{II}(saloph). Indeed the characteristic triplet resonance at δ 3.72 was observed in the first instance, and another at δ 3.53 appeared over a period of 15 min in the second instance. These observations are consistent with the facile redox transfer of alkylcobalt(III) complexes with cobalt(II),[34,35] e.g.,



(16)

However, after several hours, we could find no evidence of the appearance of rearranged cyclopentylmethyl derivatives by their characteristic ^1H resonances at δ 3.45 and 3.62. While it is not possible to rigorously exclude the catalysis of alkyl exchange by traces of cobalt(II) impurities in the first series of experiments, the requirement for substantial amounts of ferrocenium salt [which readily destroys cobalt(II)] and the simultaneous observation of hexenyl rearrangement [which is strongly inhibited by cobalt(II)] argue against this possibility.

In order to examine the importance of redox transfer of alkyl ligands as in eq 16, we examined the thermolysis of (5-hexenyl)Co^{III}(saloph) by heating a solution of it in pyridine-d_5. The homolysis of the n-propyl derivative ($R = CH_3CH_2CH_2$) was earlier found by Halpern and co-workers[36] to have a first-order rate constant $k_1 = 4.7 \times 10^{-4}\ s^{-1}$ at 70 °C. We wished to compare the reactivity of IX with the known rate of homolysis in eq 17.

$$RCo^{III}(saloph)(py) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co^{III}(saloph)(py) + R^\bullet \quad (17)$$

The hexenyl rearrangement was monitored by following the disappearance of the vinyl resonances in the ^1H NMR spectrum relative to that of the internal standard 2,4-dichlorotoluene. A half-life of 80 min was observed from which the hexenyl rearrangement rate constant is taken to be $1 \times 10^{-4}\ s^{-1}$. After 7 h at 70 °C, the tube was reexamined and found to contain a prominent doublet resonance at δ 4.30 (J = 5.3 Hz) for (cyclopentylmethyl)Co^{III}(saloph)(py). We judge from these results that hexenyl rearrangement proceeded at a rate that was comparable to that of homolysis (eq 17, $R = CH_2CH_2CH_2CH_2CH{=}CH_2$). It is useful to note that the homolysis rate constant k_1 may be extrapolated to 25 °C from the activation parameters reported earlier for the n-propyl analogue.[36] The value of $k_1 = 3 \times 10^{-7}$ s^{-1} which corresponds to a half-life of 26 days was substantially slower than the ferrocenium-induced rearrangement of 40% within 2 h. Thus the induced rearrangement of IX qualitatively proceeded at a rate that was many orders of magnitude faster than its rate of hexenyl homolysis.

Discussion

Ligand rearrangements of organocobalt complexes show distinctive reactivity patterns which are structurally dependent on the equatorial Schiff base and on the alkyl moiety. Thus we find that the alkyl rearrangement that transforms the cyclopropylmethyl group to the 3-butenyl group occurs much more readily than the related rearrangement of the 5-hexenyl group to the cyclopentylmethyl group in a common series of salen cobalt(III) derivatives I and IV. Both conversions are facile when contrasted against the complete reluctance of the (5-hexenyl → cyclopentylmethyl) rearrangement to occur in the related $(dmgH)_2Co^{III}$ derivative (III). These general observations, coupled with the

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[32] The ferrocenium ion was present in 18 mol% relative to the total organocobalt(III) concentration.

[33] Note the resonance at δ 3.45 also includes a contribution from the dideuteriocyclopentylmethyl derivative derived by intermolecular exchange. Similarly the resonance of δ 3.62 includes a contribution for (cyclomethylpentyl)Co^{III}(7,7-Ph_2salen).

[34] Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664.

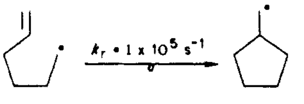
[35] Mestroni, G.; Cocevar, C.; Costa, G. *Gazz. Chim. Ital.* **1973**, *103*, 273. Van Den Bergen, A.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1971**, 52.

[36] Tsou, T.-T.; Loots, M.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 623.

extremely complex pattern of experimental variables (Table I) which affects the rearrangement of (hexenyl)Co^{III}(salen)(py) (I), underscore the occurrence of unusually interesting mechanisms for such process(es).

Conceptually, the rearrangement of an alkyl ligand may proceed by either a concerted pathway or a stepwise process involving the prior cleavage of the alkyl–metal bond. As applied to organocobalt complexes of the types examined in this study, both classes of mechanisms have been presented.[37] However, the alkyl rearrangement of (5-hexenyl)Co^{III}(salen)(py) (I) is unique, and we wish to establish that it occurs by a homolytic chain mechanism.[38]

I. Alkyl Radicals as Prime Intermediates. The transformation of a 5-hexenyl group to a cyclopentylmethyl group is highly symptomatic of an alkyl radical or radical-like (e.g., a caged radical pair) intermediate.[39-41]

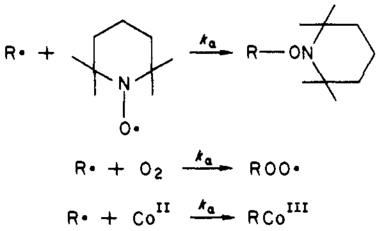


(18)

By contrast, the alternative heterolytic scission of the hexenyl–cobalt bond would result in either a hexenyl cation which rearranges to a cyclohexyl cation[42] or a hexenyl anion which is slower to rearrange.[43,44] The situation is not as clearly delineated with the cyclopropylmethyl ligand since the corresponding alkyl radical, cation, and anion are all known to rearrange spontaneously to the butenyl moiety.[41,45,46] However, there are other concerted pathways which might regiospecifically generate a cyclopentylmethyl group without prior homolysis (vide infra).

II. Mechanistic Significance of the Experimental Variables. Therefore let us consider the mechanistic significance of the diverse experimental observations for the hexenyl rearrangement as they derive from (a) the strong inhibition by additives as different as TEMPO, dioxygen, and cobalt(II), (b) the initiation and facilitation by chemical and electrochemical oxidation, (c) the stabilization by prereduction, (d) the ineffectiveness of alkyl–cobalt bond homolysis, (e) the intermolecular character of the rearrangement and the accompanying alkyl exchange, and finally (f) the dichotomous effect of pyridine.

(a) The inhibition of the hexenyl rearrangement in I by TEMPO, dioxygen, and cobalt(II) is established by their effect on freshly prepared samples of (5-hexenyl)Co^{III}(salen)(py) (I), as shown by the results in Table I. Among these inhibitors, the cobalt(II) additive introduced as Co^{II}(salen)(py) is the most effective. Thus the presence of as little as 0.5 mol % is sufficient to squelch completely the rearrangement of a freshly prepared sample of I for prolonged periods (Table IV). Such an observation establishes the occurrence of a chain process for the hexenyl rearrangement, the kinetic chain length (kcl) of which must be >200.[47] 9,10-Dihydroanthracene has an intermediate effect of retarding the hexenyl rearrangement in measure with the amount added (Table V). A limiting value of the efficiency is not attained until more than 2 equiv (>200 mol %) of dihydroanthracene is present, which suggest a limited kcal of <5. We propose that the differing efficiencies are related to the effectiveness with which the active chain carrier is intercepted by TEMPO, dioxygen, cobalt(II), or dihydroanthracene. The characteristics of these additives differ, some are oxidants (TEMPO and O$_2$) whereas others are reducing agents (Co^{II} and DHA). However, they are all known to be uniformly susceptible to the alkyl radical R•.[48] Thus the scavenging of alkyl radicals by TEMPO, dioxygen, and cobalt(II) occurs at or close to diffusion-controlled rates to generate more stable adducts,[49-51] i.e.,

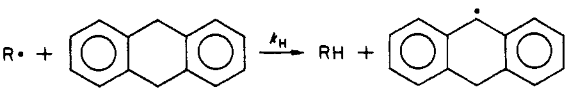


(19)

$$R\bullet + O_2 \xrightarrow{k_a} ROO\bullet \tag{20}$$

$$R\bullet + Co^{II} \xrightarrow{k_a} RCo^{III} \tag{21}$$

where R = 5-hexenyl, cyclopentylmethyl, etc. By way of comparison, 9,10-dihydroanthracene is known to transfer a hydrogen atom to alkyl radicals with a second-order rate constant k_H, i.e.,



(22)

which is at least 6 orders of magnitude less than the values for k_a in eq 19–21.[52] Such a difference in rates accounts for the strong inhibitory effects of TEMPO, O$_2$, and Co^{II} and the rather mild retarding effect of DHA on the radical chain process for 5-hexenyl rearrangement.

(b) The initiation and facilitation of hexenyl rearrangement by chemical and electrochemical oxidation relates to the production of the active chain carrier. Thus alkylcobalt(III) complexes are known to undergo 1-electron oxidation to metastable alkylcobalt(IV) species as a result of both electrochemical and chemical stimulation.[53-57] The subsequent fragmentation of the alkylcobalt(IV) species affords alkyl radicals,[58] i.e.,

Scheme I

$$RCo^{III}S \xrightarrow{-e} RCo^{IV}S^+ \tag{23}$$

$$RCo^{IV}S^+ \xrightarrow{\text{fast}} R\bullet + Co^{III}S^+ \tag{24}$$

S represents the coordinated Schiff base

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(37) For example, see ref 9a, 12a, 13, and 14.

(38) For another type of homolytic chain mechanism, see: (a) Gupta, B. D.; Funabiki, T.; Johnson, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 6697. (b) Crease, A. E.; Gupta, B. D.; Johnson, M. D.; Moorhouse, T.-J. *J. Chem. Soc., Dalton Trans* **1978**, 182. (c) Bougeard, P.; Gupta, B. D.; Johnson, M. D. *J. Organomet. Chem.* **1981**, *206*, 211. (d) Crease, A. E.; Johnson, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 8013 and related papers.

