Isotopic Investigation of Hydrogen Transfer Related to Cobalt-Catalyzed Free-Radical Chain Transfer

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The process of cobalt porphyrin catalyzed chain transfer in methacrylate free radical polymerizations shows a deuterium kinetic isotope effect greater than 3, indicating that hydrogen atom transfer occurs in the rate-limiting step of the catalytic cycle. This step involves formation of a transient hydridocobalt(III) complex by a reversible hydrogen atom abstraction from an incoming radical; the other product is an olefin. In some cases, the resulting radical can be trapped as the alkylcobalt(III) product. The use of labeled cyclic olefins indicates that the formation of the alkylcobalt(III) species can be at least partially stereoselective in some cases, and when it is, the addition is cis. Deuterated vinylidene olefins such as methyl methacrylate-d_8 were found to exchange the hydrogen of a cobalt porphyrin hydride to deuteride under free radical conditions. This exchange reaction can be used for deuterium labeling experiments—the transient cobalt deuterides are similarly trapped by addition of protioolefins. Thermal isomerization of the labeled product with time results in gradual loss of stereoselectivity, but observation of the initial stereoselectivity of this reaction indicates an underlying limit to the reaction selectivity. The ready availability of radical homolysis products will always limit the selectivity of the products. Similar experiments with acetylenes usually result in trans-vinyl products except when steric effects dominate. This shift from cis products with olefins to trans products for acetylenes is unexplained but may be attributed to radical intermediates or may indicate a role for a second cobalt complex in the transition state.

Introduction

Chain transfer catalysis (CTC) in the free-radical polymerization of methacrylates[2] can be described with the following two equations:

$$R_n^{\bullet} + Co^{\bullet} \rightarrow P_n + Co{-}H \quad (1)$$

$$Co{-}H + M \rightarrow R_1^{\bullet} + Co^{\bullet} \quad (2)$$

Here Co is a cobalt(II) chelate, Co−H is its cobalt(III) hydride. In the case where the monomer, M, is methyl methacrylate (MMA), $R_n^{\bullet}$ is a polymeric propagating radical of n units of MMA, $R_1^{\bullet}$ is propagating radical containing only one MMA unit, and P_n is a polymeric PMMA molecule with a terminal double bond. Although the kinetics of CTC have been the subject of several investigations,[3] the mechanism of both Co−H formation and the reaction of Co−H with monomer to yield a propagating radical remain undefined.[4]

During our initial investigation of CTC we explored the reaction of macrocyclic Co(II) complexes with radicals.[5] We found that the reaction of tertiary radicals with Co(II) is a convenient source of highly reactive CoH that can form organocobalt complexes when reacted with a variety of olefins or acetylenes. This approach allows the investigation of the reaction of Co(II) species with free radicals, providing important information on the free radical chemistry of low-spin cobalt(II) chelates.

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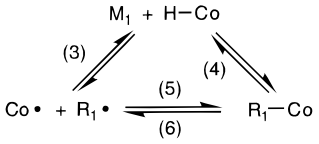
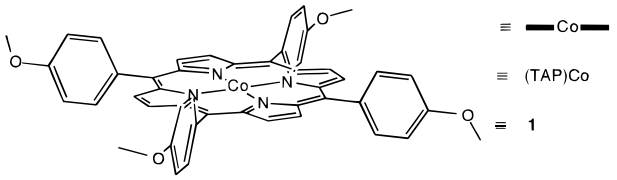
Despite the observed chemistry, the mechanism of the reaction remains a question.

