2.5 (m, 1 H), 1.8 (m, 5 H), 1.4 (m, 5 H), 1.0 (m, 3 H). Anal. Calcd for $C_{10}H_{16}N_2Br$: Br, 30.05. Found: Br, 30.28.

Cyclization of 3a. Dehydrobromination of 11.4 g (46.9 mmol) of **3a** with 5.7 g (56.3 mmol) of triethylamine in 20 mL of dichloromethane gave after workup and distillation (Kugelrohr apparatus, 0.02 mbar) 7.1 g (93%) of 2,3-dimethyl-2-propylcyclopropane-1,1-dicarbonitrile: ^{1}H NMR δ 1.6, 1.5, 1.35 (3 m). Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.04; H, 8.70; N, 17.27. Found: C, 73.87; H, 8.70; N, 17.11.

Addition of BMN to 3-Chloro-2-methylpropene (8). Irradiation of 7.25 g (50 mmol) of BMN and 4.34 g (48 mmol) of 8 in 60 mL of dichloromethane for 24 h gave after workup 9.94 g (88%) of 3-bromo-4-chloro-3-methylbutane-1,1-dicarbonitrile (**8a**): ^{1}H NMR δ 4.27 (t, J = 7 Hz, 1 H), 3.97 (s, 2 H), 2.68 (d, J = 7 Hz, 2 H), 1.97 (s, 3 H).

Cyclization of 8a. Dehydrobromination of 4.9 g (20.8 mmol) of **8a** with 2.11 g (23.7 mmol) of triethylamine in 10 mL of dichloromethane gave after workup and distillation 2.95 g (91%) of 2-(chloromethyl)-2-methylcyclopropane-1,1-dicarbonitrile: bp 110 °C (0.2 mbar); ^{1}H NMR δ 3.76, 3.59 (dd, J = 12 Hz, 2 H), 1.88 (s, 2 H), 1.62 (s, 3 H); IR (film) 2245 cm^{-1} (CN). Anal. Calcd for $C_7H_7N_2Cl$: C, 54.38; H, 4.56; N, 18.12; Cl, 22.93. Found: C, 54.34; H, 4.58; N, 18.07; Cl, 23.04.

Addition of BMN to 2,3-Dimethyl-2-hexene (9). Irradiation of 3.5 g (24.1 mmol) of BMN and 1.2 g (10.7 mmol) of **9** in 35 mL of dichloromethane for 3 h gave after workup 2.6 g (94%) of addition product as a 1:1 mixture of regioisomers 3-bromo-2,2,3-trimethylhexane-1,1-dicarbonitrile (**9a**) and 2-(1-bromo-1-methylethyl)-2-methylpentane-1,1-dicarbonitrile (**9b**): ^{1}H NMR δ 4.51 (s, 1 H), 4.4 (s, 1 H), 1.92, 1.86, 1.76 (3 s, 9 H), 1.70 (m, 4 H), 1.45 (m, 4 H), 1.43 (s, 9 H), 1.01 (m, 6 H).

Cyclization of 9a/b. Dehydrobromination of a mixture of 2.6 g (10.1 mmol) of **9a** and **9b** with 1.2 g (11.8 mmol) of triethylamine in 20 mL of dichloromethane gave after workup quantitatively 2,2,3-trimethyl-3-propyl-cyclopropane-1,1-dicarbonitrile: mp 66 °C (benzene); ^{1}H NMR δ 1.58, 1.51, 1.40, 1.36, 1.33 (2 m, 3 s, total 13 H), 1.01 (m, 3 H). Anal. Calcd for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.90. Found: C, 74.95; H, 9.05; N, 15.85.

2-(Chloromethyl)cyclopropane-1,1-dicarbonitrile. Irradiation of 7.25 g (50 mmol) of BMN and 3.93 (50 mmol) of allyl chloride in 60 mL of dichloromethane for 3 days at 28 °C yielded after workup 8.52 g (77%) of the crude addition product, which after dehydrobromination with 4.9 g (55 mmol) of triethylamine in 10 mL of dichloromethane and distillation yielded 4.3 g (60%) of 2-(chloromethyl)cyclopropane-1,1-dicarbonitrile: bp 136 °C (2 mbar); ^{1}H NMR δ 1.67-2.78 (m, 3 H, cyclopropane H), 3.38-4.06 (m, AB part of ABX spectrum, J_{AB} = 12.5 Hz, 2 H, CH_2Cl); IR (film) 2240 cm^{-1} (CN). Anal. Calcd. for $C_6H_5N_2Cl$: C, 51.26; H, 3.59; N, 19.93; Cl, 25.22. Found: C, 51.25; H, 3.64; N, 19.79; Cl, 25.05.

A fraction with a bp 76 °C (2 mbar) was identified as 1-chloro-2,3-dibromopropane (0.6 g, 5%).

Addition of BMN to 2-Methyl-3-methoxypropene. Irradiation of 4.34 g (29.9 mmol) of BMN and 2.57 g (29.9 mmol) of 2-methyl-3-methoxypropene in 60 mL of dichloromethane for 24 h at 28 °C yielded after workup 6.4 g (93%) of 3-methyl-4-methoxy-3-bromobutane-1,1-dicarbonitrile: ^{1}H NMR δ 1.87 (s, 3 H, CH_3), 2.47 and 2.73 (2 m, AB part of ABX spectrum, J_{AB} = 15 Hz, 2 H, CH_2), 3.43 (s, 3 H, OCH_3), 3.62 (dd, AB spectrum, J_{AB} = 10 Hz, CH_2O), 4.30 (t, X part of ABX spectrum, $J_{AB} = J_{BX}$ = 6 Hz, 1 H, $CH(CN)_2$).

Cyclization of the Addition Product. The addition product (4.4 g, 19.1 mmol) yielded on dehydrobromination with 2.01 g (22.6 mmol) of triethylamine in 10 mL of dichloromethane 2.5 g (81%) of 2-methyl-2-(methoxymethyl)-cyclopropane-1,1-dicarbonitrile: bp 55-57 °C (0.01 mbar); ^{1}H NMR δ 1.46 (s, 3 H, CH_3), 1.65 and 1.87 (dd, AB spectrum, J_{AB} = 6 Hz, 2 H, cyclopropane H), 3.34 and 3.60 (dd, AB spectrum, J_{AB} = 11 Hz, 3 H, CH_2O), 3.83 (s, 3 H, OCH_3); IR (film) 2240 cm^{-1} (CN). Anal. Calcd for $C_8H_{10}N_2O$: C, 64.01; H, 6.67; N, 18.67; O, 10.66. Found: C, 64.17; H, 6.70; N, 18.74; O, 10.81.