(39) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(40) Surzur, J.-M. In *Reactive Intermediates*; Abramovitch, A., Ed.; Plenum: New York, 1982; Vol. 2, p 121.

(41) Beckwith, A. L. J.; Ingold, K. U. ref 1, p 162 ff. See also: Julia, M. *Pure Appl. Chem.* **1974**, *40*, 553.

(42) Bartlett, P. D.; Clossen, W. D.; Cogdell, T. J. *J. Am. Chem. Soc.* **1965**, *87*, 1308.

(43) (a) Kossa, W. C., Jr.; Rees, T. C.; Richey, H. G., Jr. *Tetrahedron Lett.* **1971**, 3455. (b) See, however: Hill, E. A. *Adv. Organomet. Chem.* **1977**, *16*, 131. Garst, J. F.; Hines, J. B., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 6443.

(44) (a) Furthermore, the slight retarding effect of pyridine indicates that an intramolecular rearrangement of a carbenoid cobalt complex of the type suggested by Rooney and co-workers (Amir-Ebrahimi, V.; Hamilton, R.; Kulkarni, M. V.; McIlgorn, E. A.; Mitchell, T. R. B.; Rooney, J. R. *J. Mol. Catal.* **1983**, *22*, 21) for 5-hexenylcobalamine is unlikely in the present case. (b) For carbene rearrangements, see: Jones, W. M., in ref 1, p 95.

(45) Cf.: Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 856.

(46) Silver, M. S.; Shafer, P. R.; Nordlander, J. E.; Ruchardt, C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 2646. Lansbury, P. T.; Pattison, V. A.; Clement, W. A.; Sidler, J. *J. Am. Chem. Soc.* **1964**, *86*, 2247.

(47) We have taken the lower limit of the kinetic chain length to be simply the reciprocal of the equivalents of added inhibitor.

(48) Hereinafter R is used generally to indicate the alkyl (hexenyl, cyclopentylmethyl, etc.) ligand of the organocobalt(III) derivative RCo^{III}S, where S is the coordinated Schiff base.

(49) See ref 22 and 23.

(50) See: Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3043 and ref 14 therein.

(51) (a) Wilson, R. L. *Trans. Faraday Soc.* **1971**, *67*, 3008. (b) Blackburn, R.; Charlesby, A. *Trans. Faraday Soc.* **1966**, *62*, 1159. (c) Thomas, J. K. *J. Phys. Chem.* **1967**, *71*, 1919.

(52) Evaluated from the data in: Ingold, K. U. *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 38 ff.

(53) (a) Halpern, J.; Chan, M. S.; Hanson, J.; Roche, T. S.; Topich, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1606. (b) Abley, P.; Dockal, E. R.; Halpern, J. *J. Am. Chem. Soc.* **1972**, *94*, 659.

(54) Anderson, S. N.; Ballard, D. H.; Chrzastowski, J. Z.; Dodd, D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1972**, 685.

(55) Levitin, I. Ya.; Sigan, A. L.; Volpin, M. E. *J. Chem. Soc., Chem. Commun.* **1975**, 469.

(56) (a) Costa, G.; Puxeddu, A.; Tavagnacco, G.; Dreos-Garlatti, R. *Inorg. Chim. Acta* **1984**, *89*, 65. (b) Fanchiang, Y.-T. *Inorg. Chem.*, **1984**, *23*, 3983.

(57) Tamblyn, W. H.; Klingler, R. J.; Hwang, W. S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3161.

which would be effective initiators of the radical chain process. The anodic initiation described in Table I and the ferrocenium-induced initiation in Tables IV and VI represent the contribution from the electron-transfer in Scheme I.[48] Such a redox process also serves the dual function of effectively eliminating any adventitious cobalt(II) impurity which can act as an inhibitor. [Note the oxidation potential of $\mathrm{Co^{II}(salen)(py)}$ in eq 10 is less positive than that of $\mathrm{(hexenyl)Co^{III}(salen)(py)}$ in eq 12.] Indeed the ability of ferrocenium ion to overcome the deliberate inhibition of hexenyl rearrangement by added $\mathrm{Co^{II}(salen)(py)}$, as shown in Figure 3, addresses this point directly (eq 11). Owing to the dual character of oxidative initiation, it is not possible to rigorously define a kinetic chain length based on the initiation of hexenyl rearrangement. However, if we proceed strictly on the basis of the requirement for faradays of anodic current passed or the equivalents of ferrocenium consumed, a phenomenological minimum for kcl is estimated to be roughly 10.

(c) **Prereduction** at potentials of −0.8 to −1.0 V vs. SCE retards the spontaneous rearrangement of freshly prepared samples of $\mathrm{(hexenyl)Co^{III}(salen)(py)}$ (I). At these potentials, the organocobalt(III) complex I is not electroactive.[59] However, such potentials are sufficient to consume the oxidizing cobalt(III) impurities, as in eq 10. The resultant cobalt(II) species which would be generated under these conditions are capable of effectively inhibiting the hexenyl rearrangement (vide supra). It is also possible that adventitious oxidants which could initiate the chain process by the redox process in Scheme I are destroyed at these potentials.

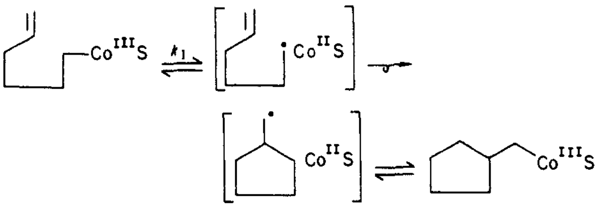
(d) **Homolytic dissociation** of an organocobalt(III) complex in eq 25, coupled with the rapid addition of alkyl radicals to cobalt(II) in eq 21, represents the quasi-equilibrium

$$\mathrm{RCo^{III}S} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{R^{\bullet} + Co^{II}S} \tag{25}$$

which is well established with various Schiff base complexes.[60,61] The efficient scavenging of propyl radicals under conditions that $k_2[\mathrm{Co^{II}S}] >> k_1$ allowed Halpern and co-workers to evaluate the rate constant $k_1 = 4.7 \times 10^{-4}\ \mathrm{s^{-1}}$ for $(n\text{-propyl})\mathrm{Co^{III}(saloph)(py)}$.[63] Our data for $\mathrm{(5\text{-}hexenyl)Co^{III}(saloph)}$ show clearly that its rate of homolysis as in eq 17 is many orders of magnitude slower than the rate of the induced rearrangement in Table VI. Therefore a mechanism involving a rate-limiting ligand homolysis followed by the rapid rearrangement and recombination as in Scheme II is precluded. Furthermore such a mechanism would not account for the chain character of the hexenyl rearrangement, as established by cobalt(II) inhibition and oxidative initiation shown above in (a) and (b), respectively.

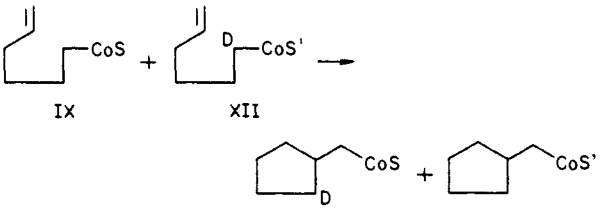
Ligand homolysis as in eq 17 cannot, by itself, be responsible for the spontaneous initiation of hexenyl rearrangement since any effect of the alkyl radical initiator will be effectively nullified by the coproduction of the cobalt(II) inhibitor. However, the extent to which the ferrocenium ion selectively destroys cobalt(II) in eq 11[64] may reflect this mode of initiation in the $\mathrm{Fc^+}$-induced rearrangements (Table IV). However, we hasten to add that such a contribution from homolysis is limited by the small magnitude of the rate constant $k_1 \cong 10^{-7}\ \mathrm{s^{-1}}$ ($\tau_{1/2} \cong 3$ weeks[65]).

Scheme II



(26)

(e) **The intermolecular character** of the hexenyl rearrangement is established by the crossover experiments with the doubly labeled hexenylcobalt(III) derivatives IX and XII, i.e.,

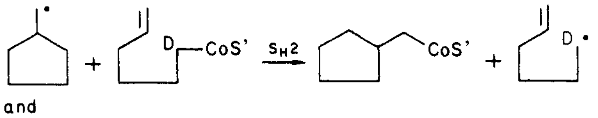


IX XII (27)

where S = saloph and S′ = 7,7′-$\mathrm{Ph_2}$salen. The extensive transfer of alkyl ligands accompanying rearrangement can be accommodated by a homolytic displacement on the alkylcobalt(III) complex, which is schematically represented as

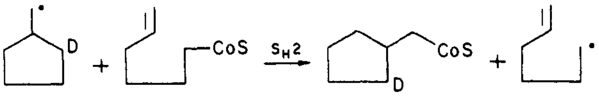
$$\mathrm{R'^{\bullet} + RCo^{III}S \rightarrow R'Co^{III}S + R^{\bullet}} \tag{28}$$

Although such a radical substitution reaction is not commonly known for transition metal–alkyls, it is well established with the main-group organometals and is designated as a $\mathrm{S_H2}$ process.[67,68] As applied to the crossover experiments in eq 27, the homolytic substitution reactions involve the rearranged cyclopentylmethyl radical, i.e.,



(29)

and



(30)

The sum of these displacement reactions plus the (hexenyl → cyclopentylmethyl) rearrangement in eq 18 represent the overall chain process for the intermolecular rearrangement as described in eq 27.