Fortunately, we are able to draw upon a wealth of related chemistry which has been developed during investigations of vitamin B_{12} chemistry.[6] Cobalt−hydrogen bond formation could occur either by radical−radical hydrogen abstraction (reaction 3) or by β-hydrogen elimination from the organometallic (reaction 4) after radical−radical coupling (reaction 5). In vitamin-B_{12} chemistry, the abstraction pathway (reaction 3) is accepted to predominate over the associative/β-elimination pathway (5,4) under specific conditions.[7] The intermediacy of a caged radical pair can be important to the explanation of this chemistry. The generality of the former mechanism for planar Co(II) complexes with macrocyclic ligands remains unclear. Whether the latter pathway can play a significant role under some reaction conditions remains to be established. The mechanism may well be controlled by the choice of complex, substrate, medium, and reaction conditions. Our continuing studies of the chemistry of cobalt(II) porphyrin complexes in the presence of olefins and radicals of the general form $^{\bullet}C(CH_3)(R)X$ are aimed at these questions. The major difference between this chemistry and vitamin-B_{12} chemistry as it is normally studied is that the free radicals and resulting organometallics may be tuned over a wider range because they are not dependent on the dissociation of the Co−C bond (reaction 6) of a preformed organometallic species. Formation of the new organometallic by reaction of the presumed Co−H with substrate olefins is the dominant pathway. Additionally, the exchange of radical species is more facile as evidenced by the observation that vitamin-B_{12} is more than two orders of magnitude less reactive than cobaloximes in catalytic chain transfer chemistry.[8]



There have been several other occasions when the reaction of Co−H with double and triple bonds has been investigated. Gaudemer found cobaloxime deuteride underwent a stereoselective cis-addition to olefins and acetylenes,[9] but his latest experiments showed a maximum of ~70% cis-addition.[10] Setsune observed cis-addition is limited to ~60% of the events when (OEP)-CoD reacts with phenylacetylene.[11]

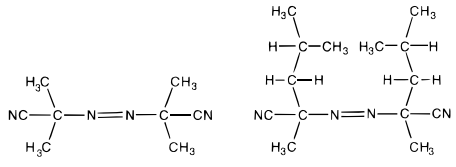
The aim of the present research is to obtain more information on the cobalt(II)−hydridocobalt(III) chemistry of cobalt porphyrins in the systems based upon (tetraanisylporphyrinato)cobalt(II) (**1**) in the presence

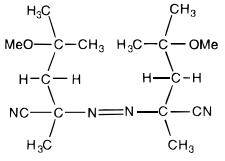


of radicals of the type $^{\bullet}C(CH_3)(R)X$, and its hydridocobalt(III) analog (**2**) in the presence of olefins and acetylenes. Previous papers in this series have dealt with the kinetics and thermodynamics of related systems. We now detail the application of isotopic labeling in probing the stereochemistry associated with the addition of Co−H species with olefins and acetylenes.

Experimental Section

Materials. (Tetra-*p*-anisylporphyrin)cobalt, (TAP)Co, and (octaethylporphyrin)cobalt, (OEP)Co (Aldrich), were recrystallized from chloroform−heptane. (Tetramesitylporphyrin)cobalt, (TMP)Co, was generously gifted by Dr. S. L. Mukerjee. Methyl methacrylate (MMA), methyl acrylate, and cyclopentene (Aldrich) were purified by multiple vacuum distillation to remove stabilizer immediately before use. Other olefins (Aldrich), as well as maleic anhydride-d_2 (Matheson), AIBN (2,2′-azobis(isobutyronitrile)) (Kodak), Vazo-52 (2,2′-azobis(2,4-dimethylpentanenitrile)) (DuPont), V-70 (2,2′-azobis(2,4-dimethyl-4-methoxypentanenitrile)) (Wako Chemicals), and $CDCl_3$ (Aldrich) were used as received. The temperatures at which their half-lives are 10 h are indicated by $T_{1/2}$).





Cyclopentene-d_8 was synthesized by modified literature procedure.[12] Purified cyclopentene (2 mL) was added into a thick-walled 25 mL flask containing mixture of 6 mL of D_2O and 3 mL of 20% solution of DCl in D_2O (deuterium content 99.5%, Aldrich). After two freeze−pump−thaw cycles the flask was sealed and immersed in a constant temperature bath at 130 °C with occasional stirring of the reaction mixture. After 3 days the flask was opened and cyclopentene was distilled out in a moderate vacuum (~10 mmHg). The partly deuterated cyclopentene obtained was dried by passing through 2 × 0.4 cm column of alumina and treated with diluted acidic solution once again as described above. The final cyclopentene-d_8 (~0.9 g) had ≥96% deuterium by NMR analysis.