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Registry No. 1, 513-81-5; 2, 763-29-1; 3, 17618-77-8; **3a**, 105694-96-0; 4, 2738-19-4; **4a**, 105694-94-8; 5, 109-67-1; (*E*)-6, 4050-45-7; (*Z*)-6, 7688-21-3; (*Z*)-7, 627-20-3; 8, 563-47-3; **8a**, 105694-98-2; 9, 7145-20-2; **9a**, 105695-00-9; **9b**, 105695-01-0; (*Z*)-10, 691-38-3; (*Z*)-11, 762-63-0; BMN, 1885-22-9; DCM, 58821-77-5; H_2C=$CHCH_2Cl$, 107-05-1; $BrCH_2CHBrCH_2Cl$, 96-12-8; H_2C=$C(CH_3)CH_2OCH_3$, 22418-49-1; $H_3COCH_2C(Br)(CH_3)CH_2CH(CN)_2$, 105695-04-3; 2,2-dimethyl-3-propylcyclopropane-1,1-dicarbonitrile, 105694-95-9; 2,3-dimethyl-2-propylcyclopropane-1,1-dicarbonitrile, 105694-97-1; 2-(chloromethyl)-2-methylcyclopropane-1,1-dicarbonitrile, 105694-99-3; 2,2,3-trimethyl-3-propylcyclopropane-1,1-dicarbonitrile, 105695-02-1; 2-(chloromethyl)cyclopropane-1,1-dicarbonitrile, 105695-03-2; 2-methyl-2-(methoxymethyl)cyclopropanedicarbonitrile, 105695-05-4.

New Synthetic Methods via Free Radicals. Free-Radical Generation via Photolytic Homolysis of Alkyl-Cobaloxime C-Co Bonds. Efficient Radical Trapping with Useful Functional Groups

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Visible-light photolyses of primary and secondary (pyridine)alkylcobalt(III) cobaloximes, R-$Co^{III}(dmgH)_2py$ (**2-7**), generate free radicals that can be trapped in good to excellent yield (75% to nearly quantitative) with radical-trapping agents PhSSPh (to produce R-SPh), PhSeSePh (to produce R-SePh), or $BrCCl_3$ (to produce R-Br). Studies with CH_2=$CH(CH_2)_4$-$Co^{III}(dmgH)_2py$ (**6**) demonstrate that a 5-hexenyl intramolecular radical-olefin cyclization can intervene between radical generation and radical trapping. At the dilute concentrations required to suppress premature radical trapping prior to 5-hexenyl cyclization, competing side reactions limit the yields of cyclized, trapped product to about 60%. Studies of *n*-decyl-$Co^{III}(dmgH)_2py$ (**2**) and *n*-pentyl-$Co^{III}(dmgH)_2py$ (**9**) photolyses in the presence of PhSSPh at various concentrations demonstrate that β-hydride elimination (4%) was the major side reaction at high concentrations (18-22 mM) and that at low concentrations (1 mM) β-hydride elimination (17-31%) and as yet uncharacterized radical-cobaloxime ligand reactions (14-26%) were the major side reactions.

Organic synthesis is the focus of a recent renaissance of radical chemistry.[1] To realize the full potential of radical-mediated organic synthesis, new methods are still needed to generate free radicals and exploit them in syn-

0022-3263/87/1952-0212$01.50/0

Scheme I. Standard Synthesis of Alkyl Cobaloximes

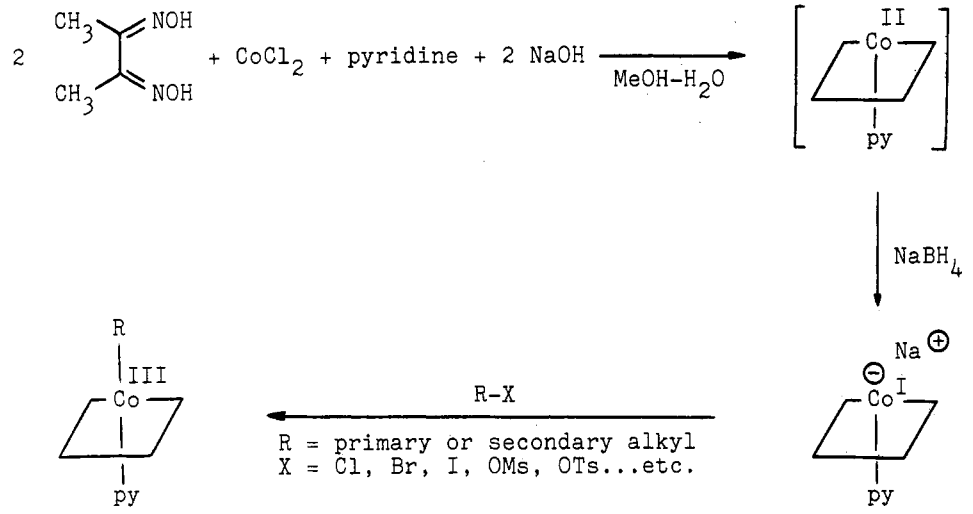


Table I. Representative Trapping Reactions of Alkyl Radicals (R•) Generated from R–$Co^{III}(dmgH)_2py$ Photolysis[a]

R–$Co^{III}(dmgH)_2py$ [mM]	radical trap [mM]	time, min	% yield[b,c]
2 [9.9]	PhSSPh [14.8]	180	82
2 [4.9]	PhSeSePh [5.9]	60	95
2 [9.9]	$BrCCl_3$ [10.2]	165	97
3 [10.6]	PhSSPh [12.7]	360	92
3 [5.3]	PhSeSePh [6.4]	90	96
3 [10.6]	$BrCCl_3$ [76.0]	165	75
4 [4.7]	PhSSPh [5.6]	30	46
4 [4.7]	PhSeSePh [5.6]	15	98
4 [4.7]	$BrCCl_3$ [51.0]	120	ca. 100
5 [5.6]	PhSSPh [6.7]	30	73
5 [5.6]	PhSeSePh [6.7]	30	81

[a] All reactions were performed in benzene saturated with deoxygenated nitrogen. [b] Yields of radical-trapped products; R–SPh from PhSSPh, R–SePh from PhSeSePh, or R–Br from $BrCCl_3$. [c] Yields were determined by ^1H NMR integration vs. Ph_3CH added as an internal standard immediately prior to ^1H NMR of total reaction product.