Furthermore the close examination of the results of the crossover experiments also revealed the occurrence of a simultaneous exchange of alkyl groups between two cobalt(III) centers concom-

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[58] (a) See ref 55 and 57 and compare with: Reisenhofer, E.; Costa, G. *Inorg. Chim. Acta* **1981**, *49*, 121. (b) In a more general context, organocobalt(IV) species suffer decomposition by at least three pathways,

$$\mathrm{RCo^{III}S \xrightarrow{-e} RCo^{IV}S^+ \rightarrow R^{\bullet} + Co^{III}S^+} \tag{a}$$

$$\mathrm{RCo^{IV}S^+ \rightarrow R^+ + Co^{II}S} \tag{b}$$

$$\mathrm{RCo^{IV}S^+ \xrightarrow{Nu} RNu^+ + Co^{II}S} \tag{c}$$

the competition among which is probably affected by the coordinated S.[83]

[59] For example, (a) CV studies show for V a quasi-reversible wave at $E_{1/2} = -1.21$ V ($\Delta E = 105$ mV at mV at 500 mV $\mathrm{s^{-1}}$) which is only slightly shifted to −1.22 V ($\Delta E = 130$ mV) in the presence of 1 equiv of added pyridine in THF solutions containing 0.2 M TBAP. (b) $\mathrm{Co^{II}(salen)}$ shows a quasi-reversible reduction at −1.13 V ($\Delta E = 90$ mV at 500 mV $\mathrm{s^{-1}}$) under the same conditions. The reduction is irreversible in $\mathrm{CH_2Cl_2}$ probably due to reaction with solvent to afford $\mathrm{ClCH_2Co^{III}S}$ complexes.

[60] Halpern, J.; Kim, S.-H.; Leung, T. W. *J. Am. Chem. Soc.* **1984**, *106*, 8317. Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. Finke, R. G.; Hay, B. P. *Inorg. Chem.* **1984**, *23*, 3043 and ref 14 therein. Finke, R. G.; Smith, B. L.; Mayer, B. J.; Molinero, A. A. *Inorg. Chem.* **1983**, *22*, 3677.

[61] Compare also the reversible homolysis of the related organochromium(III) complexes.[62] See: Blau, R. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 3530.

[62] Espenson, J. H. In *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed.; Academic Press: New York, 1982; Vol. I, pp 1–63.

[63] See ref 36.

[64] Electron transfer from cobalt(II) to $\mathrm{Fc^+}$ is facile, whereas that from primary alkyl radicals can be relatively slow. See: Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.

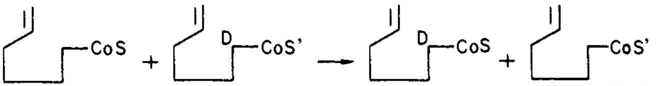
[65] Moreover the thermal homolysis of hexacoordinate species such as I is thought to be much more facile than that of the base-off pentacoordinate species V.[66]

[66] Schrauzer, G. N.; Grate, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 541. Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2274.

[67] For reviews, see: (a) Ingold, K. U.; Roberts, B. P. *Free Radical Substitution Reactions*; Wiley: New York, 1971. (b) Davies, A. G.; Roberts, B. P. *Acc. Chem. Res.* **1972**, *5*, 387, (c) Davies, A. G.; Roberts, B. P. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 547. (d) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978.

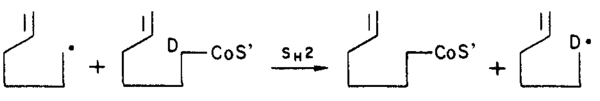
[68] For an example of a homolytic substitution on a dirhodium center, see: Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

itant with hexenyl rearrangement. This conclusion derives from the crossover of an *unrearranged* hexenyl group from one cobalt center to another, i.e.,



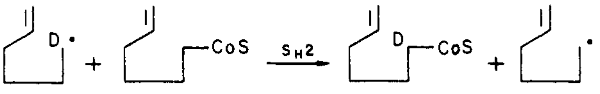
(31)

Such an alkyl exchange is inherent to the homolytic displacement in eq 28, since it merely represents the case in which the displacements occur with the unrearranged hexenyl radical, i.e.,



(32)

and



(33)

Thus the sum of eq 32 and 33 represents the chain process for the alkyl exchange, as described in eq 31.

The alkyl radical chain process for ligand exchange accompanying hexenyl rearrangement is to be distinguished from an alternative process for alkyl exchange. Thus Johnson and coworkers[34] had earlier shown that exchange of an alkyl ligand is possible between alkylcobalt(III) complexes when it is mediated by cobalt(II) species, i.e.,

$$\mathrm{RCo^{III}S + Co^{II}S' \rightarrow RCo^{III}S' + Co^{II}S} \qquad (34)$$

Indeed, (hexenyl)Co^{III}(saloph) (IX) is converted to the Ph$_2$salen derivative X by Co^{II}(Ph$_2$salen), as shown in eq 16. However, we find that hexenyl rearrangement to cyclopentylmethyl does not accompany alkyl exchange in Scheme IV. Moreover the presence of substantial amounts of ferrocenium in our system ensures the destruction of any cobalt(II) species extant. Both of these results argue against the Co^{II}-mediated process for alkyl exchange during the hexenyl rearrangement.

(f) The dichotomous effect of pyridine on the hexenyl rearrangement of the coordinatively unsaturated derivative V is shown by the strong enhancement at low concentrations (<1 equiv), the minor effect at moderate concentrations, and the slight retarding effect at high concentrations, as examined in Table III. The spectral results shown in Figure 2 indicate that (hexenyl)Co^{III}(salen)(py) (I) is readily dissociated in solution, as given by the general equilibrium

$$\mathrm{RCo^{III}S(py) \underset{}{\overset{K^{-1}}{\rightleftharpoons}} RCo^{III}S + py} \qquad (35)$$

The results at low pyridine concentrations, coupled with the magnitude of K as measured in Table II, support the hexacoordinate RCo^{III}S(py) as the active species for hexenyl rearrangement. According to the redox initiation in Scheme I the oxidized RCo^{IV}S(py) undergoes homolytic dissociation, i.e.,

$$\mathrm{RCo^{IV}S(py)^+ \rightarrow Co^{III}S(py)^+ + R^\bullet} \qquad (36)$$

to generate the stable 16-electron Co^{III}S(py). By contrast, the homolysis of the coordinatively unsaturated species RCo^{IV}S$^+$ would be unfavorable owing to the formation of the metastable 14-electron Co^{III}S$^+$.[69] In the latter, the preferred route for decomposition would be expected to be a heterolytic one,[58] e.g.,

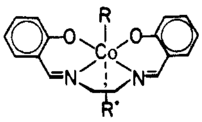
$$\mathrm{RCo^{IV}S^+ \rightarrow R^+ + Co^{II}S} \qquad (37)$$

to generate the uncharged cobalt(II) species.[70] Basically the same type of reasoning could be used in favoring the homolysis of RCo^{III}S(py) rather than that of the coordinatively unsaturated RCo^{III}S.[65]

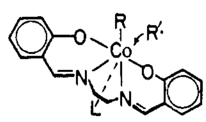
The contrasting effect at higher concentrations of pyridine can be ascribed to the chain transfer step in eq 28.[71] If so, the results in Figure 2 show that the alkylcobalt(III) complex exists as the coordinatively saturated species at the highest concentrations of pyridine. Since the hexenyl rearrangement is only slightly retarded and not quenched under these conditions, the homolytic displacement probably occurs directly on this hexacoordinate complex, i.e.,[72]

$$\mathrm{R'^\bullet + RCo^{III}S(py) \rightarrow R'Co^{III}S(py) + R^\bullet} \qquad (38)$$

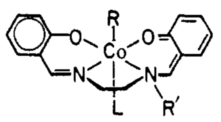
The involvement of the pentacoordinate complex is directed to the vacant axial site which is trans to the alkyl ligand in RCo^{III}S. Such an attack is conceptually attractive, and it would lead to a neutral cobalt(IV) intermediate or activated complex such as A in which the overall substitution occurs with stereochemical inversion at the cobalt center. The location of the homolytic attack on the saturated complex in eq 38 is less clear. Thus the occupation of the trans site by pyridine could direct the attack on cobalt from the same face as that occupied by the alkyl ligand to afford the 7-coordinate, cis analogue B. Alternatively, a reversible addition to the salen moiety as in C may be followed by a migratory displacement. Whatever the activated complex for homolytic displacement may be, however, it is to be distinguished from that at the carbon center leading to the displacement of cobalt(II).[73] Thus a thorough search among the reaction products showed no evidence for bihexenyl, bicyclopentylmethyl, or the mixed coupled dimeric product.[74] Furthermore, the treatment of the *n*-butyl derivative with ferrocenium salt under conditions applicable to the hexenyl rearrangement, followed by iodinolysis, afforded only *n*-butyl iodide and no octane (<0.2%).



A



B



C

III. Alkyl Radical Chain Mechanism for Hexenyl Rearrangement. Any mechanistic formulation of the hexenyl rearrangement must accommodate all of the diverse experimental observations described above. Foremost among these are (i) the primacy of alkyl radicals as reactive intermediates and (ii) the strong inhibition of hexenyl rearrangement by such structurally different additives cobalt(II), dioxygen, and TEMPO. Indeed the inhibition of an alkyl radical process establishes a chain process of which the propagation mechanism can be presented as

Scheme III

$$\mathrm{R'^\bullet + RCo^{III}S(py) \rightarrow R'Co^{III}S(py) + R^\bullet} \qquad (39)$$

$$\mathrm{R^\bullet \xrightarrow{\;k_c\;} R'^\bullet} \qquad (40)$$

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[69] Note the difference between RCo^{III}S(py) and RCo^{III}S does not lie in their oxidation potentials since the quasi-reversible CV waves occur at $E_{1/2}$ = 0.612 and 0.617 V, respectively, with $(E_p^a - E_p^c)$ = 100 mV at 500 mV s^{-1} in THF solutions. These values agree with those obtained under an acetonitrile for related penta- and hexacoordinate (alkyl)Co^{III}(salen) complexes with pyridine.[55] (b) Thus any distinction between the two in their ability to generate alkyl radicals lies in the decomposition[58] rather than in the formation of the corresponding organocobalt(IV) derivative.

(70) These arguments derive from the differences in the thermodynamic driving forces for the competition involved in the decomposition of the alkylcobalt(IV) species. See ref 58b.