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Table 1. Isotope Effect in Chain Transfer Catalysis[a]

		MMA		MMA-d_8		
temp (°C)	[Co] (10^4M)	M_n	M_w/M_n	M_n	M_w/M_n	k_H/k_D
40	4	630	1.79	2240	2.2	3.6 ± 0.3
40	2	1000	1.83	3430	2.6	3.4 ± 0.3
40	1	1670	2.06	5660	3.1	3.4 ± 0.3
60	4	590	1.89	2270	1.79	3.8 ± 0.3
80	4	680	1.86	2310	1.82	3.4 ± 0.3

[a] MMA-h_8 vs MMA-d_8 polymerization in the presence of (TAP-)Co, 10−15% conversion, [AIBN] = 0.08 M.

Synthesis of AIBN-d_{12} was conducted according to published procedures[13] from acetone-d_6 (99.5 atom % D, Aldrich) as a starting material. The final product was recrystallized from chloroform at −60 °C and had ∼97 atom % of D by NMR analysis.

Procedures. In a typical reaction procedure, 7.5 mg of (TAP)Co, 0.1−0.2 M olefin or acetylene and initiator were added to 1 mL of $CDCl_3$ in air and the resulting mixture was transferred to NMR tubes adapted for vacuum. After three freeze−pump−thaw cycles, the tubes were sealed and immersed in constant-temperature bath (±0.1 °C). Formation of organocobalt porphyrin was monitored using a 200 MHz NMR spectrometer at 23 °C.

Samples of poly(methyl methacrylate) (PMMA) were obtained by the following procedure. (TAP)Co was dissolved in $CDCl_3$ to obtain a 0.01 M solution which was injected with a precision micro syringe (Hamilton) into bulk, degassed MMA-h_8 or MMA-d_8 containing the initiator to achieve concentrations of $(1-4) \times 10^{-4}$ M of cobalt porphyrin. Sealed ampules were kept in an isothermal bath long enough to obtain 10−15% conversion. They were then opened and the polymer was isolated by removing monomer under high vacuum at room temperature. The concentration range of (TAP)Co was chosen to provide PMMA with molecular weights above 1500 to minimize the contribution from volatile low oligomers. The isotope effect reported is the ratio between chain transfer rate constant for MMA-d_8 and MMA-h_8 which were obtained as an average value of 6 experiments.

Polymer molecular weights and distributions were determined using a Water's microstyrogel column with pore sizes 100, 10^3, 10^4, and 10^5 Å on a Hewlett-Packard 1090 chromatograph with THF as solvent at 2 mL/min flow rate and RI detection against a PMMA standard. Molecular weights were high enough that there was no need to corrected for the known response factors of the low oligomers.[14]

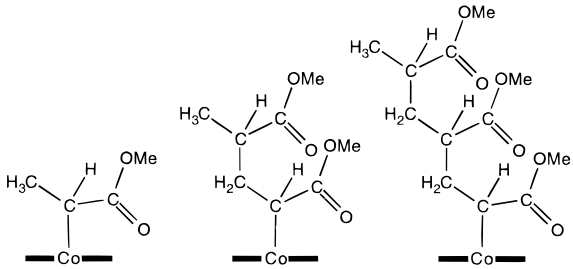
Results

Isotope Effect on Cobalt-Catalyzed Chain Transfer. When chain transfer catalysis is carried out in a methyl methacrylate free radical polymerization with relatively high concentrations of cobalt, it is possible to make oligomers with molecular weights in the hundreds or low thousands. If normal protio-MMA-h_8 is replaced with MMA-d_8, the molecular weight of the resulting oligomers increases significantly, displaying a clear kinetic isotope effect on the average polymer chain length. The k_H/k_D, which is presumably of the reaction of the polymeric free radicals with the Co(II) catalyst, is approximately 3.5 (Table 1) and relatively independent of temperature. This value of k_H/k_D is similar to the range (1.9−3.3) of kinetic isotope effects observed for hydrogen atom abstraction from a variety of substrates by different radicals by pathway 3.[15] The kinetic isotope effect would be expected to be smaller if it were observable at all if the rate-limiting step were to involve concerted β-hydride elimination as in reaction 4.[16] Nonetheless, the only definite conclusion from this series of experiments is that hydrogen atom transfer is involved in the rate-limiting step of CTC.

