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Formation of Organocobalt Porphyrin Complexes from Reactions of Cobalt(II) Porphyrins and Dialkylcyanomethyl Radicals with Organic Substrates: Chemical Trapping of a Transient Cobalt Porphyrin Hydride

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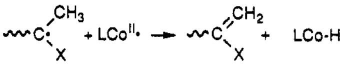
Solutions of (tetrakis(*p*-methoxyphenyl)porphyrinato)cobalt(II) ((TAP)$Co^{II\bullet}$) and alkyl radicals ($^{\bullet}C(CH_3)(CH_3)CN$, $^{\bullet}C(CH_3)(CH(CH_3)_2)CN$) formed from dialkylazo precursors react with alkenes and alkynes in $CHCl_3$, DMF, and hydrocarbon solvents to form alkyl and vinyl complexes ((TAP)Co—R, (TAP)Co—$C(R_1)$=$C(R_2)(R_3)$) and with alkyl halides and epoxides in DMF to form alkyl and β-hydroxyalkyl complexes. These reactivity patterns are indicative of forming a transient cobalt(III) hydride ((TAP)Co—H) that adds with unsaturated organic substrates or, when deprotonated, reacts as a nucleophile ($[(TAP)Co^I]^-$) with alkyl halides and epoxides. Addition reactions of (TAP)Co—H with alkenes and alkynes generally occur with high regioselectivity corresponding to formation of the most stable organic radical (Markovnikov regioselectivity). Sterically encumbering substituents which inhibit (TAP)Co binding at the same carbon center can reverse the regioselectivity (anti-Markovnikov addition). Examples of organic group isomerization that correspond to 1,2(H,Co)-shifts for secondary alkyl complexes and 1,3(H,H)-shifts for vinyl derivatives are reported and discussed. High yields of regio- and stereospecific products using simple procedures suggest the synthetic utility of this versatile methodology in forming a wide range of organocobalt complexes.

Introduction

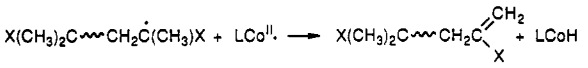
Cobalt(II) porphyrins and related low-spin cobalt(II) macrocycles are chain-transfer catalysts for regulating the molecular weight of polymers formed by free-radical polymerization.[2,3] These catalysts can produce functionalized oligomers with terminal alkene groups, and applications for the resulting macromonomers in copolymerizations[4] account for the increasing commercial importance of this technology.[5] Mechanistic studies of this process suggest that cobalt(II)-catalyzed chain transfer occurs through the intermediacy of a cobalt(III) hydride formed from reaction of cobalt(II) with the oligomer radical (eq 1).[3a,6] The cobalt hydride species formed by reaction 1 can subsequently transfer a hydrogen atom to an alkene monomer to form an alkyl radical or radical pair (eq 2), which then undergoes normal chain growth (eq 3) until terminated by reaction with Co(II) to re-form the cobalt(III) hydride (eq 4), completing the catalytic cycle.



$$\sim\sim C^{\bullet}(CH_3)X + LCo^{II\bullet} \longrightarrow \sim\sim C(=CH_2)X + LCo\text{-}H \qquad (1)$$

$$LCo\text{-}H + CH_2{=}C(CH_3)X \longrightarrow X(CH_3)_2C^{\bullet} + LCo^{II\bullet} \qquad (2)$$

$$X(CH_3)_2C^{\bullet} + (n)CH_2{=}C(CH_3)X \longrightarrow X(CH_3)_2C\sim\sim CH_2\dot{C}(CH_3)X \qquad (3)$$



$$X(CH_3)_2C\sim\sim CH_2\dot{C}(CH_3)X + LCo^{II\bullet} \longrightarrow X(CH_3)_2C\sim\sim CH_2C(=CH_2)X + LCoH \qquad (4)$$

Intermediate cobalt hydrides have not yet been directly observed in the Co(II)-catalyzed chain transfer in radical polymerization, but the polymer products and kinetic–mechanistic studies are fully compatible with a cycle involving reactions 1–4. Reactions of dimethylcyanomethyl radicals with cobalt(II) phthalocyanine and cobalt(II) oximes[7] that produce cobalt(I) complexes in donor solvents such as DMF and DMSO (eqs 5 and 6) support

$$LCo^{II\bullet} + {}^{\bullet}C(CH_3)_2CN \rightarrow LCo{-}H + CH_2{=}C(CH_3)CN \qquad (5)$$

$$LCo{-}H + B \rightarrow [LCo^I]^- + BH^+ \qquad (6)$$

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the plausibility of producing cobalt hydride species from radical pathways such as those depicted by reactions 1 and 4. Thermal and photolytic alkene-forming reactions of cobalt(III) alkyl complexes[8] are thought to occur by a closely related pathway that involves formation of a cobalt(III) hydride by β-hydrogen atom transfer from an alkyl radical to a cobalt(II) unit within a geminate radical pair ($[\mathrm{Co^{II}}\bullet\ \bullet\mathrm{CX_2CHY_2}] \rightarrow \mathrm{Co{-}H} + \mathrm{CX_2{=}CY_2}$).[8a–e]

The chemistry of cobalt porphyrin hydrides is underdeveloped compared with that of hydrides of cobaloxime and cobalt salen derivatives[9] because of the lack of convenient preparative procedures. In contrast with cobal(II)oximes, cobalt(II) porphyrins fail to react with either H_2 (P_{H_2} = 1 atm; T = 298 K) to form observable concentrations of cobalt(III) porphyrin hydrides or BH_4^- to form cobalt(I) porphyrin species.[10,11] Protonation of cobalt(I) porphyrin complexes formed by sodium amalgam reduction of cobalt(II) porphyrin derivatives has provided limited information on the formation and reactivity of cobalt porphyrin hydrides, but producing the cobalt(III) hydride in this manner results in bimolecular elimination of H_2 and substrate reactions of cobalt(I) species in competition with the cobalt(III) hydride.[11] Evidence for occurrence of a transient (por)Co—H species (por = porphyrin) has been obtained for solutions of cobalt(III) porphyrin species in contact with $NaBH_4$ and oxidizing agents by observing reactions with alkenes and alkynes that form organocobalt porphyrin derivatives.[13] This article reports that solutions of cobalt(II) porphyrins in the presence of dialkylcyanomethyl radicals function as a convenient source for cobalt(III) hydrides that react with alkenes and alkynes in $CHCl_3$, DMF, and hydrocarbon solvents to produce alkyl and vinyl complexes, respectively, and with organic halides and epoxides in DMF to form alkyl and β-hydroxyalkyl complexes.[12] These results provide evidence for the intermediacy of cobalt(III) hydride species in cobalt(II)-catalyzed chain transfer in radical polymerizations and illustrate that chemical trapping of transient cobalt(III) hydrides can be a versatile method for the preparation of a wide variety of organocobalt porphyrin and related macrocycle and chelate complexes.

Experimental Section

Vinyl monomers (Aldrich) containing hydroquinone or other stabilizing compounds were purified by multiple vacuum distillations to remove the stabilizer immediately before use. AIBN (2,2′-azobis(isobutyronitrile)) (Kodak), VAZO-52 (2,2′-azobis(2,4-dimethylpentanenitrile)) (DuPont), and all other reagents and solvents (Aldrich) were used as purchased.

General Procedures. In a typical reaction procedure, 7.5 mg of (tetrakis(*p*-methoxyphenyl)porphyrinato)cobalt(II) ((tetra-*p*-anisylporphyrinato)cobalt(II), (TAP)Co), a 20–100-fold molar excess of organic substrate, and 13.1 mg of AIBN were added to ~0.9 mL of solvent in air, and the resulting mixture was transferred to a reaction ampules adapted for vacuum. After three freeze–pump–thaw cycles, the ampules were sealed and immersed in a constant-temperature bath (±0.1 °C). In the case of VAZO-52-initiated reactions, the procedure was the same as that described for AIBN except that 20 mg of initiator was used. Unless otherwise noted in the text, chloroform was used as solvent in the reactions of $\mathrm{(TAP)Co^{II}}$ and AIBN with alkenes and alkynes, and DMF was used for reactions of alkyl halides and epoxides. The specific solvents were selected for their ability to maintain the reactants and products in solution. Experiments in toluene or benzene resulted in the same organocobalt(III) products as experiments in chloroform, but reduced solubility makes observation of the products by ^{1}H NMR less convenient. (TAP)Co was selected for this investigation because of the relatively high solubility in $CHCl_3$ and hydrocarbon solvents. The reaction times reported in Table I correspond to the period in which the maximum yield of the initial organometallic product is obtained. Longer reaction times may result in a decrease in the yield of the initial organometallic product accompanied by appearance of several different organometallic species. These additional organocobalt species result from isomerization of (TAP)Co—R to (TAP)Co—R′ and reactions of organic radicals with excess alkene substrates. Time intervals given in Tables I–III indicate a steady-state formation of the initial organocobalt species during the time interval. Specific times given in Tables I–III indicate that longer reaction times result in observable quantities of additional organocobalt complexes.