(71) The extent to which pyridine affects the initiation step in Scheme I is reflected in the diversion of the (alkyl)cobalt(IV) species from homolytic scission as in eq 24 to non-radical-producing processes such as nucleophilic displacement (see eq c in ref 58b). Compare also eq 36 and 37.

(72) It is also possible that the limited amounts of rearrangement observed at low pyridine concentration is strictly due to the inefficiency of the initiation step, as described in eq 37. If so, the results in Figure 2 could be interpreted in terms of an S$_H$2 substitution on a pentacoordinate species if (a) the rate constant (i.e., R'$^\bullet$ + RCoS → R'CoS + R$^\bullet$) were substantially faster than that in eq 38 and (b) the kinetic chain length in Scheme III were limited. However the results in Figure 3 indicate a long kinetic chain length for hexenyl rearrangement. An independent source of alkyl radical would help to resolve this ambiguity.

(73) Bury, A.; Cooksey, C. J.; Funabiki, T.; Gupta, B. D.; Johnson, M. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1050.

(74) Cf.: Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 4395.

where R and R′ represent 5-hexenyl and cyclopentylmethyl, respectively. According to Scheme III, the alkyl radical is the sole reactive intermediate responsible for the propagation of the chain process. It includes both of the key steps in the hexenyl rearrangement, namely, the rearrangement of the alkyl radical and the homolytic displacement on the alkylcobalt(III) complex, as described in eq 18 and 38, respectively. Most importantly, it readily accommodates the observation of the intermolecular nature of hexenyl rearrangement (eq 27) and the concurrent alkyl exchange (eq 31) both of which are otherwise difficult to explain. (See eq 29,30 and 32,33, respectively). With (hexenyl)$\mathrm{Co^{III}}$(salen)(py), the rate of homolytic displacement in eq 39 is roughly comparable to the rate of the radical rearrangement in eq 40,[75] since the scrambling of the hexenyl ligands can be detected simultaneously with hexenyl rearrangement.

Since the alkyl radical is solely responsible for chain propagation in Scheme III, any process or additive which removes alkyl radicals would terminate the chain. The effectiveness of dioxygen, TEMPO, cobalt(II), and even dihydroanthracene accords with this conclusion as represented in eq 19–21 and 22. Likewise any process or additive which leads to alkyl radicals, such as chemical or anodic oxidation (eq 12 and 13), would lead to chain initiation by the mechanism in Scheme I.

IV. Alternative Mechanisms for Hexenyl Rearrangement. The stipulation that alkyl *radicals* are prime intermediates in a *chain* process for hexenyl rearrangement does limit the mechanistic possibilities to essentially that propagation cycle presented in Scheme III. For example, there are other chain processes such as that evolving from electron transfer (see eq 23), i.e.,

Scheme IV

$$\mathrm{RCo^{III}S(py) + Co^{III}S(py)^+ \rightarrow RCo^{IV}S(py)^+ + Co^{II}S(py)} \qquad (41)$$

$$\mathrm{RCo^{IV}S(py)^+ \rightarrow R^{\bullet} + Co^{III}S(py)^+}, \text{ etc.} \qquad (42)$$

which is tantamount to the catalytic homolysis of the alkylcobalt(III) precursor, i.e.,

$$\mathrm{RCo^{III}S(py) \rightarrow R^{\bullet} + Co^{II}S(py)} \qquad (43)$$

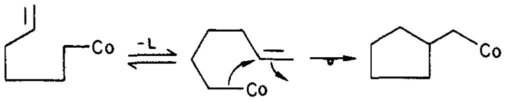
The extent to which eq 43 is reversible allows the hexenyl rearrangement to take place, viz.,

$$\mathrm{R^{\bullet}} \xrightarrow{k_r} \mathrm{R'^{\bullet}} \qquad (44)$$

$$\mathrm{R'^{\bullet} + Co^{II}S(py)} \xrightarrow{\text{fast}} \mathrm{R'Co^{III}S(py)} \qquad (45)$$

A key factor in this mechanism, is the oxidative role played by the cobalt(III) salt $\mathrm{Co^{III}S(py)^+}$ as the chain carrier. Although alkyl radicals are involved, they are not the principal carriers. Thus radical scavengers do not quench the chain but merely serve to divert the alkyl radicals into side products (e.g., see eq 19 and 20). The chain reaction can only be quenched by the destruction of the cobalt(III) salt—most likely by reducing agents. Thus cobalt(II) additives would suppress the rearrangement by a secondary effect in eq 21, which could only serve to decrease the lifetime of hexenyl radicals, i.e., [$\mathrm{R^{\bullet}}$], and thus lead to an increase in the number of cycles necessary for successful rearrangement in eq 44 and 45. However, Scheme IV does not explain the ability of O_2 and TEMPO to inhibit and dihydroanthracene to retard the hexenyl rearrangement of I, since none of these are able to destroy cobalt(III) salts.[76] Futhermore the deliberate addition of $\mathrm{Co^{III}(salen)(py)_2{}^+PF_6{}^-}$ in Table I did not induce hexenyl rearrangement.

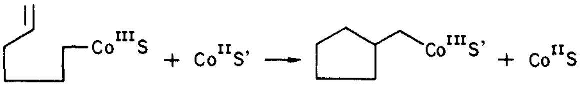
We also emphasize that the requirement of a chain process by itself imposes a severe limitation sufficient to exclude molecular mechanisms for the hexenyl rearrangement. Thus the cyclopentylmethyl derivative could arise conceivably from a regiospecific, intramolecular insertion of the hexenyl double bond into the cobalt–carbon linkage, e.g.,



(46)

This type of molecular mechanism is facilitated by a vacant coordination site cis to the cobalt–carbon bond to permit prior olefin coordination.[80] Indeed similar insertions have been recently invoked to rationalize the formation of cyclized products from organonickel and organopalladium complexes.[80,81] However, it is not clear how such an intramolecular process could be affected by TEMPO, dioxygen, cobalt(II), or dihydroanthracene. Furthermore, it should be optimum in the coordinatively unsaturated derivative $\mathrm{RCo^{III}S}$. Instead, the promotion by pyridine (see Figure 2) indicates the hexenyl rearrangement to proceed from the coordinatively saturated adduct $\mathrm{RCo^{III}S(py)}$. Finally this mechanism is incompatible with the intermolecular scrambling of the alkyl ligands which occurs during the hexenyl rearrangement.

The hexenyl → cyclopentylmethyl rearrangement of I is somewhat reminiscent of the rearrangement of (1-methyl-3-butenylcobaloxime)(pyridine) to its 2-methyl-3-butenyl isomer.[8,9] By analogy, a cyclopentylmethyl ligand might be generated by specific attack at the hexenylcobalt(III) center by cobalt(II) in such a way as to induce simultaneous rearrangement and alkyl transfer, e.g.,



(47)

This type of process was also invoked to explain alkyl interchanges between organocobaloximes.[82] However, Johnson and co-workers demonstrated that while cobalt(II) does react with (alkyl)$\mathrm{Co^{III}}$ complexes to afford alkyl exchange it does not induce ring closure in 5-hexenylcobaloxime.[82] In our system, the observation of strong inhibition by cobalt(II) rigorously excludes the possibility of eq 47.

Summary and Conclusions

The rearrangement of the alkyl ligand in (5-hexenyl)cobalt(III) complexes is demonstrated to be a chain process in which the alkyl radical is the sole chain carrier. Indeed the primacy of alkyl radicals as the reactive intermediate and the chain character of hexenyl rearrangement severely limit the mechanistic possibilities to essentially that presented for the propagation sequence in Scheme III. The necessity of proposing the homolytic displacement or $\mathrm{S_H2}$ process in eq 28 and 38 is well accommodated in the crossover experiments by the intermolecular nature of hexenyl rearrangement (eq 27) and the observation of alkyl exchange (eq 31)—the simultaneity of which would be difficult to explain other than by eq 29,30 and eq 32,33, respectively.

The clear-cut delineation of the alkyl radical chain mechanism for hexenyl rearrangement in Scheme III is made possible by the fortuitous matching of the relative rates of radical rearrangement in eq 18 and homolytic displacement in eq 38. Thus if one of these processes were either much slower or much faster than the other, the chain mechanism for rearrangement of an alkylcobalt(III) complex would be experimentally difficult to observe under the conditions described in this study. It is possible that the absence of rearrangement of (5-hexenyl)$\mathrm{Co^{III}(dmgH)_2(py)}$ in eq 5 and

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[75] By rates, we refer qualitatively to an overall change since these processes have different kinetic orders.