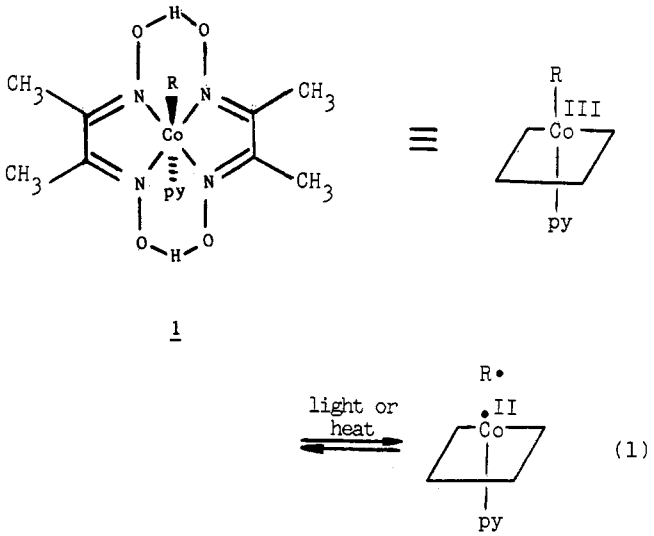
Table II. Concentration Dependence of Uncyclized 7 vs. Cyclized 8 in 5-Hexenyl Radical–Olefin Cyclizations from Photolysis of $CH_2{=}CH(CH_2)_4$–$Co^{III}(dmgH)_2py$ (6) + PhSSPh (eq 2)[a]

concn 6, mM	concn PhSSPh, mM	% yield[b] 7	8	total % yield [7 + 8]	8:7 ratio
20.0	20.0	52	34	86	0.65
15.0	21.1	39	39	78	1.00
6.5	8.9	25	43	68	1.72
1.0	1.1	5	61	66	12.2

[a] All reactions were performed in benzene saturated with deoxygenated argon. [b] Yields were determined by ^1H NMR integration vs. Ph_3CH added as an internal standard immediately prior to ^1H NMR of total reaction product.

thetically useful ways.

(Pyridine)alkylcobalt(III) cobaloximes [1 = R–Co^{III}(dmgH)$_2$py; dmgH = dimethylglyoxime monoanion) should be nearly ideal free-radical precursors for use in organic synthesis, reversibly generating R· + $Co^{II}(dmgH)_2py$ upon photolysis with visible light (eq 1).[2] R–$Co^{III}(dmgH)_2py$



(R = primary or secondary alkyl) can be prepared easily in high yields from the corresponding alkyl halides or sulfonate esters + in situ generated $Co^I(dmgH)_2py$ "supernucleophile" anion (Scheme I).[3] Orange crystalline R–$Co^{III}(dmgH)_2py$ can be handled as common organic

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reagents or synthetic intermediates; for example, they are stable to storage at room temperature in foil-wrapped vials under Ar, to weighing in air under room light, to silica gel TLC, and to silica gel flash chromatography. $Co^{I}(dmgH)_2py$ supernucleophile anion can be inexpensively prepared for about \$50/mol, approximately one-tenth the price for commercially available n-Bu_3SnH, the least expensive reagent for triorganotin radical chemistry.[1]

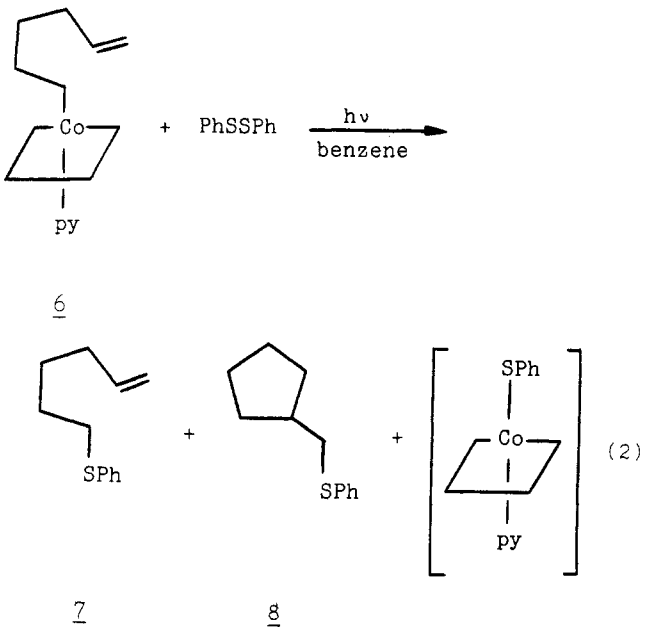
Results and Discussion

When our studies were initiated, it was known that R· generated from photolysis of $R-Co^{III}(dmgH)_2py$ could be trapped with PhSSPh (to generate R–SPh) or PhSeSePh (to generate R–SePh),[4] but it was unclear how general such reactions were or how well the reactions might be optimized for efficient trapping of R· in competition with other reactions of R· (vide infra).

High-Yielding Radical-Trapping Reactions from Photolyses of $R-Co^{III}(dmgH)_2py$ + Radical Traps at High Reactant Concentrations. We have found that under the appropriate conditions (Table I) anaerobic photolyses of benzene solutions of representative $R-Co^{III}(dmgH)_2py$ [**2**, R = $CH_2(CH_2)_8CH_3$; **3**, R = CH_2CH_2Ph; **4**, R = $CH(CH_3)(CH_2)_8CH_3$; **5**, R = $\overline{CH(CH_2)_4CH_2}$] efficiently generated free radicals that were trapped in high yields within a few hours at room temperature using PhSSPh (to generate R–SPh), PhSeSePh (to generate R–SePh), or $BrCCl_3$ (to generate R–Br). All photolyses in Table I and in the rest of this paper were easily performed by standard bench top or fume hood inert-atmosphere techniques in Pyrex tubes with 300- or 500-W incandescent light bulbs as visible light sources (visible light of 400–450 nm is known to cause $R-Co^{III}(dmgH)_2py$ C–Co homolysis).[5] The key to the success of the high-yielding reactions of Table I is the use of sufficiently high concentrations of $R-Co^{III}(dmgH)_2py$ and radical-trapping agent to make radical trapping the dominant pathway, thereby suppressing other potentially competitive side reactions (vide infra).