Conversion of $\mathrm{(TAP)Co^{II}}$ to organocobalt porphyrin derivatives was monitored by comparison of the meta phenyl proton signal of $\mathrm{(TAP)Co^{II}}$ at ~9 ppm with the ortho phenyl proton signal of $\mathrm{(TAP)Co^{III}{-}X}$ complexes at ~8 ppm ($CDCl_3$) or the meta phenyl proton at ~7 ppm (DMF-d_7) at 295 K using a 200-MHz NMR spectrometer. For systems where all species remain soluble, this method of quantification provides relative concentrations of the $\mathrm{(TAP)Co^{II}}$ and organocobalt(III) species. The classes of organometallic derivatives formed in this solution reactivity study have literature precedents such that ^{1}H NMR provides definitive identification of the solution species. The small quantities of materials required for these studies make the isolation, purification, and chemical analysis of the organometallic products impractical.

The concentration of AIBN chosen for this study (13.1 mg/mL, 0.08 M) produces 4.2×10^{-3} mol/(L·h) of radicals that enter the reaction medium at 60 °C.[14] A period of 135 min is required to produce 9.4×10^{-3} mol/L of free radicals, which is the initial concentration of $\mathrm{(TAP)Co^{II}}$ usually employed in this study. The rate of free-radical production from VAZO-52 can be estimated from reactions of 1-hexene in $CHCl_3$ and 1-hexynenitrile in DMF, which were found to form the corresponding organocobalt complexes with effectively equal rates that correspond to the rate of radical formation.

Results and Discussion

Reaction of $\mathrm{(TAP)Co^{II}\bullet}$ with $\bullet\mathrm{C(CH_3)(R)CN}$. (Tetra-*p*-anisylporphyrinato)cobalt(II), $\mathrm{(TAP)Co^{II}}$, couples with the dimethylcyanomethyl radical, $\mathrm{(CH_3)_2(CN)C\bullet}$, from

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Table I. Formation of Alkylcobalt Porphyrins by Reaction of Co(II) Porphyrins with Alkenes in the Presence of Organic Radicals from Azo Initiators in CHCl$_3$[a]

	(TAP)Co—CR$_1$R$_2$R$_3$							
compd. no.	R$_1$	R$_2$	R$_3$	yield (%)	alkene	[alkene] (mol L^{-1})	reacn time (min)	initiator/*T* (°C)
1	CH$_3$	CH$_3$	CN	13	CH$_2$=C(CH$_3$)CN	0.8	30–40	AIBN/60
1[b]	CH$_3$	CH$_3$	CN	46	CH$_2$=C(CH$_3$)CN	0.8	420–1000	VAZO-52/25
2	CH$_3$	CH(CH$_3$)$_2$	CN	<2			60–1000	VAZO-52/25
3	CH$_3$	CH$_3$	CO$_2$CH$_3$	<2	CH$_2$=C(CH$_3$)CO$_2$CH$_3$	2.0	30–120	AIBN/60
4	H	H	(CH$_2$)$_4$CH$_3$	23	CH$_2$=CH(CH$_2$)$_3$CH$_3$	0.8	180	AIBN/60
5	CH$_3$	H	Bu	42				
5	CH$_3$	H	Bu	>95	CH$_2$=CH(CH$_2$)$_3$CH$_3$	0.8	380–480	VAZO-52/40
6	H	H	(CH$_2$)$_3$OH	28	CH$_2$=CH(CH$_2$)$_2$OH	1.2	120–150	AIBN/60
7	CH$_3$	H	CH$_2$CH$_2$OH	52				
7	CH$_3$	H	CH$_2$CH$_2$OH	>95	CH$_2$=CH(CH$_2$)$_2$OH	1.2	300–360	VAZO-52/40
8	H	H	CH$_2$C(CH$_3$)$_2$OH	>95	H$_2$C=CHC(CH$_3$)$_2$OH	1.9	360–420	AIBN/60
8[b]	H	H	CH$_2$C(CH$_3$)$_2$OH	>95	H$_2$C=CHC(CH$_3$)$_2$OH	1.9	1800–2400	VAZO-52/25
9[b]	CH$_3$	H	(CH$_2$)$_{10}$CH$_3$	>95	CH$_2$=(CH$_2$)$_{10}$CH$_3$	0.4	1800–2400	VAZO-52/25
10	–(CH$_2$)$_5$–		H	40	Cyclohexene	0.3	80–180	AIBN/60
11	CH$_3$	H	Ph	47	CH$_2$=CH(C$_6$H$_5$)	0.9	90–120	AIBN/60
12	CH$_3$	H	CO$_2$CH$_3$	70	CH$_2$=CHCO$_2$CH$_3$	0.8	90	AIBN/60
13	CH$_3$	H	CHO	50	CH$_2$=CH(CHO)	1.5	100	VAZO-52/40
14	–OC(O)OCH$_2$–		H	65	vinylene carbonate	2.0	120	AIBN/60
15	CH$_3$	H	NCH$_2$CH$_2$CH$_2$CO	70	*N*-vinylpyrrolidone	0.9	90	AIBN/60
16	CH$_3$	H	CN	62	CH$_2$=CHCN	1.5	1800	VAZO-52/25

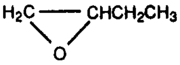
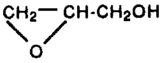
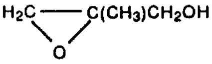
[a] [(TAP)Co] = 9.4 × 10^{-3}M unless otherwise noted. [b] [(TAP)Co] = 4.7 × 10^{-3}M.

Table II. Formation of Alkenylcobalt Porphyrins by Reaction of Co(II) Porphyrins with Alkynes in the Presence of Organic Radicals from Azo Initiators in CHCl$_3$[a]

	(TAP)Co—CR$_1$=CHR$_2$						
compd no.	R$_1$	R$_2$	yield (%)	alkyne	[alkyne] (mol L^{-1})	reacn time (min)	initiator/*T* (°C)
17	(CH$_2$)$_3$CN	H	>95	HC$\equiv$C(CH$_2$)$_3$CN	0.9	150–180	AIBN/60
18	C$_6$H$_5$	H	60	HC$\equiv$CPh	0.9	80	AIBN/60
19	(CH$_2$)$_3$CH$_3$	H	>95	HC$\equiv$CBu	0.9	4200–4800	VAZO-52/25
19	(CH$_2$)$_3$CH$_3$	H	84	HC$\equiv$CBu	0.9	120	AIBN/60
20	CH$_3$	(CH$_2$)$_2$CH$_3$	4				
21	CH$_2$CH$_3$	CH$_2$CH$_3$	80	EtC$\equiv$CEt	0.9	120	AIBN/60
22	H	Si(CH$_3$)$_3$	>95	HC$\equiv$CSi(CH$_3$)$_3$	0.7	240–270	AIBN/60
22[b]	H	Si(CH$_3$)$_3$	>95	HC$\equiv$CSi(CH$_3$)$_3$	0.7	1800–2400	VAZO-52/25
23	CH$_2$OH	H	60	HC$\equiv$CCH$_2$OH	0.9	120	AIBN/60

[a] [(TAP)Co] = 9.4 × 10^{-3}M unless otherwise noted. [b] [(TAP)Co] = 4.7 × 10^{-3} M.

Table III. Formation of Alkylcobalt Porphyrins by Reaction of Co(II) Porphyrins with Alkyl Halides and Epoxides in the Presence of Organic Radicals from Azo Initiators[a]