[76] For example, (a) (salen)$\mathrm{Co^{III}}$ salts can actually be prepared by the aerial oxidation of $\mathrm{Co^{II}}$(salen) in the presence of added ligands.[77] (b) The $E_{1/2}$ in eq 10 is much less than that of 9,10-dihydroanthracene.[78] (c) However, the $E_{1/2}$ of TEMPO is 0.33 V vs. Ag/AgCl in acetonitrile.[79]

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[78] $E_{1/2}$ for DHA is estimated to be 2.37 V vs. NHE in trifluoroacetic acid by comparison with that of *o*-xylene. See: Howell, J. O.; Goncalves, J.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

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[82] Dodd, D.; Johnson, M. D.; Lockman, B. L., in ref 34.

the extremely facile rearrangement of (cyclopropylcarbinyl)-Co^{III}(salen)(py) in eq 6 may be examples of such kinetics extrema. It is of course possible that other mechanisms pertain, as presented earlier.[9] No doubt a key question which must be resolved in order to establish this point is the role of the Schiff base structure in mediating the rates of homolytic displacement.[83] Indeed this point may be immediately relevant to the mechanism of the cobalamine-dependent enzymatic processes since there is increasing evidence for the importance of carbon-centered radicals as reactive intermediates.[84]

Experimental Section

Materials. The cobalt complexes Co^{II}(salen),[85] Co^{II}(salen)(py),[86] and Co^{III}(salen)(py)$_2$$^+PF_6$$^-$[77] were prepared by literature procedures. Co^{II}-(7,7'-Ph$_2$salen) and Co^{II}(saloph) were prepared from the complexation of 7,7'-Ph$_2$salenH$_2$ and salophH$_2$ with Co^{II}(OAc)$_2$·4H$_2$O by using the same procedure as that employed for Co^{II}(salen).[85]

1-Bromo-5-hexene was prepared from 5-hexen-1-ol (Columbia Organic Chemicals) as follows.[87] 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 solvent, 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[88] 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 which 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.[89] (Bromomethyl)cyclopentane[90] was prepared from cyclopentaneacetic acid (Aldrich) by initial reduction to the alcohol with lithium aluminum hydride. A solution of 3.0 g (30 mmol) of cyclopentanemethanol was converted to the bromide with 8.4 g (32 mmol) of triphenylphosphine and bromine[91] to afford 3.0 g (61%) of bromomethylcyclopentane: 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 iodomethylcyclopentane with 6.2 g (15 mmol) of phosphorus triiodide (Alfa) by a procedure analogous to that used for the bromide. Yield was 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), 1.59 (m, 2 H), 1.22 (m, 2 H). 1-Bromohex-5-ene-*1,1*-d_2 was prepared by the reduction of 5-hexenoic acid (2.3 g, 20 mmol) with LiAlD$_4$ (0.92 g, 22 mmol) followed by bromination of the crude product with PBr$_3$(0.72 mL, 7.7 mmol) to yield 0.72 g (4.4 mmol) of product. ^{1}H NMR (80 MHz, CDCl$_3$): δ 5.8 (m, 1 H), 5.14–4.9 (m, 2 H), 2.1–1.5 (m, 6 H). 1-Iodo-but-3-ene was prepared from 6.0 g (83 mmol) of 3-buten-1-ol (Aldrich) and a slurry of PI$_3$ (14 g, 33 mmol) in ether (50 mL) at −78 °C. After the mixture was stirred overnight at room temperature, it was extracted with saturated solution of aqueous K$_2$CO$_3$, washed with water, and dried over anhydrous Na$_2$SO$_4$. The solvent was removed in vacuo and the residue distilled under reduced pressure to yield 4.9 g of product. Bp 32 °C (0.5 mm). ^{1}H NMR (90 MHz, CDCl$_3$): δ 5.8 (m, 1 H), 5.2–4.9 (m, 2 H), 3.16 (dt, J = 1, 7 Hz, 2 H), 2.60 (m, 2 H). The ^{13}C NMR spectrum also agreed with the reported spectrum.[89] Cyclopropylmethyl iodide was prepared by nucleophilic displacement of cyclopropylmethyl tosylate with iodide.[92] ^{1}H NMR (90 MHz, CDCl$_3$): δ 3.10 (d, J = 7.6 Hz, 2 H), 1.3 (m, 1 H), 0.8 (m, 2 H), 0.3 (m, 2 H).

Synthesis of Organocobalt(III) Complexes. The organocobalt(III) complexes were prepared by a slight modification to the procedure described by Costa et al.[93] 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 pyridine 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-hexenyl)Co^{III}(salen)(py) 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. (5-Hexenyl)Co^{III}(salen)(py) ^{1}H NMR (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 (using 2,4-dichlorotoluene as the internal standard) indicated the presence 0.52 equiv of methylene chloride of crystallization. Anal. Calcd for C$_{27}$H$_{30}$O$_2$N$_3$Co·$^1/_2$CH$_2$Cl$_2$: C, 62.33; H, 5.90. Found: C, 63.54; H, 6.09.[94]

(Cyclopentylmethyl)Co^{III}(salen)(py) 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, 2H), 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$_3$O$_2$Co: C, 66.52; H, 6.20. Found: C, 66.34; H, 6.25. (5-Hexenyl)Co^{III}(7,7'-Ph$_2$salen)(py) was prepared by the same procedure from the appropriate cobaltate(I) salt in 63% yield. ^{1}H NMR (360 MHz, CDCl$_3$): δ 8.6 (d, J = 5 Hz, 2 H), 7.7 (t, J = 7 Hz, 1 H), 7.5–7.8 (m, 16 H), 6.6 (~d, J = 9 Hz, 2 H), 6.35 (t, J = 7 Hz, 2 H), 5.6 (m, 1 H), 4.8 (m, 2 H), 3.72 (~t, J = 8 Hz, 2 H), 3.3 (m, 2 H), 3.1 (m, 2 H), 2.0 (~q, J = 8 Hz, 2 H), 1.55 (~qn, J = 8 Hz, 2 H), 0.85 (~qn, J = 8 Hz, 2 H). (5-Hexenyl)Co^{III}(saloph) was also prepared similarly from the appropriate cobaltate(I) salt in 81% yield. ^{1}H NMR (360 MHz, CDCl$_3$): δ 8.57 (s, 2 H), 8.0–7.2 (m, 10 H), 6.6 (m, 2 H), 5.5 (m, 1 H), 4.8 (m, 2 H), 3.53 (~t, J = 8.2 Hz, 2 H), 1.8 (m, 2 H), 1.65 (m, 2 H), 0.63 (m, 2 H). (5-Hexenyl-α,α-d_2)-Co^{III}(7,7'-Ph$_2$salen)(py) was also prepared from the sodium amalgam reduction of 480 mg (1.0 mmol) of Co^{II}(7,7'-Ph$_2$salen) to afford 420 mg (0.66 mmol, 66%) of the product. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.7 (d, J = 5 Hz, 2 H), 7.7 (t, J = 8 Hz, 1 H), 7.5–7.0 (m, 16 H), 6.6 (d, J = 9 Hz, 2 H), 6.4 (t, J = 8 Hz, 2 H), 5.7 (m, 1 H), 4.9 (m, 2 H), 3.3 (m, 2 H), 3.1 (m, 2 H), 2.0 (~q, J = 8 Hz, 2 H), 1.6 (~qn, J = 8 Hz, 2 H), 0.90 (t, J = 8 Hz, 2 H). No resonance was observed at δ 3.7.

(5-Hexenyl)Co^{III}(dmgH)$_2$(py)[95] was prepared from the reduction of 3.0 g (11.5 mmol) of ClCo^{III}(dmgH)$_2$(py)[96] in 50 mL of methanol at 0 °C with a degassed solution of NaOH (65 mmol) and sodium borohydride (0.48 g, 12 mmol) in 75 mL of 12% vol aqueous methanol, followed by the addition of 4.4 g (29 mmol) of 5-hexenyl bromide. After stirring for 1 h at 0 °C, water (100 mL) and pyridine (10 mL) were added. The yellow insoluble oil was extracted with CH$_2$Cl$_2$ (100 mL) and the extract dried with anhydrous Na$_2$SO$_4$ and reduced in volume to ~5 mL in vacuo. Addition of hexane, gave 1.2 g (2.6 mmol) of the product as yellow crystals, which were purified by column chromatography on neutral alumina (Woelm grade IV) by eluting with 5% pyridine

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[83] A qualitative indication of the importance of the Schiff base structure in homolysis lies in the difference between (hexenyl)Co^{III}(salen) and (hexenyl)Co^{III}(saloph) as described in the Results. A similar indication is found in nucleophilic substitution of hydroxocobalt(III) complexes, as qualitatively noted by: Saussine, L.; Brazi, E.; Robine, A.; Mimoun, H.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1985**, *107*, 3534.

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[94] The variable amounts of CH$_2$Cl$_2$ occluded (vide infra) undoubtedly account for this mediocre analysis.

[95] Dodd, D.; Johnson, M. D.; Lockmann, B. L., in ref 34.

[96] Schrauzer, G. N. *Inorg. Synth.* **1968**, *11*, 61.

in CH_2Cl_2. ^1H NMR (360 MHz, $CDCl_3$): δ 18.2 (s, 2 H), 8.55 (d, *J* = 5.2 Hz, 2 H), 7.67 (m, 1 H), 7.27 (m, 2 H), 5.7 (m, 1 H), 4.8 (m, 2 H) 2.08 (s, 12 H), 1.93 (m, 2 H), 1.58 (m, 2 H), 1.25 (m, 2 H), 0.89 (m, 2 H). Analysis by quantitative ^1H NMR spectrophotometry using *p*-dimethoxybenzene as internal standard indicated 99% purity.

(Cyclopropylcarbinyl)Co^{III}(salen)(py) (IV) was prepared as follows. A slurry of 0.65 g (2.0 mmol) of Co^{II}(salen) in 100 mL of THF under argon was stirred at 25 °C with an amalgam prepared from 100 mg of sodium in 5 mL of mercury. The green solution was cooled to -78 °C and added via a stainless steel cannula to a cold solution of 0.68 g (3.0 mmol) of cyclopropylcarbinyl tosylate in 20 mL of THF. The solution was stirred for 1 h at -78 °C without apparent reaction, and the temperature then was raised to 0 °C for 30 min. To the red solution was added 5 mL of pyridine and the volume of the solution reduced to ~50 mL in vacuo at 0 °C. The mixture was then quickly (flash) chromatographed over neutral alumina at -78 °C and eluted with 5% pyridine in CH_2Cl_2. The eluted red band was rapidly reduced in volume at 0 °C and cold pentane added. The solution upon standing at -78 °C overnight afforded a red powder which was filtered while cold and washed with pentane. Yield: 0.77 g (84%). ^1H NMR (90 MHz, $CDCl_3$): δ 8.6 (d, *J* = 5 Hz, 2 H), 7.9 (s, 2 H), 7.4–7.0 (m, 9 H), 6.6–6.4 (m, 2 H), 3.9–3.7 (m, 4 H), 3.6 (d, *J* = 7 Hz, 2 H), 0.5 (m, 1 H), 0.2 (m, 4 H). Additional resonances arising from (3-butenyl)Co^{III}(salen) were observed at δ 8.6 (d, *J* = 5 Hz, 2 H), 7.9 (s, 2 H), 7.4–7.0 (m, 9 H), 6.6–6.4 (m, 2 H), 5.8 (m, 1 H), 4.8 (m, 2 H), 3.45 (~t, *J* = 8 Hz, 2 H), 1.54 (q, *J* = 8 Hz, 2 H). Integration indicated that the butenyl isomer was present to an extent of 20% of the total cobalt alkyl content, even when the ^1H NMR spectrum was obtained within 5 min after dissolution of the sample. After longer periods (~1 h in vacuo), the nearly complete conversion of IV to the butenyl isomer was noted. The solid sample of IV was assayed for purity by the iodinolysis procedure (vide infra) which indicated 77% cyclopropylcarbinyl iodide and 18% butenyl iodide. Stability to rearrangement during iodinolysis was examined by allowing a 0.02 M solution of IV in $CDCl_3$ to rearrange in air for 1 h. ^1H NMR analysis indicated a ratio of 3-butenylcobalt(III) to (cyclopropylcarbinyl)cobalt(III) to be 0.93. Addition of iodine (50 mg, 10 equiv) followed by extraction with saturated aqueous $Na_2S_2O_3$ gave a solution which analyzed for the presence of 3-butenyl iodide and cyclopropylcarbinyl iodide in a ratio of 0.90.