Application to Radical–Olefin Cyclization. Radical–olefin cyclizations have been extensively studied in triorganotin chemistry, particularly n-Bu_3SnH radical chain reductions of "5-hexenyl" halides, xanthates, and related functional groups.[1] Radical–olefin cyclizations via $R-Co^{III}(dmgH)_2py$ (eq 2) are fundamentally different in that overall radical generation and then radical trapping is a nonchain process, in principle more versatile since various radical traps can functionalize the transient radicals without the necessity of concomitantly perpetuating a radical chain.[6] The stoichiometric use of the cobaloxime ligand in a preformed metal–alkyl complex is not a disadvantage since even triorganotin radical chain reactions, catalytic in radical initiator, consume a full 1 equiv of n-Bu_3SnH or other triorganotin reagent, and, as already mentioned, $R-Co^{III}(dmgH)py$ chemistry can be performed at approximately one-tenth the cost per mole of triorganotin chemistry using Bu_3SnH.

As the results in Table II for the anaerobic photolysis of benzene solutions of $CH_2{=}CHCH_2CH_2CH_2CH_2{-}Co^{III}(dmgH)_2py$ (**6**) + PhSSPh demonstrate, a 5-hexenyl radical–olefin cyclization can intervene between radical generation and radical trapping, low substrate concentrations favoring the formation of cyclized **8** over uncyclized **7**, as expected for competition between premature bimolecular trapping of $CH_2{=}CHCH_2CH_2CH_2CH_2{\cdot}$ + PhSSPh, leading to **7**, and unimolecular cyclization of $CH_2{=}CHCH_2CH_2CH_2CH_2{\cdot}$, leading to **8** after PhSSPh trapping of the cyclized radical.



Quantitation of Side Reactions under Low Substrate Concentration (5-Hexenyl Cyclization) Conditions. The increased yield of cyclized **8** at low substrate concentrations, from 34% at 20 mM to 61% at 1 mM, is accompanied by a 20% drop in total yield of radical-trapped products (**7** + **8**), from 86% at 20 mM to 66% at 1 mM. The drop in total yield of radical-trapped products might be accounted for by side reactions such as (1) combination of two R· to form R–R and concomitant disproportionation of two R· to form R–H + R· minus H (i.e., an olefin),[7] (2) β H atom elimination between R· and $Co^{II}(dmgH)_2py$ to form an olefin + $H-Co^{III}(dmgH)_2py$, (3) reactions of R· with impurities in the solvent (including oxygen),[8] and (4) reactions of R· with the cobaloxime ligand.

Attempts to quantitate side reactions by capillary GC for photolyses of **6** + PhSSPh failed because it was not possible to resolve some of the most important potential byproducts, cyclized and uncyclized alkenes and alkanes, from the enormous benzene solvent peak when dilute benzene reaction solutions were injected directly onto the GC. n-Pentyl-$Co^{III}(dmgH)_2py$ (**9**) and n-decyl-$Co^{III}(dmgH)_2py$ (**2**) were chosen for quantitative GC product studies because potential alkane and alkene byproducts could be resolved from the benzene solvent peak even when dilute reaction solutions were injected directly onto the gas chromatograph. It was first necessary to determine with **2** and **9** whether the concentration dependence of yields was a general feature of radical trapping in $R-Co^{III}(dmgH)_2py$ photolyses. In a series of photolyses run at high concentrations in deoxygenated Ar-saturated benzene, 20 mM PhSSPh + 20 mM **6** produced **7** + **8** in

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(7) Gibian, M. J.; Corley, R. C. *Chem. Rev.* **1973**, *73*, 441.

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Table III. Capillary GC Quantitation of Products from Photolyses of R–$Co^{III}(dmgH)_2py$ (2, R = *n*-decyl; 9, R = *n*-pentyl) + PhSSPh at High and Low Concentrations[a]

R–$Co^{III}(dmgH)_2py$ [mM]	concn PhSSPh, mM	% yield				
		R–SPh[b,c]	alkene[b,d]	alkane[b,e]	R–R dimer[b,f]	total product[b,g]
2 [16.8]	17.8	90	4	<1		95
2 [1.0]	1.0	62	17	7		86
9 [10.6]	21.8	85	4	3	0	92
9 [1.0]	1.1	35	26	13	0	74
9 [1.0]	1.1	44	20	10	0	74
9 [1.0]	1.1	38	24	14	0	76
9 [1.0]	1.1	38	31	18	0	87
9 [1.0]	1.1	37	27	13	0	77

[a] All reactions were run in benzene saturated with deoxygenated argon. [b] All yields were determined by capillary gas chromatography. [c] $PhS(CH_2)_9CH_3$ from 2 and $PhS(CH_2)_4CH_3$ from 9. [d] $CH_2{=}CH(CH_2)_7CH_3$ from 2 and $CH_2{=}CH(CH_2)_2CH_3$ from 9. [e] $CH_3(CH_2)_8CH_3$ from 2 and $CH_3(CH_2)_3CH_3$ from 9. [f] $CH_3(CH_2)_{18}CH_3$ from 2 (not determined) and $CH_3(CH_2)_8CH_3$ from 9 (not detected at all). [g] R–SPh + alkene + alkane percent yields.

86% total yield (Table II), 20 mM PhSSPh + 20 mM 2 produced *n*-decyl–SPh in 79% yield (Table III), and 15.6 mM PhSSPh + 13.9 mM 9 produced *n*-pentyl–SPh in 87% yield (Table III). In a series of photolyses run at low concentrations in deoxygenated Ar-saturated benzene, 1.1 mM PhSSPh + 1.0 mM 6 produced 7 + 8 in 66% total yield (Table II), 1.1 mM PhSSPh + 1.0 mM 2 produced *n*-decyl–SPh in 62% yield (Table III), and 1.1 mM PhSSPh + 1.0 mM 9 produced *n*-pentyl-SPh in 35%, 38%, and 44% yields in three separate runs (Table III).