	(TAP)Co—CHR$_1$R$_2$							
compd no.	R$_1$	R$_2$	yield (%)	substrate	[substrate] (mol L^{-1})	solvent	reacn time (min)	initiator/*T* (°C)
4	H	(CH$_2$)$_4$CH$_3$	>95	CH$_3$(CH$_2$)$_4$CH$_2$I	1.0	DMF	200–260	AIBN/60
24	H	H	5	CH$_3$I	1.6	CHCl$_3$	400	AIBN/60
			>95	CH$_3$I	1.6	DMF	180–240	AIBN/60
25	Cl	H	50	CH$_2$Cl$_2$	1.5	DMF	120–160	AIBN/60
26	Cl	Cl	<2	CHCl$_3$	12.5	CHCl$_3$	100–500	AIBN/60
			>95	CHCl$_3$	1.3	DMF	180–240	AIBN/60
27	CH$_3$	H	<2	C$_2$H$_5$I	1.3	CHCl$_3$	300	AIBN/60
			>95	C$_2$H$_5$I	1.3	DMF	180–240	AIBN/60
28	CH$_3$(CH$_2$)$_2$	H	>95	CH$_3$(CH$_2$)$_3$I	1.0	DMF	180–240	AIBN/60
			80	CH$_3$(CH$_2$)$_3$Br	1.0	DMF	240–320	AIBN/60
29	CH$_3$	CH$_3$	16	(CH$_3$)$_2$CHBr	1.0	DMF	80–120	AIBN/60
			47	(CH$_3$)$_2$CHI	1.0	DMF	60–100	AIBN/60
			>95	(CH$_3$)$_2$CHI	1.0	DMF	240–320	VAZO-52/40
30	CH$_3$	CH$_2$CH$_3$	92	CH$_3$CH(I)CH$_2$CH$_3$	0.9	DMF	260–320	VAZO-52/40
31	H	(CH$_2$)$_2$CO$_2$CH$_3$	>95	Br(CH$_2$)$_2$CO$_2$CH$_3$	1.5	DMF	300–380	VAZO-52/40
32	H	CH$_2$CH(OH)CH$_2$CH$_3$	<2		1.4	CHCl$_3$	100–200	AIBN/60
			65			DMF	180–240	AIBN/60
			84			DMF	500–660	VAZO-52/40
33	–CH(OH)(CH$_2$)$_4$–		<2	epoxycyclohexane	1.0	CHCl$_3$	90–180	AIBN/60
			<2			DMF	90–180	AIBN/60
34	H	CH(OH)CH$_2$OH	<2		1.3	DMF	90–180	AIBN/60
35	H	C(CH$_3$)(OH)CH$_2$OH	88		1.1	DMF	180–240	AIBN/60

[a] [(TAP)Co] = 9.4 × 10^{-3} M.

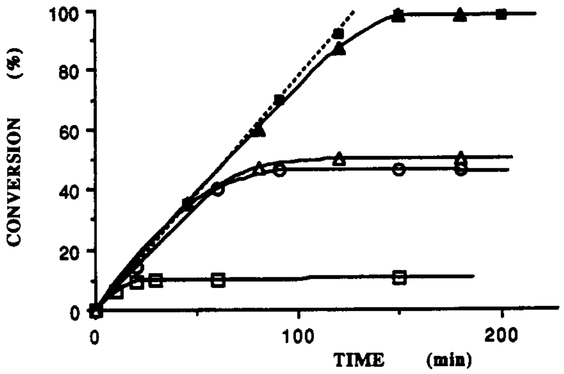


Figure 1. Time dependence for the conversion of (TAP)Co^{II} in $CDCl_3$ to organocobalt(III) complexes ($T = 60$ °C) ([AIBN] = 0.08 M; [(TAP)Co] = 9.4×10^{-3} M): (○) [styrene] = 0.9 M; (△) [cyclohexene] = 0.3 M; (▲) [methyl acrylate] = 0.8 M; (■) [vinylpyrrolidone] = 0.9 M; (□) no alkene added. The dotted line corresponds to the theoretical line for quantitative use of the alkyl radicals from AIBN in forming organocobalt(III) derivatives.

AIBN (353 K) to form an alkyl complex, (TAP)Co—$C(CH_3)_2CN$ (1) (eq 7). Formation of 1 is observed in $CHCl_3$

$$(CH_3)_2(CN)C^{\bullet} + (TAP)Co^{II\bullet} \rightleftharpoons (TAP)Co{-}C(CH_3)_2CN \quad (7)$$

solution by appearance of a characteristic high-field ^1H NMR peak (β_{CH_3}(1) −5.00 ppm) (Table I). Increasing the AIBN concentration increases the fraction of (TAP)Co converted to 1 before achieving a steady-state concentration. Compound 1 is an unusual example of a tertiary alkyl–cobalt(III) complex.[11,13,15] Dimethylcyanomethyl radicals have previously been observed to have one-electron reactions at either the carbon radical center or the nitrile nitrogen ($((CH_3)_2(CN)C^{\bullet} \leftrightarrow (CH_3)_2C{=}C{=}\dot{N}{:})$).[16] No evidence was obtained for an organometallic product resulting from (TAP)Co^{II} reacting at the nitrile nitrogen. Exposure of solutions of 1 to O_2 (295 K) results in the immediate conversion to a new (TAP)Co^{III} species displaying a singlet at −1.36 ppm in the ^1H NMR, which is tentatively assigned to a peroxy complex, (TAP)Co—$OOC(CH_3)_2CN$, in analogy with previously reported reactions of cobalt(III) alkyls with dioxygen.[17,18] Thermal insertion of O_2 into the Co—C bond of 1 results from the facile Co–alkyl bond homolysis associated with sterically demanding alkyl groups. Solutions of (TAP)Co^{II} and $^{\bullet}C(CH_3)(CH_2CH(CH_3)_2)CN$ and $^{\bullet}C(CH_3)_2CO_2CH_3$ derived from azo precursors failed to produce ^1H NMR observable quantities of organometallic complexes (compounds 2 and 3; Table I) which undoubtedly result from the large steric demands for the organic groups.

Reactions of (TAP)Co$^{II\bullet}$ and $^{\bullet}C(CH_3)(R)CN$ with Alkenes, Alkynes, Alkyl Halides, and Epoxides. Chloroform solutions containing (TAP)Co$^{II\bullet}$, AIBN (333 K) or VAZO-52 (313 K) as a source of $^{\bullet}C(CH_3)(R)CN$ radicals, and an alkene or alkyne react respectively to produce alkyl and vinyl complexes of (TAP)Co (eqs 8 and 9) (Tables I and II; Figures 1–5).

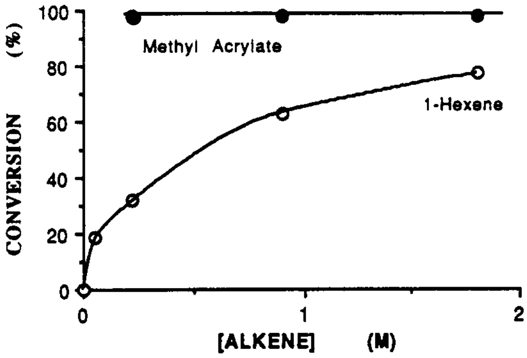


Figure 2. Dependence for the conversion of (TAP)Co^{II} into organocobalt(III) complexes on the concentration of alkene in chloroform at 60 °C ([AIBN] = 0.08 M; 150 min; [(TAP)Co] = 9.4×10^{-3} M).

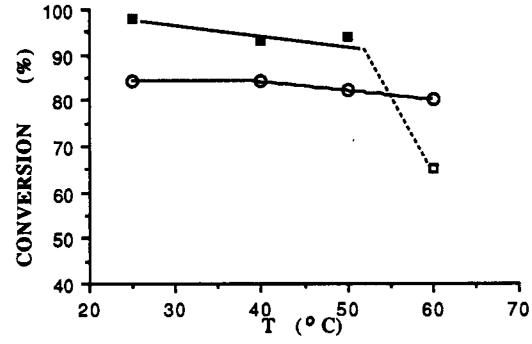


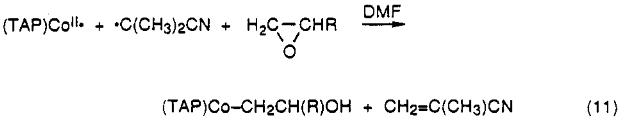
Figure 3. Dependence for the steady-state conversion of (TAP)Co^{II} in $CDCl_3$ to organocobalt(III) complexes on the reaction temperature ([(TAP)Co] = 9.4×10^{-3} M; [AIBN] = 0.08 M; [VAZO-52] = 0.08 M): (○) 3-buten-1-ol, AIBN; (□) 1-hexene, AIBN; (■) 1-hexene, VAZO-52.

$$(TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)(R)CN + CH_2{=}CHX \xrightarrow{CHCl_3} (TAP)Co{-}CH(CH_3)X + CH_2{=}C(R)CN \quad (8)$$

$$(TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)(R)CN + HC{\equiv}CX \xrightarrow{CHCl_3} (TAP)Co{-}C(X){=}CH_2 + CH_2{=}C(R)CN \quad (9)$$

DMF solutions of (TAP)Co$^{II\bullet}$ and AIBN (353 K) are observed to react with alkyl halides and epoxides to form alkyl and β-hydroxyalkyl complexes, respectively (eqs 10 and 11; Table III). This general method for producing organocobalt complexes from reactions of a cobalt(II) complex with a tertiary alkyl radical and an organic substrate we call the *tertiary radical synthesis*.

$$(TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)_2CN + R{-}X \xrightarrow{DMF} (TAP)Co{-}R + CH_2{=}C(CH_3)CN + HX \quad (10)$$



$$(TAP)Co^{II\bullet} + {}^{\bullet}C(CH_3)_2CN + H_2C\overset{O}{-}CHR \xrightarrow{DMF} (TAP)Co{-}CH_2CH(R)OH + CH_2{=}C(CH_3)CN \quad (11)$$

Appearance of the organocobalt porphyrin complexes and concomitant loss of (TAP)Co$^{II\bullet}$ are conveniently followed by ^1H NMR. Structures for the organocobalt porphyrin derivatives in solution were assigned by analysis

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[15] (a) Jensen, F. R.; Buchanan, D. H. *J. Chem. Soc., Chem. Commun.* **1973**, 153. (b) Eckert, M.; Lenoir, D.; Ugi, I. *J. Organomet. Chem.* **1977**, *141*, C23. (c) Schrauzer, G. N.; Deutsch, E. *J. Am. Chem. Soc.* **1969**, *91*, 3341.