Owing to the rapid homolysis of (5-hexenyl)Co^{III}(saloph) (IX), a modified procedure was required for the rapid removal of the cobalt(II) impurity required to obtain material of sufficient purity for rearrangement studies. Typically a solution of 100 mg of IX in 5 mL of 5% pyridine in CH_2Cl_2 was filtered rapidly through a 5-mm pad of silica gel (EM Industries 60 F) supported on a glass frit directly into 100 mL of cold (-78 °C) hexane. After an additional quick rinse with 5 mL of the solvent, the precipitate was collected and dried in vacuo. It was stored at -15 °C and used within a day. Thin-layer chromatography of IX on 0.2-mm plates of precoated silica (EM 60F) with 5% pyridine in CH_2Cl_2 as eluent indicated that Co^{II}(saloph) was immobile (R_f 0). To avoid the formation of Co^{II}(saloph) during TLC, it was necessary to pretreat the silica gel plates with 5% pyridine in CH_2Cl_2.

The coordinatively unsaturated alkylcobalt(III) complexes were prepared from the hexacoordinate complex by acid removal of pyridine. Typically, 100 mg (0.22 mmol) of (*n*-butyl)Co^{III}(salen)(py) in 20 mL of CH_2Cl_2 was extracted with a chilled (0 °C) solution of 0.10 M HBF_4 (3 × 10 mL aliquots) and water (10 mL). The solution was dried over anhydrous K_2CO_3 and Na_2SO_4 and then evaporated in vacuo to reduce the volume. Addition of hexane afforded a bronze-colored solid (63 mg, 0.16 mmol) which contained 0.1 equiv of CH_2Cl_2 of crystallization. ^1H NMR (360 MHz, $CDCl_3$): δ 8.0 (s, 2 H), 7.4–7.0 (m, 6 H), 6.6 (t, *J* = 7 Hz, 2 H), 3.9 (m, 2 H), 3.6 (m, 2 H), 3.55 (~t, *J* = 8 Hz, 2 H), 1.3 (m, 2 H), 0.72 (t, *J* = 7 Hz, 3 H), 0.65 (m, 2 H). The ^1H resonances of coordinated pyridine characteristically at δ 8.7 and 7.7 were absent. Similarly (5-hexenyl)Co^{III}(salen)(py) (250 mg, 0.48 mmol) was treated with HBF_4 to give 190 mg (0.46 mmol) of (5-hexenyl)Co^{III}(salen) as a bronze-colored solid. ^1H NMR (90 MHz, $CDCl_3$): δ 7.9 (s, 2 H), 7.4–7.0 (m, 6 H), 6.5 (m, 2 H), 5.5 (m, 1 H), 4.8 (m, 2 H), 4.0–3.6 (m, 4 H), 3.5 (m, 2 H), 1.8 (m, 2 H), 1.4 (m, 2 H), 0.6 (m, 2 H).

Instrumentation. ^1H NMR spectroscopy was performed on either a Nicolet NT-360 or NT-300 or a JEOL FX-90Q spectrometer. UV-vis spectra were recorded on a Hewlett-Packard 8450 diode array spectrometer. Gas chromatography and GC-MS analysis were carried out on a Hewlett-Packard 5890 chromatograph with FID detection and a 12.5-m cross-linked dimethylsilicone capillary column and a Hewlett-Packard 5970 mass spectrometer. The latter allowed the organic products to be characterized by comparison of the mass spectra with those of authentic samples. Bulk electrochemistry was performed on a Princeton Applied Research (PAR) Model 173 potentiostat equipped with a Model 176 current-to-voltage converter which provides feedback compensation for ohmic drop between the working and reference electrodes. The charge passed during prereduction or the oxidatively induced experiments were measured with a PAR Model 179 digital coulometer. The voltage follower amplifier (PAR Model 178) was mounted external to the potentiostat with a minimum length of high-impedance connection to the reference electrode to ensure minimum or low noise pickup. Some of the bulk electrolyses were conducted with a Vacuum Atmosphere glovebox in which the electrodes were connected to the voltage follower amplifier by means of wires running through an Apiezon W wax seal constructed in an air-tight Cajon pipe fitting mounted in a utility port. Coulometry was conducted in a three-compartment cell in which the working and counter electrodes were separated by a Nafion (Du Pont) membrane, and a platinum gauze basket was the working electrode. Cyclic voltammograms were obtained with an IR-compensated potentiostat of local construction, coupled with a PAR Model 175 universal programmer. The electrochemical cell was constructed according to Van Duyne and Reilley.[97] The distance between the platinum working electrode and the salt bridge was <5 mm. The SCE reference electrode was connected through a capacitor to a platinum wire electrode located between the working and counter electrodes to facilitate IR compensation of the ohmic drop in the nonaqueous solutions. All operations and manipulations were conducted under argon or prepurified nitrogen with 0.2 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte in tetrahydrofuran or methylene chloride.

Analysis by Iodinolysis of (Organo)Co^{III} Complexes. The procedure is exemplified by the cleavage of (*n*-butyl)Co^{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 stirring the mixture for 5 min, the solution 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. In each case, the identity of the organic iodide was confirmed by GC-MS analysis and comparison with authentic samples. In order to establish the iodinolysis under rearrangement conditions, 0.0236 mmol of (*n*-butyl)Co^{III}(salen)(py) was treated with 0.0118 (0.5 equiv) of $Fc^+BF_4^-$ in 1.0 mL of CH_2Cl_2 for 120 min under argon. Iodinolysis, followed the GC analysis, indicated the presence of 0.0172 mmol (73%) of *n*-butyl iodide and $<5 \times 10^{-6}$ mmol (<0.2%) of *n*-octane.

Spectral Titration of (Alkyl)cobalt(III) with Donor Ligands. In a typical example, the titration of the base-off form (*n*-butyl)Co^{III}(salen) was conducted by measuring the change in absorbance of the 665-nm band (ϵ 1350 M^{-1} cm^{-1}) upon the incremental addition of pyridine and other donor ligands to a methylene chloride solution containing 0.2 M TBAP. For example, into a 1-mm cuvette was placed 1.0 mL of a 2×10^{-3} M solution of (*n*-butyl)Co^{III}(salen) in methylene chloride. At 665 nm the absorbance (*A*) was 0.281. The addition of 5×10^{-3} mmol (0.404 μL) of pyridine to this solution changed the absorbance to 0.252. Further additions of pyridine gave the following absorbances: [py] = 2×10^{-2} M, *A* = 0.203; [py] = 5×10^{-2} M, *A* = 0.157; [py] = 2×10^{-1} M, *A* = 0.068; [py] = 1.0 M, *A* = 0.014. From these data, the equilibrium constant for the formation of the pyridine adduct was calculated to be $K = 22$ M^{-1}. This value of *K* corresponds to 84% dissociation at 1×10^{-2} M. The formation constants of the adducts from other ligands are listed in Table II.

Oxidative Induced Rearrangement of (5-Hexenyl)Co^{III}(salen)(py). All studies of the rearrangement of (alkyl)cobalt(III) complexes were conducted either in Schlenk vessels under an argon atmosphere using standard benchtop techniques or in air-tight culture tubes fitted with teflon-lined screw caps and prepared in a Vacuum Atmospheres HE-43-2 glovebox equipped with a MO 40-1 gas purifier under dinitrogen or in NMR tubes sealed in vacuo. The experiments were carried out in subdued room or dim red light. The methylene chloride was distilled from P_2O_5 under argon. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon. Pyridine was distilled from CaH_2 and chloroform which was first degassed by several freeze–pump–thaw cycles was then vacuum transferred from P_2O_5. All solvents were either stored in Schlenk vessels under argon or in a glovebox under nitrogen. Three general procedures were developed for the oxidative initiation of hexenyl rearrangement. Typical examples of each are described in the following.

Procedure A. Electrochemical Prereduction and Chemical Oxidation. A typical procedure is described for the evaluation of dihydroanthracene on the hexenyl rearrangement. To a argon-filled electrochemical cell is added 243 mg (0.413 mmol) of (5-hexenyl)Co^{III}(salen)(py) and 1.37 g (4.0 mmol) of TBAP. The cell was evacuated and refilled with argon

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(97) Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142.