To address the radical–radical combination/disproportionation question (potential side reaction 1), the photolysis of 9 + PhSSPh was studied, with capillary GC analysis for the production of *n*-pentane, 1-pentene, and *n*-decane. If radical–radical combination/disproportionation were occurring, 1-pentene and *n*-pentane would be produced in equal amounts by radical–radical disproportionation and *n*-decane would be produced by radical–radical combination in several-fold excess over 1-pentene or *n*-pentane, since the combination/disproportionation ratio of free alkyl radicals in solution generally favors combination over disproportionation several-fold.[7] When 1.0 mM 9 + 1.1 mM PhSSPh in benzene were photolyzed under standard low-concentration radical-trapping conditions, no detectable amounts of *n*-decane were formed in several reproducible experiments (Table III). The absence of *n*-decane demonstrates that radical–radical combination is not occurring, and since radical–radical disproportionation inevitably accompanies radical–radical combination,[7] radical–radical disproportionation can also be eliminated as a side reaction of any significance.

Since 1-pentene production from photolysis of 9 + PhSSPh is clearly not due to radical–radical disproportionation, it seems safe to conclude that olefins are produced (1-pentene from 9 and 1-decene from 2) by β H atom elimination between R· and $Co^{II}(dmgH)_2py$ (potential side reaction 2). As summarized in Table III, β-hydride elimination was found to be a minor side reaction (4%) under the high-concentration conditions that lead to high yields of radical-trapped products, and it was found to be a major side reaction (17–31%) under the low concentration conditions (5-hexenyl cyclization conditions) that lead to lower yields of radical-trapped products.[9]

In the experiments summarized in Table III, alkane production (*n*-pentane from 9 and *n*-decane from 2) was reproducibly low (1–3%) at high substrate concentrations and reproducibly significant (7–18%) at low substrate concentrations. Since radical–radical disproportionation is not occurring, there must be a source of H atoms in the system other than via radical–radical disproportionation. It is unclear from the set of experiments summarized in Table III what the source of H atoms leading to alkane production is.

One possible source of H atoms could be reactions with the solvent, either the solvent molecules themselves or trace impurities in the solvent. A survey of the solvent dependence of the yield of 8 from photolysis of 1 mM 6 + 1 mM PhSSPh at low concentrations (5-hexenyl cyclization conditions) showed that many solvents (or solvent impurities) react with the radicals, resulting in significantly lowered yields of radical-trapped cyclized 8: nitromethane (22%), acetonitrile (23%), tetrahydrofuran (28%), acetone (38%), diethyl ether (44%), *tert*-butyl alcohol (44%), *p*-dioxane (45%). In several solvents the yield of cyclized 8 was similar to that in benzene (61%): ethanol (57%), methanol (62%), and *tert*-butyl methyl ether (65%). Since all of these best solvents gave similar yields of 8, it is likely that the lowered yield of radical-trapped products under dilute conditions in these solvents is an intrinsic feature of R–$Co^{III}(dmgH)_2py$ chemistry and is not due to competing side reactions with the solvent or impurities in the solvent.

Under even the best conditions, anaerobic atmospheres and deoxygenated solvents still contain traces of O_2 contamination. Although the Ar or N_2 gases used in all of these studies were catalytically deoxygenated (over hot BASF catalyst R3-11) immediately prior to use, it was possible that in dilute solution the amount of O_2 contamination might become significant compared to the amounts of starting materials used. This possibility seemed unlikely since in none of the successful reactions that are described herein could any of the characteristically brown O_2-inserted ROO–$Co^{III}(dmgH)_2py$ be seen by silica gel TLC analysis of reaction progress of low concentration reactions even though brown ROO–$Co^{III}(dmgH)_2pyr$ could easily be observed, invariably at lower R_f than R–$Co^{III}(dmgH)_2py$, in reactions that were intentionally contaminated with O_2. To quantitatively investigate the significance of O_2 contamination, 6 + PhSSPh + freshly distilled benzene were placed separately in a Vacuum Atmospheres inert-atmosphere glovebox, and the N_2 atmosphere of the box (<1 ppm O_2) was bubbled through the benzene for 20 min. A Pyrex tube equipped with a ground-glass joint was charged with 6, PhSSPh, and benzene to make a standard dilute (1 mM) solution in both 6 and PhSSPh. The tube was then tightly sealed with a well-greased ground-glass stopper that was then securely taped down. The hermetically sealed tube was removed from the inert-atmosphere box,

(9) The β-hydride elimination at the lower concentration conditions was not entirely unexpected since β-hydride elimination is known to occur when R–$Co^{III}(dmgH)_2py$ are photolyzed anaerobically in the absence of any radical trap: (a) Golding, B. T.; Kemp, T. J.; Sheena, H. H. J. *Chem. Res. Synop.* **1981**, 34. (b) Duong, K. N. V.; Ahond, A.; Merienne, C.; Gaudemer, A. *J. Organomet. Chem.* **1973**, *55*, 375.

and then the reaction was photolyzed as usual. The yield of cyclized **8** that was obtained under these highly deoxygenated conditions was not improved compared to that obtained without these special precautions, indicating that under the usual photolytic conditions loss of free radicals due to reaction with O_2 contamination is insignificant.

The cobaloxime ligand is the only remaining possibility as a source of H atoms for alkane production (pentane from **9**, *n*-decane from **2**), to account for the 14–26% of radicals missing from the mass balance at low concentrations. The CH_3 and OH groups on the cobaloxime ligand are potential sources of H atoms for alkane production.[10] It is unclear at this time in what other ways the ligand could react with 14–26% of the radicals, yet other uncharacterized products, presumably derived from the ligand, are formed since dark-colored polar material is produced that adheres to silica gel when the reactions are prefiltered prior to ^1H NMR or GC analyses. Further efforts are being directed toward the identification and suppression of these side reactions and toward the further development of R–$Co^{III}(dmgH)_2py$ chemistry for specific synthetic applications.