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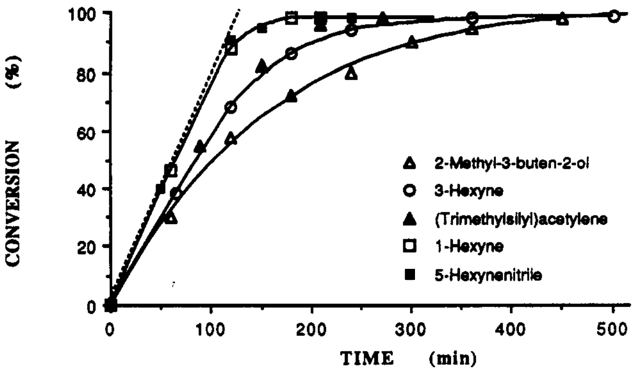


Figure 4. Time dependence for the conversion of (TAP)Co^{II} to organocobalt(III) complexes ([(TAP)Co] = 9.4 × 10^{-3} M; chloroform; 60 °C; [AIBN] = 0.08 M; [alkyne] ≈ 0.5 M). The dotted line corresponds to the theoretical line for quantitative use of the alkyl radicals from AIBN in forming organocobalt(III) derivatives.

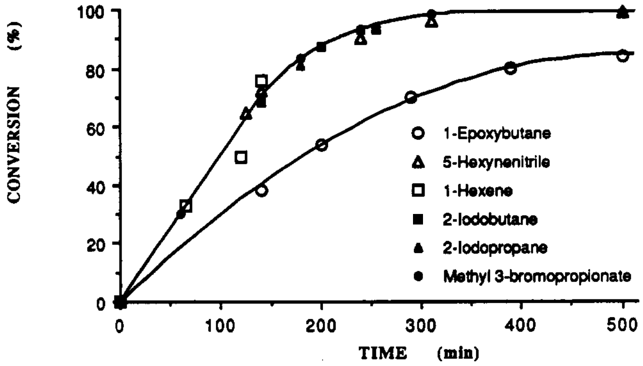


Figure 5. Time dependence for the conversion of (TAP)Co^{II} in DMF to organocobalt(III) complexes (T = 40 °C; [VAZO-52] = 0.08 M; [(TAP)Co] = 9.4 × 10^{-3} M; [organic substrate] ≈ 1 M). $CDCl_3$ solvent was used for 1-hexene.

of the characteristic high-field ^{1}H NMR spectra resulting from the porphyrin ring current effects on groups bonded with the cobalt (Table IV; Figures 6–9). ^{1}H NMR was used to distinguish between addition of H$^\bullet$ or an initiator radical along with (TAP)Co$^{II\bullet}$ to unsaturated organic substrates and also to provide evidence for the regio- and stereoselectivity for the addition reactions. Resolution of H–H coupling for the α-C—H groups in (TAP)Co—R complexes is adequate to make these structural distinctions, which contrasts with (OEP)Co—R derivatives, where the α-C—H resonances are usually too broad to resolve the proton coupling.[11] Integration of the ^{1}H NMR spectra for (TAP)Co—R derivatives and the H–H coupling patterns are uniquely compatible with addition of the constituents of (TAP)Co—H with both alkenes and alkynes. The reaction of (TAP)Co$^{II\bullet}$ and AIBN with acrylonitrile provides an example where there is exclusive formation of the secondary alkyl complex (TAP)Co—$CH(CH_3)CN$, which is demonstrated by the quartet pattern for the α-C—H and the doublet CH_3 group resulting from mutual coupling (Figure 7, Table IV). The primary and secondary cobalt alkyl complexes that can potentially be produced by addition of (TAP)Co—H with vinyl substrates ($CH_2{=}CHX$) are easily distinguished by the chemical shift and coupling patterns, and the effects associated with a chiral carbon center that occurs in many secondary alkyl complexes. ^{1}H NMR spectra for (TAP)Co—$CH_2(CH_2)_4CH_3$ and (TAP)Co—$CH(CH_3)(CH_2)_3CH_3$ illustrate several of the spectral features useful for structural assignments (Figure 6, Table IV). The ^{1}H NMR resonances for the 1-hexyl group in (TAP)Co—$CH_2(CH_2)_4CH_3$ appear at relatively high field positions (δ −4.64 to +0.10) and show equivalence for each of the sets of CH_2 hydrogens (Table IV). The β-CH_2 group is at a higher

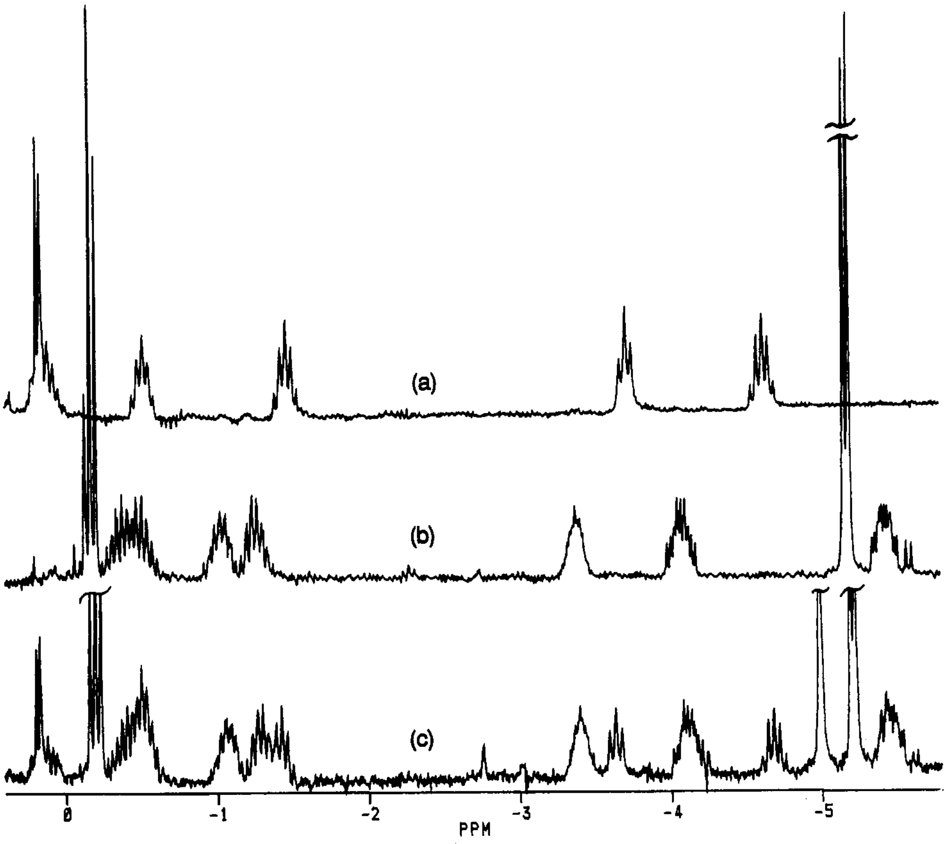
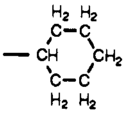
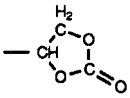
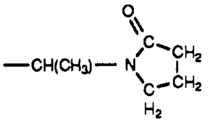
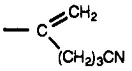


Figure 6. ^{1}H NMR spectra: (a) 1-hexyl-(TAP)Co; (b) 2-hexyl-(TAP)Co; (c) reaction mixture of 1-hexene, (TAP)Co^{II} (9.4 × 10^{-3} M), and AIBN (0.08 M) after heating for 90 min at 60 °C.