3 times, and 20 mL of methylene chloride containing 65.8 mg of undecane was added with the aid of a hypodermic syringe through an air-tight septum. The solution was prereduced at −1.0 V vs. SCE with the current initially at 0.40 mA falling to 0.02 mA after 25 min. The total charged passed of 8 × 10^{-3} mF corresponds to less than 0.5% of the (alkyl)cobalt(III) present. An aliquot (2.5 mL) was withdrawn via a hypodermic syringe and transferred to a septum-capped Schlenk vessel containing 1.36 mg (5 × 10^{-3} mmol) of $Fc^+BF_4^-$ and variable amounts (0–36 mg) of dihydroanthracene under argon. The solution was stirred for 120 min and quenched with 50 mg of iodine. After stirring for 10 min, the solution was extracted with saturated aq $Na_2S_2O_3$ and analyzed by GC–MS. Alternatively, an aliquot was immediately quenched with iodine immediately after prereduction or it was stirred for 120 min without additives before being quenched. The experiment was repeated with different amounts of dihydroanthracene. The results are included in Table V and in Table I, entry 10.

Similar experiments were performed to establish the efficacy of $Co^{III}(salen)(py)_2PF_6$ (Table I, entry 4) and Co^{II}(salen)(py) (entry 5). The effects of different concentrations of $Fc^+BF_4^-$ (entries 6–8) and the effects of pyridine and temperature of the Fc^+-initiated rearrangements are included in entries 9 and 11. In entry 9, 100 equiv of degassed pyridine was added to the sample with the aid of a microsyringe after the prereduced aliquot was added in combination with the oxidant. In entry 11, the prereduced aliquot was added to a mixture of $Fc^+BF_4^-$ and TEMPO.

Independent confirmatory experiments were also carried out by following the spectral changes in the visible region. Thus by monitoring the 620-nm band of 4 × 10^{-3} M ferrocenium tetrafluoroborate in CH_2Cl_2 under an argon atmosphere, we found that Fc^+ is inert to 4 × 10^{-2} M dihydroanthracene and 1 × 10^{-1} M TEMPO over a 3-h period. However, ferrocenium ion does react with 2 M pyridine under the same conditions at a rate which consumes 50% of it within a 30-min period. No absorption band of ferrocene (λ_{max} 440 nm) was seen to be growing in. Moreover, the 665-nm band of 4 × 10^{-3} M (5-hexenyl)Co^{III}(salen)(py) in methylene chloride under argon was monitored and the complex was found to react rapidly with 4 × 10^{-3} M Fc^+. Under these conditions, 50% of the cobalt complex disappeared within less than 1 min, and all of it was consumed in ~30 min. Ferrocene was apparent by the appearance of its 440-nm absorption band. (5-Hexenyl)Co^{III}(salen)(py) is inert to 3 × 10^{-2} M TEMPO under the same conditions over a 1-h period.

Procedure B. Electrochemical Prereduction Followed by Anodic Oxidation. The efficacy of electrochemical oxidation in the initiation of hexenyl rearrangement and the effects of additives were established in the following experiments, the results of which have been presented in Table I, entries 12–16. A solution of 133 mg (0.266 mmol) of (5-hexenyl)Co^{III}(salen)(py)·CH_2Cl_2 and 0.241 mmol of undecane in 12 mL of methylene chloride containing 0.2 M TBAP prepared under nitrogen in a glovebox was prereduced at −0.80 V for 15 min at which time 0.04 C or 2 × 10^{-3} F per mol of cobalt was passed. A 2.0-mL aliquot was withdrawn with the aid of a hypodermic syringe and quenched with 50 mg of iodine. Analysis indicated the presence of 17.8 mM (80%) of 5-hexenyl iodide and 2.0 mM (9%) of cyclopentylmethyl iodide. The remaining solution containing 0.222 mmol of cobalt complex was oxidized at a constant potential of +0.40 V until 1.06 C or 5 × 10^{-2} F per mol of cobalt was passed (~3 min). Portions (2.0 mL) of this solution were withdrawn and added to a vessel containing (a) 1 atm of dioxygen (entry 14), (b) Co^{II}(salen) (1.32 mg, 4.1 × 10^{-3} mmol) (entry 15), and (c) pyridine (147 mg, 1.85 mmol) (entry 16) which were all stirred for 120 min prior to iodinolysis.

Procedure C. Chemical Oxidation without Prereduction. This procedure was used to determine the effects of (a) pyridine and Co^{II}(salen)(py) as additives to the ferrocenium-initiated rearrangement of (5-hexenyl)Co^{III}(salen) described in Figure 2 and Table III, (b) (5-hexenyl)Co^{III}(salen)(py) in Figure 3 and Table IV, and (c) (5-hexenyl)-Co^{III}(saloph) in Table VI. For (a), the reaction vessels containing 16.4 mg (0.040 mmol) of (5-hexenyl)Co^{III}(salen) and 1.1 mg of $Fc^+BF_4^-$ were treated with 2.0 mL of CH_2Cl_2 and variable amounts (0–50 equiv) of pyridine under nitrogen in a glovebox. After stirring the mixture for 120 min, the samples were quenched with 50 mg of iodine and analyzed by gas chromatography using undecane as the internal standard. For (b), to vessels containing 11 mg (0.021 mmol) of (5-hexenyl)Co^{III}(salen)(py) were added 1 mL of CH_2Cl_2 and varying amounts of a stock solution of 0.2005 M $Fc^+BF_4^-$ in CH_2Cl_2. After the mixture was stirred for 60 min, the reactions were quenched with 50 mg of iodine and analyzed. Two sets of identical reactions were also set up, and to these were added 10 and 20 μL (0.5 and 1.0 mol % with respect to cobalt) of a stock solution of 0.1005 M Co^{II}(salen)(py) in CH_2Cl_2. The solution of cobalt(II) was added before the ferrocenium solution. Following reaction for 60 min, the mixture was quenched with iodine and analyzed. For (c), the vessels containing 6.9 mg (0.015 mmol) of freshly purified (5-hexenyl)Co^{III}(saloph) and 0.99 mg of $Fc^+BF_4^-$ (24% with respect to cobalt(III) complex) and 3.5 μL of undecane were dissolved in 0.50 mL of CH_2Cl_2 and stirred for 120 min prior to quenching with iodine.

Since procedures A and B were carried out in the presence of supporting electrolyte (TBAP) whereas procedure C was not, it was necessary to establish that the hexenyl rearrangement was not subject to salt effects in the following way. A pair of identical solutions consisting of 0.020 mmol of (hexenyl)Co^{III}(salen)(py) and 0.0020 mmol (0.10 equiv) of $Fc^+BF_4^-$ were prepared under argon in 1.0 mL of methylene chloride. TBAP (0.2 M) was added only to one reaction mixture, and both reactions were allowed to proceed for 120 min. Iodinolysis followed by the usual workup afforded 0.164 (79%) and 0.003 38 (16%) mmol of cyclopentylmethyl and 5-hexenyl iodide, respectively, in the reaction without TBAP and 0.0141 (70%) and 0.0512 mmol (25%), respectively, in the reaction with TBAP. Within experimental uncertainty, the results are the same.

Oxidative Rearrangement of (Hexenyl)$Co^{III}(dmgH)_2$(py). Attempts to effect the rearrangement of (5-hexenyl)$Co^{III}(dmgH)_2$(py) by electrochemical and chemical methods of initiation are described as follows. (5-Hexenyl)$Co^{III}(dmgH)_2$(py) 47.1 mg (0.104 mmol) was placed in an electrochemical cell which was flushed with argon, and 20 mL of air-free CH_2Cl_2 containing 0.2 M TBAP was added in the dark. A constant anodic current (2.5 mA) was passed for 16.1 min [which corresponds to 0.25 F per mol of cobalt(III)], during which time the potential at the anode increased from 0.746 to 0.760 V vs. SCE. The current was interrupted and solution was stirred for an additional 45 min. The cell was then exposed to air and the contents were washed with CH_2Cl_2 into a volumetric flash and the solution diluted to 25 mL. A 5.0-mL aliquot was concentrated to ~2 mL with a stream of argon; iodinolysis followed by extraction with $Na_2S_2O_3$ and addition of internal standard (1-bromohexane, 0.0282 mmol) yielded a solution which upon gas chromatographic analysis indicated the presence of 0.0149 mmol (71% recovery) of 5-hexenyl iodide. No cyclopentylmethyl iodide was detected. TLC analysis of another aliquot on silica gel with 2% pyridine in CH_2Cl_2 showed a yellow spot (R_f 0) which could be either a cobalt(II) or a cobalt(III) salt. Most of the material (R_f 0.5) was assigned to (5-hexenyl)$Co^{III}(dmgH)_2$(py).

Alternatively, a Schlenk vessel containing 49.1 mg (0.109 mmol) of (5-hexenyl)$Co^{III}(dmgH)_2$(py) and 6.36 mg (0.0233 mmol) of $Fc^+BF_4^-$ was flushed with argon and 20 mL of air-free CH_2Cl_2 was added in the dark. The mixture was stirred for 45 min under argon, opened to air, and transferred quantitatively to a 25-mL volumetric flask. A 5.0-mL aliquot was cleaved with iodine and analysis indicated the presence of 0.0211 mmol (97% recovery) of 5-hexenyl iodide without detectable amounts of cyclopentylmethyl iodide. A similar result was obtained by direct ^1H NMR analysis of the reaction mixture using *p*-dimethoxybenzene as the internal standard.

Intermolecular Alkyl Exchange and Rearrangement of (Hexenyl)cobalt(III) Complexes. The rearrangement of (5-hexenyl)Co^{III}(7,7′-Ph_2salen)(py) (IX) was carried out as follows. In a glovebox, a sample of IX (13 mg, 0.02 mmol) was dissolved in 0.95 mL of $CDCl_3$ directly in a NMR tube and 50 μL of a stock solution of 0.02 M $Fc^+BF_4^-$ in $CDCl_3$ added. The tube was sealed with a rubber septum. After 4 h at 23 °C, the resonance at δ 3.72 of IX was completely replaced by the resonance at δ 3.62 for the cyclopentylmethyl isomer. (No vinyl resonances were visible.) The spectral lines were broadened by paramagnetic impurities, and ferrocene (δ 4.15) was apparent. Iodine (25 mg) was added to the tube, and the doublet resonance at δ 3.2 (*J* = 7 Hz) for cyclopentylmethyl iodide was identified and cnfirmed by GC-MS analysis. Repetition of the experiment with the deuteriated analogue XII showed the appearance of the same resonance at δ 3.62 without an additional resonance at δ 3.72 which would have arisen if deuterium scrambling had occurred in the unrearranged XII.