Experimental Section

All reagents were purchased from Aldrich Chemical Co. with the following exceptions: dimethylglyoxime (Lancaster Synthesis); pyridine, NaOH (J. T. Baker); $CoCl_2·6H_2O$ (Mallinckrodt). All solvents were reagent grade from J. T. Baker with the following exceptions: *n*-pentane (Fisher); *tert*-butyl methyl ether (Aldrich). Solvents were distilled immediately prior to use with the exception of benzene, which was refluxed over basic aqueous $KMnO_4$ for 2 days, then washed with water, dried over anhydrous $MgSO_4$, and then distilled from sodium benzophenone ketyl under Ar. Analytical thin-layer chromatography was performed on Merck (#5554) aluminum-backed F_{254} silica gel 60 plates. Ar and N_2 were deoxygenated by passage through a heated column of BASF R3-11 catalyst (Chemical Dynamics Corp.) in the black (reduced) form and then through a column of activated Davison 3-Å molecular sieves. Solvents were deoxygenated in the reaction vessels by rapid bubbling with deoxygenated Ar or N_2 for 10–15 min immediately prior to starting reactions. ^1H NMR spectra were recorded on either a Varian XL-100 spectrometer (100 MHz) or a General Electric QE-300 spectrometer (300 MHz). ^{13}C NMR spectra were measured on the QE-300 instrument at 75.48 MHz. Elemental analyses were performed by MicAnal in Tucson, AZ. GC analyses were performed on a Hewlett-Packard 5790A gas chromatograph equipped with a Hewlett-packard 3390A plotter/integrator.

General Information on R–$Co^{III}(dmgH)_2py$. All R–$Co^{III}(dmgH)_2py$ were orange solids. All had similar chromatographic properties, with typical R_f values (EtOAc) of 0.4 on silica gel TLC plates. Visualization of R–$Co^{III}(dmgH)_2py$ spots on TLC plates was done either with visible light (orange spot), with 254-nm UV light, or by dipping in vanillin (2.5 wt %)–glacial acetic acid (2.0 wt %)–concentrated sulfuric acid (3.5 wt %)–95% EtOH followed by heating with a heat gun. Pure R–$Co^{III}(dmgH)_2py$ are invariably orange; a brown discoloration indicates contamination with oxygen-inserted ROO–$Co^{III}(dmgH)_2py$. The presence of ROO–$Co^{III}(dmgH)_2py$ can be confirmed by observation of a brown spot at R_f 0.1–0.2 on silica gel TLC using EtOAc for development. The formation of ROO–$Co^{III}(dmgH)_2py$ is a significant problem only with moist, partially purified samples; the reaction is not a problem with chromatographically purified or recrystallized dry free-flowing solids. Pure dry free-flowing solid R–$Co^{III}(dmgH)_2py$ can be stored for months under Ar in foil-wrapped amber bottles at room temperature without significant decomposition. All compounds described in this paper were easily obtained as pure stable orange solids.

Representative Preparations of R–$Co^{III}(dmgH)_2py$. The standard R–$Co^{III}(dmgH)_2py$ preparation[3,11] was followed with several different modifications given in the representative following procedures. All R–$Co^{III}(dmgH)_2py$ were known compounds,[3b,11a-d] with the exception of **4** which was characterized by ^1H NMR and elemental microanalysis.

Preparation of $CH_3(CH_2)_9$–$Co^{III}(dmgH)_2py$ (2).[11a] A deoxygenated suspension of $CoCl_2·6H_2O$ (238 mg, 1.00 mmol) and dimethylglyoxime (235 mg, 2.02 mmol) in 7 mL of CH_3OH at room temperature was treated with 50% aqueous KOH (230 mg of KOH, 2.05 mmol of KOH) and pyridine (80 mg, 1.0 mmol). N_2 was bubbled through the resulting red suspension for another 10 min, then $NaBH_4$ (70 mg, 1.8 mmol) was added, and the resulting green mixture was stirred for 10 min. A deoxygenated solution of *n*-decyl bromide (225 mg, 1.02 mmol) in 3 mL of CH_3OH was added via cannula, and the resulting mixture was stirred under N_2 for 1 h, 20 min. Another 40 mg of $NaBH_4$ was added, and the mixture was stirred overnight. The orange suspension was then diluted with 25 mL of acetone and adsorbed onto a few grams of silica gel followed by rotary evaporation of the solvent, and then the silica gel was placed on top of a short silica gel column (10–20 g), which was eluted with deoxygenated EtOAc. Deoxygenated N_2 was bubbled through the solution of **2** as it was collected. The solvent was removed on a rotary evaporator to give **2** as an orange solid: 381 mg, 0.748 mmol (73%); ^1H NMR ($CDCl_3$) δ 0.8 (m, 5 H), 1.2 (br m, 14 H), 1.7 (m, 2 H), 2.1 (s, 12 H), 7.3 (m, 3 H), 7.7 (m, 1 H), 8.6 (d, J = 4.8 Hz, 2 H), 19 (br s, 2 H, OHO bridge).

By a directly analogous procedure $CH_3(CH_2)_4$–$Co^{III}(dmgH)_2py$ (**9**)[11b] was prepared in 48% isolated yield (unoptimized) from *n*-pentyl bromide: ^1H NMR ($CDCl_3$) δ 0.79 (t, J = 6 Hz, 3 H), 0.9 (m, 2 H), 1.20 (m, 4 H), 1.64 (m, 2 H), 2.12 (s, 12 H), 7.31 (m, 3 H), 7.71 (m, 1 H), 8.60 (br d, J = 5 Hz, 2 H), 17.9 (br s, 2 H, OHO bridge); ^{13}C NMR ($CDCl_3$) δ 12.0, 14.1, 22.4, 30.3, 32.9 (br, CCo), 32.9, 125.1, 137.4, 149.0, 150.0.

By a directly analogous procedure $CH_3(CH_2)_8CH(CH_3)$–$Co^{III}(dmgH)_2py$ (**4**) was prepared in 36% isolated yield (unoptimized) from $CH_3(CH_2)_8CH(CH_3)Br$: ^1H NMR ($CDCl_3$) δ 0.43 (d, J = 6.8 Hz, 3 H), 0.89 (br t, J = 6.8 Hz, 3 H), 1.25 (br s, 17 H), 2.14 (s, 12 H), 7.29 (t, J = 6.0 Hz, 2 H), 7.69 (t, J = 7.3 Hz, 2 H), 8.59 (d, J = 5.1 Hz). Anal. Calcd for $C_{24}H_{42}N_5O_4Co$: C, 55.06; H, 8.09; N, 13.38. Found: C, 55.02; H, 8.40; N, 13.29.