Table IV. ^{1}H NMR Parameters for the Organic Substituents in Organocobalt(III) Chelates[a]

compd. no.	structure of substituent	solvent	organic group ^{1}H NMR[b]
1	$-C(CH_3)_2CN$	CDCl$_3$	CH$_3$, s, −5.00
4	$-CH_2(CH_2)_4CH_3$	DMF-d_7	α-CH$_2$, t, −3.73, J = 8.0; β-CH$_2$, m (5), −4.64, J = 7.5; γ-CH$_2$, m (5), −1.45, J = 7.3; δ-CH$_2$, m (5), −0.50, J = 7.0; ϵ-CH$_2$, m, 0.11; CH$_3$, m, 0.10
5	$-CH(CH_3)CH_2CH_2CH_2CH_3$	CDCl$_3$	CH, bs, −3.5; β-CH$_3$, d, −5.27, J = 6.5; β-CH$_2$(A), b, −4.20; β-CH$_2$(B), b, −5.55; γ-CH$_2$(A), m, −1.40; γ-CH$_2$(B), m, −1.1; δ-CH$_2$, bm, −0.5; ϵ-CH$_3$, t, −0.28, J = 6.0 Hz
8	$-CH_2CH_2C(CH_3)_2OH$	CDCl$_3$	α-CH$_2$, t, −3.65, J = 8.7; β-CH$_2$, t, −4.70, J = 8.6; CH$_3$, s, −0.68
9	$-CH(CH_3)(CH_2)_{10}CH_3$	CDCl$_3$	CH, b, −3.5; β-CH$_3$, d, −5.25, J = 6.5; β-CH$_2$(A), b, −4.2; β-CH$_2$(B), b, −5.5; γ-CH$_2$(A), b, −1.4; γ-CH$_2$(B), b, −1.1; δ-CH$_2$, bm, −0.6; ϵ-CH$_2$, m (5), −0.02; J = 7.1; θ-CH$_2$, m (5), 0.45, J = 7.1
10		CDCl$_3$	CH, b, −3.38; β-CH$_2$, bq, −4.30, J = 10 and bd −4.52, J = 10; γ-CH$_2$, bm, −0.8; δ-CH$_2$, b, −0.13
11	$-CH(CH_3)Ph$	CDCl$_3$	CH, q, −2.33, J = 7.0; CH$_3$, d, −5.14, J = 7.0
12	$-CH(CH_3)COOCH_3$	CDCl$_3$	CH, q, −3.38, J = 3.8; CH$_3$, d, −5.42, J = 3.8
13	$-CH(CH_3)CHO$	CDCl$_3$	CH, q, −3.11, J_1 = 7.1, J_2 = 1.8; CH$_3$, d, −5.65, J = 7.1; CHO, d, 2.98, J = 1.8
14		CDCl$_3$	CH, bm, −1.0; CH$_2$(A), bm, −1.0; CH$_2$(B), d, −3.10, J = 10.2
15		CDCl$_3$	CH, q, −1.11, J = 6.2; CH$_3$, d, −4.88, J = 6.2; α-CH$_2$, t, −2.04, J = 6.3; CH$_2$CH$_2$, bm, 0.2
16	$-CH(CH_3)CN$	CDCl$_3$	CH, q, −3.75, J = 7.3; CH$_3$, d, −5.95, J = 7.3
17		CDCl$_3$	=CH$_2$ (trans), m, −0.54; =CH$_2$ (cis), d, −2.45, J = 4.2; β-CH$_2$, dt, −3.59, J_1 = 7.2, J_2 = 1.0; γ-CH$_2$, m (5), −1.36, J = 7.2; δ-CH$_2$, t, 0.11, J = 7.2
17		DMF-d_7	=CH$_2$ (trans), s, −0.34; =CH$_2$ (cis), d, −2.43, J = 3.0; β-CH$_2$, t, −3.58, J = 7.1; γ-CH$_2$, m (5), −1.38, J = 7.3; δ-CH$_2$, t, 0.45, J = 7.3
18	$-C(Ph){=}CH_2$	CDCl$_3$	=CH$_2$(trans), d, −0.49, J = 2.9; =CH$_2$ (cis), d, −2.1, J = 2.9
19	$-C(Bu){=}CH_2$	CDCl$_3$	=CH$_2$ (cis), d, −2.63, J = 4.5; =CH$_2$ (trans), m, −0.67; β-CH$_2$, t, −3.91, J = 7.0; γ-CH$_2$, m (5), −1.50, J = 7.3; δ-CH$_2$, m (6), −0.52, J = 7.5; CH$_3$, t, −0.15, J = 7.4
21	$-C(Et){=}CHEt$	CDCl$_3$	β-CH$_2$, q, −4.01, J = 7.3; =CH (trans), bt, −0.55, J = 7.6; γ-CH$_3$, t, −0.88, J = 7.2; γ-CH$_2$, m (5), −2.65, J = 7.2; δ-CH$_3$, t, −1.54, J = 7.2
22	$-CH{=}CHSi(CH_3)_3$	CDCl$_3$	α-CH, d, −0.79, J = 7.8; β-CH, d, −2.90, J = 7.8; CH$_3$, s, −2.30
22		DMF-d_7	α-CH, d, −0.74, J = 7.2; β-CH, d, −2.85, J = 7.1; CH$_3$, s, −2.30
23	$-C(CH_2OH){=}CH_2$		=CH (cis), d, −2.41, J = 3.9; =CH (trans), m, −0.15; CH$_2$, d, −1.92, J = 4.6; OH, bt, −0.74
24	$-CH_3$	DMF-d_7	s, −4.80
24		CDCl$_3$	s, −4.49
25	$-CH_2Cl$	DMF-d_7	s, −2.15
26	$-CHCl_2$	DMF-d_7	s, −1.08
27	$-CH_2CH_3$	DMF-d_7	CH$_2$, q, −3.71, J = 7.7; CH$_3$, t, −4.97, J = 7.7
28	$-CH_2CH_2CH_2CH_3$	DMF-d_7	CH$_2$, t, −3.75, J = 8.0; CH$_2$, m (5), −4.68, J = 7.3; γ-CH$_2$, m(6), −1.46, J = 7.2; CH$_3$, t, −0.80, J = 7.0
29	$-CH(CH_3)_2$	DMF-d_7	CH, m, −3.42; CH$_3$, d, −5.03, J = 6.0
30	$-CH(CH_3)CH_2CH_3$	DMF-d_7	CH, b, −3.54; β-CH$_2$(A), b, −4.15; β-CH$_2$(B), b, −5.2; β-CH$_3$, d, −5.15, J = 6.6; CH$_3$, t, −1.53, J = 7.4
31	$-CH_2CH_2CO_2CH_3$	DMF-d_7	α-CH$_2$, b, −3.8; β-CH$_2$, b, −3.8
32	$-CH_2CH(OH)CH_2CH_3$	DMF-d_7	α-CH$_2$(A), t, −3.77, J = 5.3; α-CH$_2$(B), t, −4.00, J = 6.2; β-CH, b, −2.97; γ-CH$_2$(A), m, −1.82, J = 7.3; γ-CH$_2$(B), m, −2.54; OH, d, 0.12, J = 4.6; CH$_3$, t, −0.86, J = 7.1
35	$-CH_2C(OH)(CH_3)CH_2OH$		α-CH$_2$, s, −3.96; CH$_3$, s, −2.51; β-OH, s, 0.04; γ-CH$_2$, d, −0.54, J = 5
36	$-C({=}CH_2)(CH_2)_3$	CD$_3$C$_6$D$_5$	=CH (cis), d, −1.77, J = 2.3; β-CH$_2$, t, −3.03, J = 7.8; γ-CH$_2$, m (5), −0.38, J = 7.3; δ-CH$_2$ + CH$_3$ + =CH (trans), bm, −0.1 to +0.25
		CDCl$_3$	=CH (cis), d, −2.50, J = 4.3; =CH (trans), m, −0.53; β-CH$_2$, t, −3.67, J = 7.6; γ-CH$_2$, m (5), −0.90, J = 7.6, δ-CH$_2$, m(5), −0.33, J = 7.4; CH$_3$, t, −0.18, J = 7.4
37	$-CH(COOC_2H_5)CH_2COOC_2H_5$	CDCl$_3$	α-CH + β-CH$_2$(A), bm, −3.0 to −3.5; β-CH$_2$(B), bm, −4.4
38	$-CH(CH_3)(CH_2)_3CH_3$	CDCl$_3$	CH, b, −3.2; β-CH$_2$(A), b, −4.1; β-CH$_2$(B), b, −5.5; γ-CH$_2$(A), b, −1.3; γ-CH$_2$(B), b, −1.5; δ-CH$_2$, bm, −0.8; θ-CH$_3$, m, −0.65; β-CH$_3$, m, −5.4
39	$-C({=}CH_2)(CH_2)_3CN$	CDCl$_3$	broad signals at −4.2, −3.0, −1.9, −1.7, −1.0, and −0.4 ppm
40	$-C({=}CH_2)(CH_2)_3CN$	CDCl$_3$	=CH (trans), m, −0.87; =CH (cis), d, −3.01, J = 2.3; β-CH$_2$, dt, −4.12, J = 7.3, J_2 = 0.8; γ-CH$_2$, m (5), J = 7.5; δ-CH$_2$, t, −0.25, J = 7.7

[a] Compound numbers correspond to the entries in Tables I–III and VI. Resources are given in units of ppm and J values in Hz. [b] Notations of cis and trans are with respect to the Co center.