It would have been of interest to use isotopic measurements to determine the relative roles of hydrogen abstraction from radicals and hydrogen addition to olefins—the termination or initiation of polymer chains, respectively. This would require cross isotopic studies but the extensive isotopic scrambling which is discussed later in this paper precluded at least the straightforward versions of this experiment.

Reaction of CoH With Olefins. (a) Methyl Acrylate. The mild conditions of organometallic synthesis with tertiary-radicals allows the facile preparation of a variety of organocobalt(III) porphyrin complexes.[5b] Methyl acrylate figured prominently in that work. Methyl acrylate serves as a good example of complications that can arise in the isotopic studies later in this paper, so it will be discussed in some detail. Simple addition of the olefin to the Co−H bond accounts for most of the observed organometallic species, but with polymerizable olefins, secondary reactions can lead to more complex product mixtures.

When (TAP)Co^{II} is reacted with methyl acrylate in the presence of $^{\bullet}C(CH_3)_2CN$ radicals from AIBN, the initial dominant product is (TAP)Co−$CH(CH_3)COOMe$, **3**. The addition product, (TAP)Co−$C(CH_3)_2CN$, is not



3 **4** **5**

observed even though it is observed in the absence of acrylate. When the reaction is allowed to proceed for longer times, new products, **4**, **5**, and products bearing higher oligomers, based upon radicals derived from poly(methyl acrylate) are observed, finally complicating the spectrum to the point where interpretation becomes difficult.

This can be attributed to the dissociation of the Co−C bond and incorporation of additional monomer into the free radical chain. The conditions under which this polymerization reaction can become "living" have been detailed in another publication.[17] Typical NMR spectra obtained during radical polymerization of acrylates (Figure 1S in Supporting Information) can be used in the assignment of certain proton NMR signals of orga-

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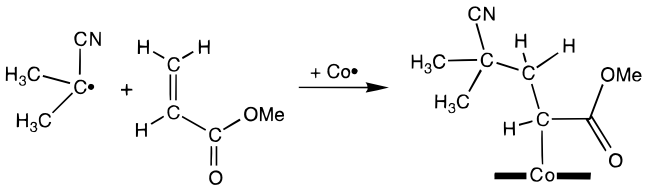
nocobalt porphyrins. The region around −1 ppm is attributed to resonances of the δ-methyl of the organocobalt groups. At the beginning of the polymerization some quantity of compound **6** forms (Figure 1S); the



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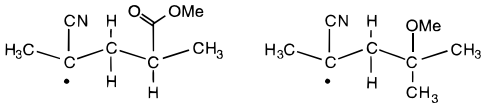
readily apparent diastereomers will be useful later in this paper. As the polymerization proceeds, the resonance of **6** is replaced by the characteristically broad NMR signals of oligo(methyl acrylate) complexes.

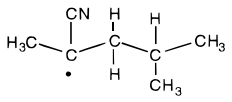
Formation of the poly(methyl acrylate) complexes can be suppressed by copolymerization with methacrylonitrile, clarifying the NMR assignments of oligomers up to pentamer and possibly higher. When methacrylonitrile is added to the methyl acrylate under otherwise identical conditions, the major product is again **6**. While some Co(III) cyanoisopropyl must be formed, rapid homolysis[5c] liberates Co(II) which is ultimately trapped as the more stable complexes with methyl acrylate or the cyanoisopropyl adduct of methyl acrylate, **6**.

Organocobalt porphyrin **6** has an optically active site which causes a diastereotopic splitting of the two methyl resonance of the cyanoisopropyl group (in Figure 2S: CH, bd, −3.40, J = 8; CH_2(A), d, −6.77, J = 13.5; CH_2-(B), t, −2.91, J = 10.8; CH_3, ds, −0.54 and −0.57). These chemical shifts of the methyl hydrogen resonances are consistent with the chemical shifts of the δ-CH_3 of other substrates which are observed at −0.7 ppm.[5b,18] By chance, the concentrations of the two diastereomers are equal within the limits of our measurements. As will be shown later in this paper, the characteristic doublet of the β-cyanoisopropyl end group is relatively independent of the nature of the monomer which has been inserted between it and the metal center.