Preparation of $PhCH_2CH_2$–$Co^{III}(dmgH)_2py$ (3).[11c] In an ice–water-cooled 50-mL three-neck flask under N_2 were suspended $CoCl_2·6H_2O$ (1.0 g, 4.2 mmol) and dimethyl glyoxime (1.02 g, 8.82 mmol) in 15 mL of CH_3OH. Pyridine (0.398 g, 5.04 mmol) and 50% aqueous NaOH (0.403 g of NaOH, 10.1 mmol of NaOH) were added, followed by a solution of $NaBH_4$ (0.33 g, 8.8 mmol) in 3 mL of H_2O. The suspension had not been deoxygenated, so excess $NaBH_4$ was used to scavenge O_2 through formation of reduced $Co^I(dmgH)_2py$ anion, which would react with O_2 followed by rereduction with $NaBH_4$ to form $Co^I(dmgH)_2py$ anion again. The red–brown suspension rapidly turned green when the $NaBH_4$ was added. Neat $PhCH_2CH_2Br$ (0.885 g, 4.62 mmol) was added by syringe; within 10 min the mixture had turned orange. Half of the solvent was evaporated with a stream of deoxygenated N_2, and then the mixture was diluted with an approximately equal volume of water. The orange solid **3** was collected by filtration: 1.62 g, 3.42 mmol (82%); ^1H NMR ($CDCl_3$) δ 1.6–1.9 (m, 4 H), 2.1 (s, 12 H), 7–7.5 (m, 3 H + $CHCl_3$), 8.60 (d, 2 H, J = 4 Hz).

By a directly analogous procedure $\overline{CH_2(CH_2)_4CH}$–$Co^{III}(dmgH)_2py$ (**5**)[3b] was prepared from cyclohexyl bromide in 60% isolated yield: ^1H NMR ($CDCl_3$) δ 0.7–2.0 (m, 11 H), 2.14 (s, 12 H), 7.26 (m, 2 H), 7.66 (m, 1 H), 8.56 (d, J = 4 Hz, 2 H).

Preparation of CH_2=$CH(CH_2)_4$–$Co^{III}(dmgH)_2py$ (6).[11d] At room temperature, deoxygenated Ar was bubbled for several minutes through a suspension of $CoCl_2·6H_2O$ (1.48 g, 6.22 mmol) and dimethylglyoxime (1.74 g, 15.0 mmol) in 25 mL of CH_3OH. After the addition of pyridine (0.49 g, 6.1 mmol) and 2 equiv of 50% aqueous NaOH solution, deoxygenated Ar was bubbled

(10) EPR studies of photolyses of $PhCH_2$–$Co^{III}(dmgH)_2py$, selective deuteriation studies using $PhCH_2$–$Co^{III}(dmgH)_2py$, and studies on $PhCH_2$–Co^{III}(diphenylglyoximato-H)$_2$py have identified the OH bridges as a primary source of H atoms: Maillard, P.; Giannotti, C. *Can. J. Chem.* **1982**, *60*, 1402. Our quantitative GC studies corroborate these qualitative (or semiquantitative) EPR studies.

(11) (a) Maillard, P.; Massot, J. C.; Giannotti, C. *J. Organomet. Chem.* **1978**, *159*, 219. (b) Giannotti, C.; Gaudemer, A.; Fontaine, C. *Tetrahedron Lett.* **1970**, *37*, 3209. (c) Schrauzer, G. N.; Kohnle, J. *Chem. Ber.* **1964**, *97*, 3056. (d) Jensen, F. R.; Kiskis, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 5825.

through the dark red–brown mixture for several more minutes and then $NaBH_4$ (0.324 g, 8.53 mmol) was added. After it was stirred for 10 min at room temperature, a solution of CH_2=C-H$(CH_2)_3CH_2OSO_2CH_3$ (0.924 g, 5.19 mmol) in 7 mL of CH_3OH, through which deoxygenated Ar had been bubbled for several minutes, was added via cannula. After 2-h stirring at room temperature, an additional 20 mg of $NaBH_4$ was added, the same was done again after 4 h, and then the mixture was stirred overnight. The resulting suspension was diluted with acetone and adsorbed onto a few grams of silica gel followed by rotary evaporation of the solvents, and then the silica gel was placed at the top of a short silica gel column (10–20 g), which was eluted with petroleum ether (30–60 °C) and then with 3:1 ether–petroleum ether. Deoxygenated N_2 was bubbled through the orange solution of **6** as it was collected. The solvent was removed on a rotary evaporator, giving **6** as an orange solid: 1.77 g, 3.91 mmol (75%); ^{1}H NMR ($CDCl_3$) δ 0.93 (m, 2 H), 1.35 (m, 2 H), 1.7 (m, 2 H), 1.95 (m, 2 H), 2.13 (s, 12 H), 4.9 (m, 2 H), 5.8 (m, 1 H), 7.3 (m, 3 H), 7.7 (m, 1 H), 8.6 (d, 2 H) 17.6 (br s, 2 H, OHO bridge); ^{13}C NMR ($CDCl_3$) δ 12.1, 14.2, 22.5, 30.4, 32.4 (bd, C-Co), 33.0, 125.2, 137.5, 149.0, 150.1.

General Information on Photolyses. Photolyses were performed in Pyrex tubes equipped with ground-glass joints and fitted with rubber septa under a positive pressure of deoxygenated Ar or N_2 (syringe needle through the septum) in magnetically stirred Ar- or N_2-saturated solutions, prepared by bubbling the gas through the solutions for 10–15 min. Solvent or reagent additions were performed with syringes or cannulas by standard anaerobic transfer techniques. Each reaction tube was immersed in a beaker of water that was cooled with cold tap water running through a coil of copper tubing immersed in the beaker surrounding the reaction tube. The water in the beaker was magnetically stirred along with the reactions. The light source was either a Sylvania 300-W incandescent lamp or a GE 500-W incandescent lamp, mounted in a ceramic socket. The end of the light source was placed 3–6 in. from the outside of the beaker. The entire apparatus was wrapped in foil during the photolysis, and the light bulb was cooled with a stream of air blown over the bulb from behind. Silica gel TLC for R–$Co^{III}(dmgH)_2$py disappearance was performed by removing small samples of the reaction mixtures by a long needle inserted through the septum. Whenever a crude reaction mixture was filtered through silica gel prior to ^{1}H NMR or GC analysis, petroleum ether or methylene chloride was used as solvent for eluting the desired product(s) from the silica gel without eluting the polar byproducts.