field ($\delta_{\beta CH_2}$ −4.64) than the α-CH$_2$ group ($\delta_{\alpha CH_2} = -3.73$), and their mutual coupling is relatively large ($J_{\alpha H-\beta H} = 8.0$ Hz). A regular decrease in upfield shift and H–H coupling occurs on proceeding further away from the metal center ($\delta_{\beta CH_2}$ −1.52; $\delta_{\delta CH_2}$ −0.50; $\delta_{\epsilon CH_2}$ 0.11; δ_{CH_3} 0.10; J_{H-H} = 7.0–7.5 Hz). The secondary 2-hexyl complex (TAP)Co—CH(CH$_3$)(CH$_2$)$_3$CH$_3$ has a chiral center at the α-carbon, and each of the CH$_2$ groups are diastereotopic and appear as AB spin patterns (Figure 6). The β-CH$_2$ protons are widely split ($\delta_{\beta CH_2(A)}$ −5.55; $\delta_{\beta CH_2(B)}$ −4.20), and the magnitude of the CH$_2$ splitting decreases regularly with distance from the chiral center ($\delta_{\gamma CH_2(A)}$ −1.40, $\delta_{\gamma CH_2(B)}$ −1.10; $\delta_{\delta CH_2(A)}$ −0.62, $\delta_{\delta CH_2(B)}$ −0.45). The splitting for the CH$_2$ hydrogens becomes negligible when the CH$_2$ group is five

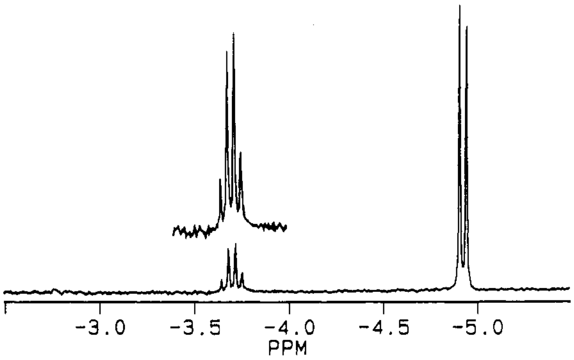


Figure 7. ^{1}H NMR spectrum in $CDCl_3$ illustrating the formation of (TAP)Co—$CH(CH_3)CN$ from the reaction of (TAP)Co^{II} (9.4×10^{-3} M), VAZO-52 (0.08 M), and acrylonitrile (1.5 M) (30 h; 25 °C).

Table V. Proton Chemical Shift Ranges for Methyl and Methylene Groups in Unsubstituted (TAP)Co–Alkyl Complexes[a]

H position[b]	approx $\delta(CH_3)$	approx $\delta(CH_2)$
α (1)	–4.5 to –4.8	–3.6 to –3.7
β (2)	–5.0 to –5.3	–4.6 to –4.7
γ (3)	–1.5	–1.4 to –1.5
δ (4)	–0.7 to –0.8	–0.5 to –0.6
ϵ (5)	–0.2 to –0.3	0.0 to +0.1
θ (6)	+0.1	+0.45

[a] Values are taken from Table IV. [b] Denotes attachment of hydrogen to the α–θ-carbon atoms, where the α-carbon atom is bonded to the cobalt.

or more atoms removed from the chiral site, as illustrated by the ^{1}H NMR for (TAP)Co—$CH(CH_3)(CH_2)_{10}CH_3$ (compound **9**, Table IV). The range of ^{1}H NMR chemical shifts observed for CH_2 and CH_3 groups in (TAP)Co—alkyl complexes as a function of the number of carbons removed from the cobalt center is a useful guide in assigning the ^{1}H NMR for (por)Co—R complexes (Table V). When the CH_2 or CH_3 group is adjacent to a double bond or an electronegative substituent, there is a substantial downfield shift (~0.7–1.2 ppm) (Table IV) compared to the values for saturated alkyl groups which are generalized in Table V.

Structures of the vinyl complexes that result from alkyne reactions are based on previously reported ^{1}H NMR assignments for analogous (por)Co—vinyl derivatives[11,13] (e.g. (OEP)Co—$CH_\alpha{=}CH_{\beta_1}H_{\beta_2}$: $\delta_{H\alpha}$ –0.81, $\delta_{H\beta_1}$(trans to Co) –0.26, $\delta_{H\beta_2}$(cis to Co) –2.00; $J_{H_\alpha H_{\beta 1}} = 4$ Hz, $J_{H_\alpha H_{\beta 2}} = 13$ Hz, $J_{H_{\beta 1}H_{\beta 2}} = 4$ Hz[11]). Reactions for solutions of (TAP)$Co^{II\bullet}$ and $^\bullet C(CH_3)_2CN$ with alkynes produce the addition of the constituents of (TAP)Co—H, as shown by the number and intensity of chemically inequivalent hydrogens in the ^{1}H NMR of the resulting vinyl complexes (**17–23**, Tables III and IV). A representative example is the reaction of 1-hexyne, which forms a vinyl complex with two equal-intensity inequivalent vinyl hydrogens (δ –2.63, –0.67) with a relatively small H–H coupling constant (J = 4.5 Hz). The largest upfield shift (δ –2.63) is uniquely characteristic of a vinyl β-CH cis to (por)Co, and the other hydrogen (δ –0.67) could be on the β-C trans to cobalt or on the α-C center.[11] The relatively small H–H coupling (J = 4.5 Hz) clearly favors assigning both hydrogens to the β-C center, (TAP)Co—C(Bu)$=CH_2$, and the chemical shift for β-CH_2 (δ –3.91) places this group adjacent to the double bond. Reaction of (TAP)Co—H with EtC≡CEt results in a vinylic β-CH at δ –0.55, which indicates that hydrogen entered the position trans to (TAP)Co. Addition of (TAP)Co—H with HC≡$CSi(CH_3)_3$ results in an organometallic complex with vinylic hydrogen doublets at δ –0.79 and –2.90 and a mutual H–H coupling of 7.8 Hz. This observation is most consistent with the presence of one hydrogen on each of the α- and β-carbons in a trans configuration, which is the organometallic product that would be produced by anti-Markovnikov cis addition of (TAP)Co—H.

Reactions 8–11 are found to be general for tetrapyrrole macrocycles of cobalt(II). Example reactions for a series for cobalt(II) tetraphenylporphyrin derivatives, including cobalt tetramesitylporphyrin ((TMP)Co), cobalt octaethylporphyrin ((OEP)Co), and cobalt tetra-*tert*-butylphthalocyanine (((*t*-Bu)$_4$Pc)Co) are given in Table VI. The *tertiary radical synthesis* is a highly versatile method for obtaining a diverse variety of organocobalt(III) complexes because it utilizes easily prepared cobalt(II) complexes with a diversity of readily available alkenes, alkynes, and alkyl halide substrates.

Reactions of Alkenes. Solutions of (TAP)Co^{II} with tertiary alkyl radicals ($^\bullet C(CH_3)_2CN$,$^\bullet C(CH_3)(CH_2C(CH_3)_3)$-

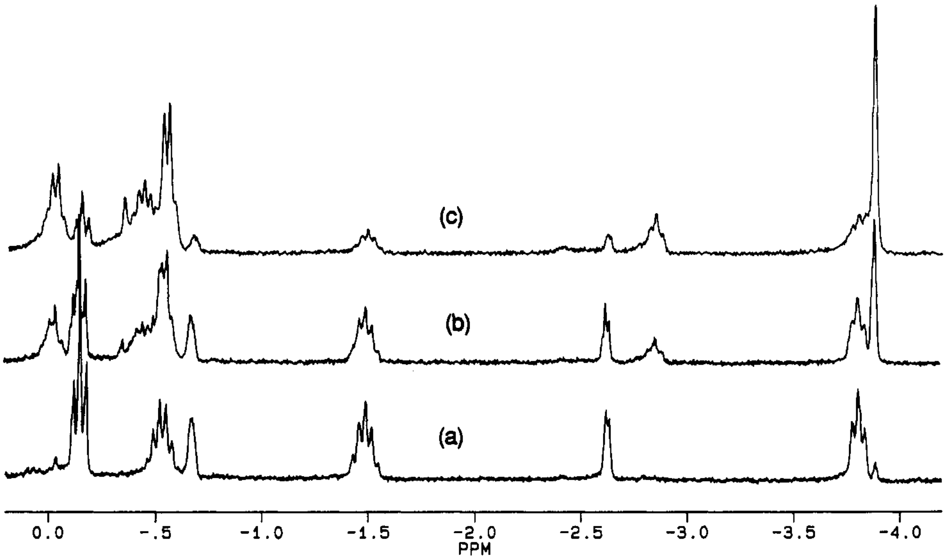


Figure 8. ^{1}H NMR spectra illustrating the formation and isomerization of (TAP)Co—C($=CH_2$)Bu to (TAP)Co—C(CH_3)$=CH(CH_2)_2CH_3$ from a $CDCl_3$ solution that initially contained [1-hexyne] = 0.9 M, [AIBN] = 0.08 M, and [(TAP)Co] = 9.4×10^{-3} M after heating at 60 °C for a series of time periods: (a) 120 min; (b) 180 min; (c) 480 min.