The selectivity of this reaction is at first confusing—analysis of the organic products would indicate that additional organometallic species could easily have been formed, but yet, they are not observed. For instance, radical **7** would result from addition of the methyl



7 **8**



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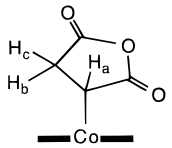
acrylate radical to methacrylonitrile. Addition of **7** to Co(II) would yield a complex which is an isomer of **6**, but the organometallic product from this likely radical species was not observed. The structurally similar radicals **8** and **9** were produced by thermal decomposition of the azo species, $T_{1/2}$-30 and $T_{1/2}$-52, respectively. The reactions were attempted under a variety of conditions known from previous experience with cyanoisopropyl complexes from AIBN. Under no conditions were organocobalt complexes of these species detected using either (TAP)Co or (OEP)Co. Thus it became clear that while there can be strong electronic influences on the stability of the Co−C bonds,[19] small increases in the size of the alkyl groups (from methyl to monosubstituted methyl in this case) can lower the stability of the organometallic complexes to the point that they unobservable under the conditions of this study. This steric effect will be utilized later in this investigation.

(b) Maleic Anhydride. The generality of organocobalt synthesis using tertiary radicals allows the facile synthesis of a variety of organocobalt(III) porphyrin species which could provide an insight into the stereoselectivity of the Co−H reaction with olefins. Particularly interesting are cyclic olefins contained a five-member ring because they give organometallic products with readily identified chemical shifts due to the shielding effect of the porphyrin ring currents.

Reaction of maleic anhydride with an *in-situ*-generated Co−H provides a quantitative yield of organocobalt porphyrin complex, **10**.



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This synthesis demonstrates versatility of syntheses employing tertiary radicals. Anhydride-bearing organocobalt porphyrins are difficult to synthesize by other methods. The structure has been confirmed in a preliminary X-ray determination.[20] Its proton NMR

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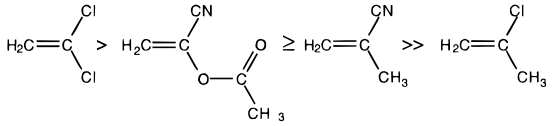
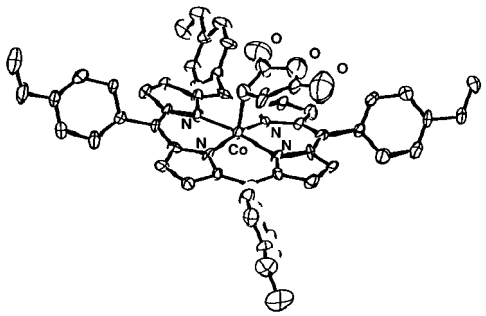
(19) The stability of the complexes resulting from addition of several olefins to Co−H were in the order



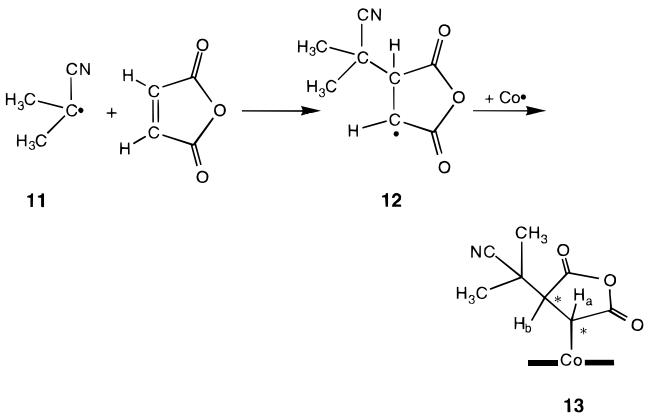
despite the fact that all formed tertiary alkyl complexes. Thus electronics are demonstrated to play a very important role in the bond dissociation energies of the resulting complexes.