Alkyl exchange studies were conducted as follows. Chloroform-*d* (1 mL) was degassed by a freeze–pump–thaw cycle and then vacuum transferred from P_2O_5 into a vacuum storage vessel containing 7.3 μL (0.09 mmol) of distilled pyridine. The vessel was thoroughly degassed by several freeze–pump–thaw cycles and then transferred into a NMR tube containing 14.4 mg (0.032 mmol) of freshly purified (hexenyl)-Co^{III}(saloph) (IX) and 19.0 mg (0.030 mmol) of (α,α-dideuterio-5-hexenyl)Co^{III}(7,7′-Ph_2salen) (XII) and 3.1 mg (0.011 mmol) of $Fc^+BF_4^-$. To begin reaction, the tube was thawed to allow the contents to mix, and the ^1H NMR spectrum was recorded at 500-s intervals over a period of an hour. At this point, the apparent ratio of ^1H resonances at δ 3.53 and 3.45 was ~2.5 and the resonance at 3.62 had grown at a comparable rate. Throughout this period, a new resonance at δ 3.71 (t, *J* = 8 Hz) grew in together with those of the rearranged products. The limiting ratio of the resonances at δ 3.53 and 3.71 was 2.4. Line broadening and the appearance of the ferrocene resonance were also noted. In the control experiment, a mixture (α,α-dideuteriohexenyl)Co^{III}(7,7′-Ph_2salen)(py)

Table VII. Ligand Rearrangement of (Cyclopropylcarbinyl)Co^{III}(salen)(py)

prep[a]	solvent	t,[b] min	rearrangement,[c] P, %	$\tau_{1/2}$,[d] min
V	$CDCl_3(Me_4Si)$[e]	7–15	57	15
		20–40	72	
V	py-d_5 (2 M)[f]	7–15	24	40
		20–40	47	
V	py-d_5 (12.5 M)[g]	2–10	11	
		20–40	11	
		7 days	~50	
A	$CDCl_3(Me_4Si)$[e]	5–15	24	40
		20–40	46	

[a] Method of preparation: V = in vacuo at 0.01 mmHg. A = air. [b] Acquisition time, see text. [c] Rearrangement to butenyl isomer, see text. [d] Approximate. [e] Containing tetramethylsilane as internal standard. [f] In $CDCl_3(Me_3Si)$. [g] Neat solvent.

(XII) and (hexenyl)Co^{III}(saloph) (IX) was allowed to interact without added ferrocenium ion, and very little scrambling or rearrangement was observed. Thus after 1 h, the apparent ratio of the ^{1}H resonances at δ 3.45 and 3.53 was only 0.13 and that at δ 3.72 and 3.53 was only 0.09. The resonance at δ 3.62 due to the rearranged cyclopentylmethyl derivatives of Co^{III}(Ph$_2$salen) was too small to integrate precisely. No line broadening was observed in these ^{1}H NMR spectra.

Redox Transfer between (Alkyl)cobalt(III) and Cobalt(II) Complexes. A mixture of 6.7 mg (0.015 mmol) of (hexenyl)Co^{III}(saloph) and 1.4 mg (0.003 mmol) of Co^{II}(Ph$_2$salen) in 0.50 mL of chloroform was treated with 3.6 μL (0.045 mmol) of pyridine under a dinitrogen atmosphere. Inspection of the ^{1}H NMR spectrum after 15 min showed the ratio of the resonance at δ 3.53 to that at 3.72 to be 0.12. However, no resonance at either δ 3.45 or 3.62 due to cyclopentylmethyl derivatives was discovered even after 4 h at 22 °C. Similarly, a mixture of 9.6 mg (0.015 mmol) of (hexenyl)Co^{III}(Ph$_2$salen) and 1.0 mg (0.0027 mmol) of Co^{II}(saloph) in 0.5 mL of chloroform was treated with 0.045 mmol of pyridine. The ratio of the resonance δ 3.53 to that at 3.72 was 0.18 after 15 min. Again no rearrangement was indicated by the absence of new resonances at either δ 3.45 or 3.62.

Thermolysis of (Hexenyl)Co^{III}(saloph). Pyridine-d_5 (Merck, 0.5 mL) over neutral alumina (Woelm, activity I) was degassed on a high-vacuum manifold and thence vacuum transferred to a NMR tube containing 11.5 mg (0.025 mmol) of (5-hexenyl)Co^{III}(saloph) (IX) and 1 μL of 2,4-dichlorotoluene as internal standard. After sealing in vacuo, the tube was heated to 70 °C. The ^{1}H NMR spectrum of the solution showed the vinyl resonance at δ 4.9 to disappear relative to the internal standard at δ 2.30—the ratio decreasing from 13.8 to 8.0 over a course of 25 min. A rate constant of 1×10^{-4} s^{-1} (correlation coefficient ($\gamma^2 = 0.95$) was evaluated on the basis of the first-order behavior. After 7 h, the vinyl resonance δ 4.9 (t, J = 8.3 Hz) had completely disappeared. Furthermore the triplet α-methylene resonance at δ 4.2 (J = 8.3 Hz) was replaced by a doublet resonance at δ 4.3 (J = 5.3 Hz), which we assign to that of the cyclopentylmethyl derivative in pyridine-d_5.

Ligand Rearrangement of (Cyclopropylcarbinyl)Co^{III}(salen)(py). Separate solutions of 22.2 mg (0.048 mmol) of (cyclopropylcarbinyl)-Co^{III}(salen)(py) (IV) in 0.7 mL of an appropriate solvent were prepared in several different ways. Some solutions were prepared under rigorous conditions in vacuo by transferring the solvent (which was degassed by several freeze–pump–thaw cycles) directly into an NMR tube containing IV at 77 K, and the tube sealed and stored at this temperature until used. Another solution was prepared in air by dissolving IV in chloroform-d_1 immediately prior to recording its ^{1}H NMR spectrum. The results presented in Table VII refer to acquisition periods t after dissolution. The rearrangement P (%) refers to the total (alkyl)cobalt(III) visible which is due to the rearranged butenyl isomer, as determined by integration of the cyclopropyl resonance at δ 0.2 (m, 4 H) relative to that of the internal standard.

The kinetics of the cyclopropylcarbinyl rearrangement was examined in a system consisting of 9.2 mg (0.02 mmol) of IV to which 1.0 mL of chloroform-d_1 was vacuum-transferred (from P_2O_5) under rigorous air-free conditions at 77 °C. The NMR tubes also contained 2 μL each of dichloromethane and tetramethylsilane as internal standards. The rate of the cyclopropylcarbinyl to butenyl conversion was determined by integrating the ^{1}H resonances of the cyclopropyl group at δ 0.2 relative to that of tetramethylsilane with time. The disappearance followed first-order kinetics with an apparent rate constant of $k_1 = 6.9 \times 10^{-4}$ s^{-1} (correlation coefficient $\gamma^2 = 0.99$, $\tau_{1/2} = 16.9$ min.)

When the experiment was repeated with 15.6 mg (5 equiv) of added TEMPO, broad lines were observed in the ^{1}H NMR spectrum, but no resonances due to the butenyl isomer was observed. Despite the limited quality of the data, the rate was estimated as $k_1 \cong 1 \times 10^{-4}$ s^{-1} ($\tau_{1/2} \sim$ 130 min) which is only a factor of about 6 slower than that observed without the nitroxide trap.

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Registry No. py, 110-86-1; DHA, 613-31-0; TEMPO, 2564-83-2; Co^{II}(salen), 14167-18-1; (5-hexenyl)Co^{III}(salen)(py), 101859-88-5; (cyclopentylmethyl)Co^{III}(salen)(py), 101859-89-6; (5-hexenyl)Co^{III}(7,7′-Ph$_2$salen)(py), 102920-62-7; Co^{II}(7,7′-Ph$_2$salen), 102920-63-8; (5-hexenyl)Co^{III}(saloph), 102920-64-9; Co^{II}(saloph), 39836-45-8; (5-(hexenyl-α,α-d_2)Co^{III}(7,7′-Ph$_2$salen)(py), 102920-65-0; (5-hexenyl)Co^{III}-(dmgH)$_2$(py), 42568-40-1; ClCo^{III}(dmgH)$_2$(py), 23295-32-1; (cyclopropylcarbinyl)Co^{III}(salen)(py), 102920-66-1; (3-butenyl)Co^{III}(salen), 102920-67-2; (5-hexenyl)Co^{III}(saloph), 102920-68-3; (n-butyl)Co^{III}-(salen)(py), 15608-77-2; (n-butyl)Co^{III}(salen), 39043-95-3; (5-hexenyl)Co^{III}(salen), 102920-69-4; n-BuCo^{III}(salen)(Im), 102920-70-7; n-BuCo^{III}(salen)(quinuclidine), 102920-71-8; $Fc^+BF_4^-$, 1282-37-7; O_2, 7782-44-7; 1-bromo-5-hexene, 2695-47-8; 5-hexen-1-ol, 821-41-0; 1-iodo-5-hexene, 18922-04-8; bromomethylcyclopentane, 3814-30-0; cyclopentaneacetic acid, 1123-00-8; cyclopentylmethanol, 3637-61-4; iodomethylcyclopropane, 27935-87-1; 1-bromo-*1,1*-d_2-hex-5-ene, 102853-21-4; 5-hexenoic acid, 1577-22-6; 1-iodobut-3-ene, 7766-51-0; 3-buten-1-ol, 627-27-0; cyclopropylmethyl iodide, 33574-02-6; cyclopropylmethyl tosylate, 1015-45-8.