Table VI. Formation of Alkylcobalt Porphyrins by Reaction of Co(II) Porphyrins with Alkenes in the Presence of Organic Radicals from Azo Initiators by $CHCl_3$[a]

compd. no.	compd	yield (%)	alkene or alkyne (concn (mol L^{-1}))	solvent	reacn time (min)	initiator	T (°C)
36	(tetramesitylporphyrinato)Co—$C(=CH_2)CH_2CH_2CH_2CH_2CH_3$	>95	1-hexyne (0.5)	toluene	180–400	AIBN	60
				$CDCl_3$	180–400	AIBN	60
37	(tetrakis(*o*-methylphenyl)porphyrinato)Co—$CH(COOC_2H_5)CH_2COOC_2H_5$	>95	diethyl maleate (0.24)	$CDCl_3$	120–150	VAZO-52	40
38	(tetrakis(*o*-chlorophenyl)porphyrinato)Co—$CH(CH_3)CH_2CH_2CH_2CH_3$	>95	1-hexene (0.5)	$CDCl_3$	120–180	VAZO-52	40
39	(tetra-*tert*-butyl)phthalocyaninato)Co—$C(=CH_2)CH_2CH_2CH_2CN$	>95	5-hexynenitrile (0.5)	$CDCl_3$	120–180	AIBN	60
40	(octaethylporphyrinato)Co—$C(=CH_2)CH_2CH_2CH_2CN$ (octaethylporphyrinato)Co—$C(CH_3)=CHCH_2CH_2CN$	85 15	5-hexynenitrile (0.5)	$CDCl_3$	150	AIBN	60

[a] The concentration for each cobalt macrocycle is 6×10^{-3} M, and the concentration of radical initiators is 0.08 M.

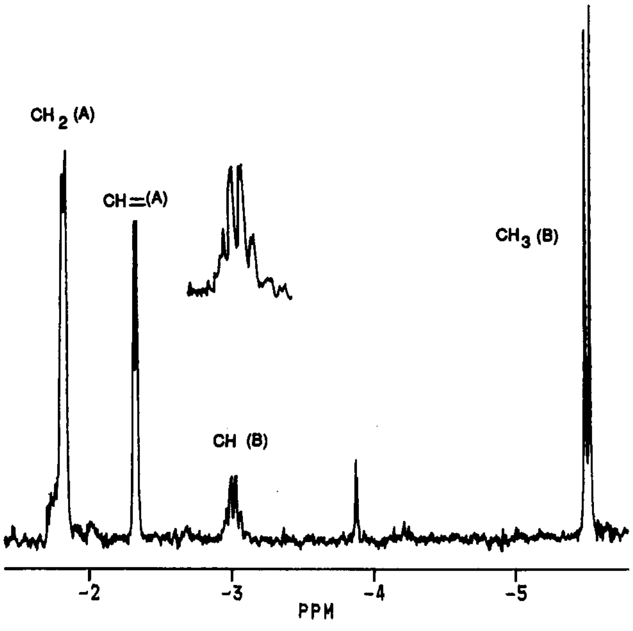


Figure 9. ^1H NMR spectrum illustrating the formation of (TAP)Co—$C(CH_2OH)=CH_2$ (A) and (TAP)Co—$CH(CH_3)$-CHO (B) in a solution initially containing [$CH\equiv CCH_2OH$] = 0.9 M, [AIBN] = 0.08 M, and [(TAP)Co] = 9.4×10^{-3} M after heating at 60 °C for 120 min.

CN), formed from the corresponding azo precursor, provide a source of (TAP)Co—H for reactions with alkenes that produce alkylcobalt porphyrin derivatives (eqs 12 and 13; Table I). Each of the alkenes studied initially reacts to

$$(TAP)Co + {}^{\bullet}C(CH_3)(R)CN \rightarrow (TAP)Co{-}H + CH_2{=}C(R)CN \quad (12)$$

$$(TAP)Co{-}H + CH_2{=}CHX \rightleftharpoons (TAP)Co{-}CH(X)CH_3 \quad (13)$$

form an alkylcobalt complex at a rate equal to the rate of alkyl radical production (Figure 1) and then achieves a near-steady-state fraction of conversion dependent on the concentration of the azo-radical precursor, the concentration of the alkene (Figure 2), and the structure of the alkyl group bonded to cobalt. These reactions usually occur with high regioselectivity favoring the Markovnikov product and are interpreted as addition of (TAP)Co—H to the alkene (eq 13). Alkenes that form the more stable Co–alkyl complex, such as methyl acrylate (Figure 1), result in nearly complete conversion of (TAP)Co^{II} to an alkyl complex during the time required to generate 1 mol of initiator radicals (${}^{\bullet}C(CH_3)(R)CN$) per mole of (TAP)Co^{II}. For these examples, most of the (TAP)Co^{II} is converted to an alkyl complex before radical termination reactions become competitive with reactions that form and add (TAP)Co—H to the alkene. Styrene produces only ~50% conversion to an alkyl complex, (TAP)Co—$CH(C_6H_5)CH_3$, under the same conditions of concentrations and temperature where $CH_2{=}CH(CO_2CH_3)$ produces near-quantitative conversion of (TAP)Co^{II} (Figure 1, Table I). This is attributed to differences in the (TAP)Co—R bond homolysis enthalpies. The high stability of the substituted benzylic radical (${}^{\bullet}CH(C_6H_5)CH_3$) results in a relatively small cobalt–alkyl bond dissociation enthalpy, which increases the rate and extent of Co—R bond homolysis compared with those for many other secondary alkyl–Co complexes. Alkenes that produce particularly weak tertiary alkyl–cobalt complexes, such as $CH_2{=}C(CH_3)CO_2CH_3$, usually do not produce ^1H NMR observable quantities of organocobalt complexes and begin polymerizing as soon as the initiator radicals are formed. Additions of (TAP)Co—H with alkenes occur with high regioselectivity and usually form the Markovnikov product which corresponds to formation of the most stable alkyl radical unit, but the alkene with the most sterically demanding substituent ($H_2C{=}CH(C(CH_3)_2OH)$) adds to (TAP)Co—H in an anti-Markovnikov regioselective fashion to form (TAP)Co—$CH_2CH_2(C(CH_3)_2OH)$ (Table I). The primary alkyl complex is probably both the kinetic and thermodynamic product, because no secondary alkyl complex was detected by ^1H NMR. The presence of the $-C(CH_3)_2OH$ group at the radical carbon center must prohibit bonding with (TAP)Co$^{II\bullet}$ and forces the reaction that forms an alkyl complex to proceed by an alternate pathway.

The normal Markovnikov regioselectivity is kinetically determined because alkene ($CH_2{=}CH(X)$) substrates generally produce secondary alkyl–cobalt complexes which are thermodynamically unstable relative to the primary alkyl complexes. This is illustrated by the reaction of 1-hexene at 40 °C that results in the exclusive and near-quantitative formation of the secondary alkyl complex (TAP)Co—$CH(CH_3)(CH_2)_3CH_3$ (Table I, Figures 3 and 6b). Carrying out the 1-hexene reaction at 60 °C produces mixtures of the primary and secondary alkyl complexes where the secondary alkyl complex dominates at an early stage, but subsequently the thermodynamically preferred primary alkyl complex, (TAP)Co—$CH_2(CH_2)_4CH_3$, becomes the predominant product (Table I, Figure 6c). Data presented in Figure 3 and Tables I–III indicate that higher yields of relatively unstable (TAP)Co—R complexes can be obtained by using lower temperature initiators.

Prolonged reaction times can result in formation of organocobalt complexes from secondary radical species; alkyl radical reactions (eqs 14 and 16) with excess alkene substrates produce alkyl radicals ($R^{*\bullet}$), which can interchange with the alkyl group in (TAP)Co—R (eqs 15 and 17). These secondary organocobalt species, (TAP)Co—R*,

$$(n+1)CH_2{=}CHX + {}^{\bullet}C(CH_3)(R)CN \rightarrow NC(R)(CH_3)C(CH_2CH(X))_nCH_2\dot{C}H(X) \quad (14)$$

$$(TAP)Co{-}R \rightleftharpoons (TAP)Co^{II\bullet} + R^{\bullet} \quad (15)$$

$$R^{\bullet} + (n+1)CH_2{=}CHX \rightarrow R(CH_2CH(X)_nCH_2\dot{C}H(X)) \quad (16)$$

$$(TAP)Co^{II\bullet} + R^{*\bullet} \rightarrow (TAP)Co{-}R^{*} \quad (17)$$

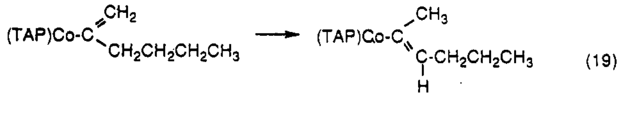
appear only after most of the $(TAP)Co^{II}$ is consumed because the reaction of $^{\bullet}C(CH_3)(R)CN$ with $(TAP)Co^{II\bullet}$ to form (TAP)Co—H and then addition of this species with alkenes to produce (TAP)Co—R are both fast compared with formation of organocobalt species by reaction 17. Organic substituent isomerizations and formation of alternate organocobalt species, (TAP)Co—R*, are both reduced by using dialkylazo compounds that produce radicals at lower temperatures (Table I).