(20) The maleic anhydride adduct of (TAP)Co crystallizes with one molecule of methylene chloride in the triclinic space group $P\bar{1}$, with a = 13.069(2) Å, b = 15.505(2) Å, c = 12.987(2) Å, α = 92.685(5)°, β = 116.607(10)°, γ = 90.728(8)°, and T = −50 °C. The methylene chloride solvent is disordered. The succinyl anhydride group also suffers a disorder resulting in unusually large thermal parameters for several atoms.



spectrum (Figure 3Sa in Supporting Information) is characterizes by three well-separated sets of resonances, making it convenient in model studies providing the resonances (1H, dd, −2.72, $J_1 = 20.5$, $J_2 = 8$; 1H, d, −3.51, $J = 8$; 1H, d, −5.32, $J = 20.5$) can be assigned with certainty. In our preceding paper, it was shown that the H_b (cis-β-hydrogen)[5b] resonance should be higher field than that of H_a (α-hydrogen). The resonance of H_c (trans-β-hydrogen) is expected to be lower field than that of H_b, so that the H_a and H_c resonances could be close or even overlapping, depending on the structure and the substituents in olefin addition studies. The coupling patterns of the H_a, H_b, and H_c hydrogen atoms are different. Due to an approximately 90° dihedral angle between atoms H_a and H_b, J_{ab} is less than 1 Hz. Hydrogen H_c couples with both hydrogen atoms H_a and H_b, resulting in a doublet of doublets pattern. The most reasonable assignment for the resonances of **10** is −3.51 ppm for H_a, −5.32 ppm for H_b, and −2.72 ppm for H_c, an assignment supported by decoupling experiments.

Further evidence for the assignment of hydrogen resonances was obtained by continuous heating of **10** in the reaction solution. On the basis of our earlier results,[5b] quantitative conversion of the (TAP)Co^{II} into organometallic Co(III) derivative should be achieved in 150−180 min at 60 °C, though in some cases, additional organometallic species are observed under these forcing conditions. When the supply of (TAP)Co^{II} in the reaction mixture is exhausted by conversion to Co(III), the cyanoisopropyl radical, **11**, formed by decomposition of



AIBN presumably adds to free maleic anhydride and the resulting radical, **12**, replaces the axial substituent of **10** or, more likely, react with traces of (TAP)Co formed by homolysis of the Co−C bond in **10** to produce the observed product, **13**. The spectrum (Figure 3Sb) has two strong, three-proton singlets at −0.46 and −0.50 ppm and two single proton singlets at −3.45 and −5.55 ppm.

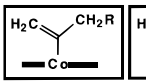
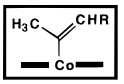
The organocobalt(III) porphyrin, **13**, has two optically active centers leading to the diastereotopic cyanoisopropyl group with two distinct methyl resonances. Because there are two optically active centers, the two diastereotopic methyl groups might have been expected to yield four methyl resonances like those shown in Figure 1S. There are two possible isomers, cis and trans addition of Co and R• across the maleic anhydride double bond, but only one is observed. The demanding steric constraints mentioned above and space-filling models

Table 2. Stereoselectivity of CoH Addition to the Double Bond of Maleic Anhydride-d_2[a]

porphyrin	initiator	temp (°C)	% cis addition
(TMP)Co	AIBN	60	50
(TAP)Co	AIBN	60	50
(OEP)Co	AIBN	60	68
(TAP)Co	Vazo-52	60	50
(TAP)Co	Vazo-52	40	87
(TAP)Co	V-70	23	93
(TAP)Co	V-70	6	>98

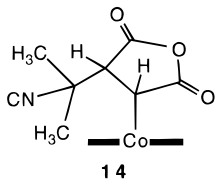
[a] In $CDCl_3$, [cobalt porphyrin] = 0.01 M, [AIBN] = 0.08 M, [VAZO-52] = 0.08 M, [V-70] = 0.065 M, 80−90% conversion.

Table 3. Organometallic Products of Cobalt Porphyrin Reaction with Acetylenes

Acetylene	Porphyrin	Time (min)	 %	 %
$HC{\equiv}C(CH_2)_3CH_3$	(OEP)Co	180	12	88
"	(TAP)Co	180	66	34
"	(TAP)Co	360	38	62
"	(TMP)Co	180-400	>99	<1
$HC{\equiv}C(CH_2)_3CN$	(OEP)Co	360	84	16
"	(TAP)Co	360	95	5
"	(TMP)Co	360-800	>99	<1

Cobalt porphyrin (0.01 M); acetylenes (0.1 M); AIBN (0.08 M) at 60°C in $CDCl_3$

of **14** indicate that the cis adduct is extremely hindered



14

and therefore unlikely. The remaining resonances correspond well with the assignment for the simple maleic anhydride product. Complex **13** is a good model for **10**, and comparison of the NMR spectrum of **6** with that of **13** confirms the assignment of the −3.51 ppm signal in **10** to the hydrogen atom labeled H_c.