Representative Procedure for All High-Yielding Radical-Trapping Reactions Summarized in Table I. In all cases the major radical-trapped products were known compounds, and unambiguous structural assignments could be made by ^{1}H NMR.

Into 20 mL of benzene in a 25-mL Pyrex tube was placed the R–$Co^{III}(dmgH)_2$py (**2–5**) and the radical-trapping agent (PhSSPh, PhSeSePh, or $BrCCl_3$) to make the final concentrations summarized in Table I. The tube was sealed with a rubber septum and the solution deoxygenated with N_2. The reactions were then photolyzed as described in the preceding section for the length of time in Table I. The tube was opened, the contents were transfered to a round-bottom one-neck flask, and the solvent was removed on a rotary evaporator. The crude product was partially purified by suction filtration through about 1 in. of silica gel in a fritted-glass funnel using petroleum ether (30–60 °C). The solvent was removed from the filtrate on a rotary evaporator, a known quantity of Ph_3CH (usually about 25 mg) was measured into the flask, then the residue was dissolved in $CDCl_3$, and the yield was determined by integrating resonances for radical-trapped products against the Ph_3CH internal standard.

Representative Run of Concentration-Dependent Photolysis of 6 in the Presence of PhSSPh (Table II). As in the general experimental for Table I a solution of **6** (67.6 mg, 0.150 mmol) and PhSSPh (45.9, 0.211 mmol, 1.40 equiv) in 10 mL benzene under Ar was photolyzed for 3 h, 15 min. The green suspension was filtered through silica gel and rinsed with benzene, and then the combined filtrates were rotary evaporated, leaving **7** + **8** in a 1:1 ratio in a total yield of 78% by as determined by ^{1}H NMR integration against Ph_3CH added as an internal standard.

Representative Experimental Procedure for Quantitative Capillary GC Product Analysis at High and Low Substrate Concentrations (Table III). A deoxygenated solution of **9** (26.2 mg, 0.0608 mmol) and PhSSPh (14.7 mg, 0.0674 mmol, 1.1 equiv) in 61 mL of benzene was photolyzed through a tap water cooled water bath with a 300-W incandescent light bulb. After 1.5 h, the green reaction mixture was filtered through a short silica gel pad with the assistance of air pressure (suction filtration was not performed to avoid evaporating volatile products). The filter was rinsed with freshly distilled deoxygenated benzene (40 mL), and the combined filtrates were analyzed by capillary gas chromatography. After the ratio of *n*-pentane to 1-pentene was established, 10 μL of *n*-pentane was added as a standard and the ratio was measured again. The *n*-pentyl–SPh was quantitated by GC integration against Ph_3CH added as an internal standard. For the GC analysis for *n*-pentane and 1-pentene, a 6 ft × $^1/_8$ in. stainless-steel column of *n*-octane/Porasil C (80/100 mesh, Alltech #2740PC) was used with 35 mL/min of N_2 carrier gas and flame ionization detection; the temperature program used was 80 °C for 5.0 min and then heating at 25 °C/min to 140 °C, where it was held until the end of the run. For the GC analysis of R–SPh products and *n*-decane, a 12.5 m × 0.2 mm fused silica column of cross-linked dimethylsilicone (Hewlett-Packard #19091-60312) was used with 1.3 mL/min of N_2 carrier flow and flame ionization detection; the temperature program used was 40 °C for 1.5 min, followed by heating at 20 °C/min to 220 °C, where the temperature was maintained until the end of the run. The response of the GC detector as a function of amount of sample injected onto the GC was independently determined for each of the products on pure authentic samples of each product; standard plots were constructed of detector response vs. amount of each compound injected. All yields reported in Table III were obtained from such plots by interpolation of observed detector responses to obtain the actual amounts of each product present in each sample.

General Experimental Procedure for Studies of the Solvent-Dependent Yields of 8 from 6 + PhSSPh under Cyclization Conditions at Low Substrate Concentrations. These reactions were all performed as in the general experimental procedure for photolyses, at 1.0 mM **6** and 1.0 mM PhSSPh. All solvents were reagent grade and were distilled immediately prior to use.

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Registry No. **2**, 68830-60-4; **3**, 55516-97-7; **4**, 105581-67-7; **5**, 28206-03-3; **6**, 42568-40-1; **7**, 39984-84-4; **8**, 100258-36-4; **9**, 37824-53-6; $CoCl_2$, 7646-79-9; $CH_3(CH_2)_9Br$, 112-29-8; $CH_3(CH_2)_4Br$, 110-53-2; $CH_3(CH_2)_8CH(CH_3)Br$, 39563-54-7; $PhCH_2CH_2Br$, 103-63-9; $\overline{CH_2(CH_2)_4CHBr}$, 108-85-0; CH_2=C-H$(CH_2)_3CHOSO_2CH_3$, 64818-36-6; PhSSPh, 882-33-7; PhSeSePh, 1666-13-3; $BrCCl_3$, 75-62-7; $CH_3(CH_2)_9SPh$, 13910-18-4; $CH_3(CH_2)_9SePh$, 61539-89-7; $PhCH_2CH_2SPh$, 13865-49-1; $PhCH_2CH_2SePh$, 65275-36-7; $CH_3(CH_2)_8CH(CH_3)SPh$, 29015-66-5; $CH_3(CH_2)_8CH(CH_3)SePh$, 61539-86-4; $\overline{CH_2(CH_2)_4CHSPh}$, 7570-92-5; $\overline{CH_2(CH_2)_4CHSePh}$, 22233-91-6; dimethylglyoxime, 95-45-4; pyridine, 110-86-1; pentyl phenyl sulfide, 1129-70-0.