Reactions of Alkynes. (TAP)Co—H formed by reaction 12 combines with alkynes to form vinylcobalt porphyrin complexes (eq 18). Kinetic factors for reaction

$$(TAP)Co{-}H + CH{\equiv}CX \rightleftharpoons (TAP)Co{-}C(X){=}CH_2 \quad (18)$$

18 are similar to those for alkenes (reaction 13), and this reaction produces vinyl complexes ((TAP)Co—C(X)=CH_2) at a rate effectively equal to that of radical production except when bulky substituents retard the reaction (Figure 4, Table II). Conversions of $(TAP)Co^{II}$ into cobalt(III) vinyl complexes are nearly quantitative because of the relatively strong Co—C bonding. The regioselectivity usually corresponds to the Markovnikov addition product as depicted by equation 18, except for the $HC{\equiv}CSi(CH_3)_3$ derivative (compound **22**, Table II), where the steric demands preclude placing both (TAP)Co and $Si(CH_3)_3$ on the same carbon center.

Although the conversion of $(TAP)Co^{II}$ to organocobalt(III) derivatives by reaction 18 is virtually quantitative, the maximum yields of the initial vinyl complexes associated with reaction 18 can be limited by rearrangements of the organic fragments. For example, the reaction of $(TAP)Co^{II}$ with AIBN and 1-hexyne (T = 353 K) produces an 84% yield of (TAP)Co—C(=CH_2)$CH_2CH_2CH_2CH_3$ (**19**) over a period of 2 h, but longer reaction times result in the appearance of (TAP)Co—C(CH_3)=CH($CH_2CH_2CH_3$) (**20**), which over a period of 6 h becomes the dominant product (Figure 8). Compound **20** occurs exclusively as the isomer with the propyl group trans to (TAP)Co, as shown by the characeristic vinylic proton resonance at −2.96 ppm (J_1 = 7.1, J_2 = 1.1 Hz). The effective 1,3(H,H)-shift which produces **20** from **19** may be thermodynamically justified by relieving the steric interactions between the geminal (TAP)Co and *n*-butyl groups in compound **19**. Reaction of propargyl alcohol ($HC{\equiv}CCH_2OH$) with (TAP)Co—H provides another example where the initially formed vinyl complex, (TAP)Co—C(CH_2OH)=CH_2 (**23**), undergoes an isomerization. In this case, **23** is found to convert to (TAP)Co—CH(CH_3)CHO (**13**). This organic fragment rearrangement is viewed as proceeding through a 1,3(H,H)-shift to (TAP)Co—C(CH_3)=CH(OH) and subsequent rapid keto–enol isomerization to **13**, which is the thermodynamically preferred form. The distribution of **23** and **13** that is observed at several reaction intervals (353 K) is illustrated in Figure 9. Reaction of $CH{\equiv}C(CH_2)_3CN$ with (TAP)Co—H in $CHCl_3$ and DMF exclusively forms the vinyl complex (TAP)Co—C((CH_2)$_3$CN)=CH_2 without any evidence for isomerization even after prolonged heating (12 h, 353 K).



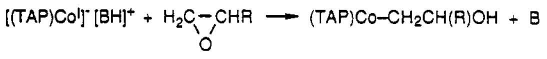
(19)

19 **20**

Reactions of Alkyl Halides and Epoxides. Solutions of $(TAP)Co^{II}$ with $^{\bullet}C(CH_3)_2CN$ radicals in $CHCl_3$ or benzene do not form organometallic products at a significant rate with alkyl halides or epoxides. However, adding Proton Sponge or changing to DMF as the solvent results in efficient conversions to organocobalt(III) complexes (Table III, Figure 5). The reactions observed for DMF solutions emulate the reactivity patterns for cobalt(I) porphyrins with alkyl halides,[11] suggesting that deprotonation of (TAP)Co—H produces a reactive $[(TAP)Co^{I}]^{-}$ species (eq 20–22). Kinetic observations for formation of organocobalt complexes by reactions 21 and 22 are presented in Figure 5. The alkyl halide reactions (eq 21) initially produce the alkylcobalt porphyrin at the same rate as initiator radical formation, implying that formation of (TAP)Co—H, deprotonation, and nucleophilic displacement are all fast compared with other potential radical reactions.

$$(TAP)Co{-}H + B \rightleftharpoons [(TAP)Co^{I}]^{-}[BH]^{+} \quad (20)$$

$$[(TAP)Co^{I}]^{-}[BH]^{+} + RX \rightarrow (TAP)Co{-}R + BHX \quad (21)$$



(22)

$$[(TAP)Co^{I}]^{-}[BH]^{+} + H_2C\overset{O}{-}CHR \rightarrow (TAP)Co{-}CH_2CH(R)OH + B \quad (22)$$

Inspection of Table III shows that, under the standard reaction conditions, alkyl iodides produce higher yields of organocobalt complexes than do alkyl bromides and chlorides (Table III). This probably results primarily from alkyl iodides having higher reaction rates rather than from thermodynamic factors.

The epoxides studied invariably react with $[(TAP)Co^{I}]^{-}$ to form β-hydroxyalkyl complexes (eq 22), but many of these organometallic derivatives fail to accumulate in observable quantities because of a subsequent reaction that forms ketones (eq 23). This type of reactivity is well

$$(TAP)Co{-}CH_2CH(X)OH \rightarrow (TAP)Co{-}H + CH_3C(O)X \quad (23)$$

established for β-hydroxyalkyl complexes of cobaloximes and cobalamines.[19,20] Epoxides that form alkyl complexes that lack a β-H can produce high yields of organocobalt complexes (compound **35**, Table III). Higher yields of β-hydroxyalkyl derivatives at lower temperatures (Table III) reinforce the assumption that decomposition by reaction 23 occurs via radical pair formation followed by β-hydrogen elimination[19] rather than by a concerted negative charge shift mechanism.[20]

Conclusions

The reactivity patterns for solutions of $(TAP)Co^{II\bullet}$ and alkyl radicals ($^{\bullet}C(CH_3)(R)CN$) with organic substrates provide indirect evidence for an intermediate cobalt(III) hydride, (TAP)Co—H. Addition reactions of (TAP)Co—H with alkenes and alkynes occur at a rate that effectively equals the rate of alkyl radical formation from the dialkylazo initiators and produce organocobalt porphyrin species with high regioselectivity that usually corresponds to the most stable organic radical fragment. The Markovnikov regioselectivity is kinetic in origin, as evidenced by examples where slow rearrangements to thermodynamically preferred organocobalt complexes are observed. Secondary alkyl complexes (TAP)Co—C(R)(R′)H have a tendency to rearrange by 1,2(Co,H)-shifts to form primary alkyl complexes, $(TAP)Co{-}CH_2R$, and vinyl complexes, $(TAP)Co{-}C(CH_2R){=}CH_2$, with a terminal double bond tending to rearrange by 1,3(H,H)-shifts to produce vinyl complexes with interior double bonds, $(TAP)Co{-}C(CH_3){=}CHR$. Diazo compounds that form alkyl radicals at lower temperatures produce higher yields of (TAP)Co—R species and minimize organic ligand isomerizations and other radical reactions that produce alternate organocobalt complexes. When formation of the Markovnikov addition product is sterically prohibited, an alternate pathway produces the anti-Markovnikov product. Reactions of (TAP)Co—H in the presence of $(TAP)Co^{II\bullet}$ with alkynes that have Markovnikov regioselectivity occur by stereoselective trans (anti) addition. Reaction of the alkyne with the most sterically demanding substituent ($HC{\equiv}CSi(CH_3)_3$) with (TAP)Co—H results in the vinyl product associated with anti-Markovnikov regioselectivity ($(TAP)Co{-}CH{=}CH(SiCH_3)_3$) and occurs by stereospecific cis (syn) addition. Highly regio- and stereoselective conversions of $(TAP)Co^{II\bullet}$ to organocobalt porphyrin derivatives obtained by convenient procedures suggest that the *tertiary radical synthesis* may find broad applications in preparing organocobalt(III) complexes.

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