Reaction of maleic anhydride-d_2 with Co(II) under free radical conditions at low temperature (6 °C) produces an organometallic species with a single proton resonance at high magnetic field (−5.32 ppm), indicating selective formation of the cis-hydrogen adduct of **10-d_2** (Table 2). Elevated temperatures (60 °C) with substituted meso-arylporphyrins reduce selectivity and the −2.7 ppm signal of the trans-adduct (hydrogen-H_c) grows in at a rate equal to that of the cis adduct; thus at 60 °C all selectivity is lost. This may be the result of isomerization of the initial cis-complex by Co−C bond cleavage of **10** to the caged radical pair. Rotation of the radical followed by recombination with cobalt would result in loss of stereoselectivity. Higher selectivity (2.1 cis/trans ratio) at 60 °C for (OEP)Co can be rationalized on the basis of slower dissociation of the Co−C bond due to the reduced steric repulsion compared with tetraaryl porphyrins such as (TAP)Co and (TMP)Co.

(c) Cyclopentene. Maleic anhydride is an unusual olefin with behavior quite unlike other olefins in many cases due to the strong electron-withdrawing effect of its conjugated carbonyl groups. For this reason, we

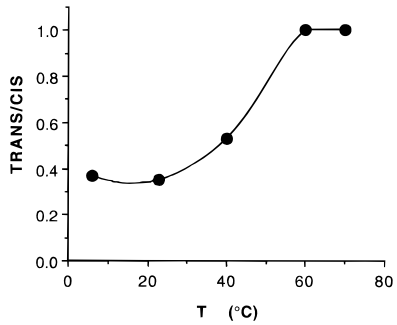


Figure 1. Temperature dependence of ratio of trans and cis addition of (TAP)CoH to the double bond of cyclopentene. Conditions: $CDCl_3$, [(TAP)Co] = 9.4×10^{-3} M, [cyclopentene-d_8] = 1.0 M; [AIBN] = 0.08 M (for 60 and 70 °C), [V-70] = 6.5×10^{-2} M (6 and 23 °C), or [VAZO-52] = 0.08 M (40 °C). The time of the reaction corresponds to a steady-state concentration of organocobalt porphyrin.

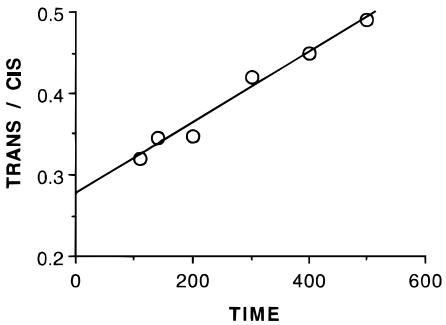
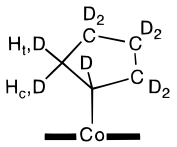


Figure 2. Dependence of the ratio of trans and cis vinylic hydrogen signals of (TAP)Co−cyclopentyl-h_1d_8 on the time of reaction. Conditions: $CDCl_3$, [(TAP)Co] = 9.4×10^{-3} M, [cyclopentene-d_8] = 1.0 M, [V-70] = 6.5×10^{-2} M, 23 °C.

decided to extend this study to other, more simple olefins. Cyclopentene reacts with (TAP)Co under free radical conditions to form the Co(III) cyclopentyl complex. Cyclopentene-d_8 reacts with (TAP)Co to form **15**



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[−2.73 (trans-β-hydrogen); −6.27 ppm (cis-β-hydrogen)]. Like maleic anhydride, there is little stereoselectivity in the cyclopentyl adduct product at temperatures above 60 °C, but at room temperature, the ratio of cis to trans is 2.8 ± 0.3. Surprisingly, this value does not seem to vary appreciably as the temperature of the reaction is lowered further (Figure 1). This limit on selectivity must be rationalized.

If the rate of cis−trans isomerization of the complex is nearly equal to the rate of formation, then it is possible that competition between formation and isomerization could account for the observed results. This model is easily tested by monitoring the kinetics of the isomerization of the reaction mixture at the temperature where the cis/trans ratio of 2.8 is formed. Once the cis/trans ratio of products is established at room temperature, the isomerization of the product to a cis/trans ratio of unity at elevated temperatures can be observed. The observed isomerizations at elevated temperatures make it clear that at room temperature and below, the thermal cis−trans exchange of labeled (TAP)Co−cyclopentyl complex is insignificant (Figure 2). Hence, isomerization after addition cannot explain the relatively low stereoselectivity of Co−H addition to the double bond of cyclopentene. There is an inherent limit to the selectivity not attributable to subsequent isomerization.

One explanation of this reduced selectivity is that the lifetime of the solvent-caged radical pair formed by reaction of olefin with Co−H is on the same order as a molecular rotation of the organic radical. The selectivity of the reaction extrapolated back to time zero is the inherent selectivity of the initial reaction. The reduced selectivity of longer reaction times is a reflection of the ability of the resulting Co(III)−R species to redissociate to the caged pair allowing further loss of selectivity.

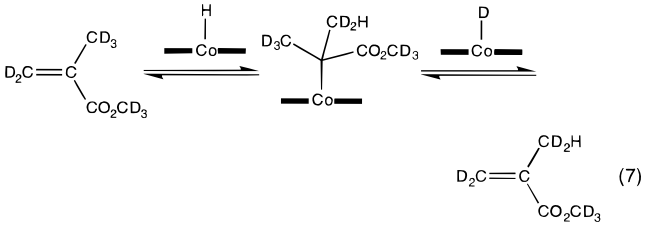
Significantly, no resonances other than those at −2.73 and −6.27 ppm appear during the isomerization experiments above 50 °C nor do they appear during long-term storage at room temperature. If β-hydride elimination and re-addition inside the radical cage was playing an important role in the isomerization process, then multistep processes involving competition between elimination from the initial CHD group or the adjacent CD_2 group would be expected to generate resonances attributable to other positions on the ring. The observation that the hydrogen label remains in the β-position whether it be cis or trans, leads to the conclusion that isomerization through β-hydride elimination and re-addition does not play a significant role in the isomerization process. Recombination of the radical pair formed by Co−C bond homolysis must also be faster than β-hydrogen abstraction from the radical because this would give results identical to β-hydride elimination and re-addition.

The time dependence of isomerization presented in Figure 2 rules out the intermediacy of Co−H in the isomerization process. Any Co−D formed by β-hydrogen abstraction would give an NMR-silent product upon reaction with the next molecule of the excess deuterated cyclopentene. In the case of formation of a Co−H intermediate followed by reaction with new cyclopentene-d_8, the cis/trans ratio should not change. This is additional evidence that cobalt combination with the radical (reaction 5) is significantly faster than cobalt hydride formation via abstraction from the radical (reaction 3) as originally suggested by initial kinetic studies.[5c]

(d) H−D Exchange with Labeled Olefins. The observed differences in the reactions of maleic anhydride and cyclopentene with Co−H bonds prompted us to study other olefins, but the number of commercially available deuterated olefins suitable for the purposes of the present research is limited. Another possible way to study stereoselectivity of Co−H reactions with olefins is to replace Co−H with Co−D and utilize nonlabeled olefins. Synthesis of Co−D is readily achieved utilizing perdeuterated AIBN. This approach is limited, however, because AIBN decomposes at reasonable rates only at temperatures above 40 °C where we have already demonstrated that extensive isomerization can complicate the investigation. In addition, at elevated temperatures the yields of products from these radical-mediated syntheses decrease leading to unacceptably low signal-to-noise levels in the NMR experiments.[5c] Synthesis of perdeuterated azo-initiators active at lower

temperatures would be an alternative approach, but their synthesis entails significant technical difficulties and expense. Fortunately, attempted labeling studies of commercial MMA-d_8 provided a ready solution to the problem.

It was observed that methacrylonitrile exchanges with Co−H hundreds of times faster than cyclopentene.[21] Methyl methacrylate and its d_8-analog would be expected to behave in a manner similar to methacrylonitrile rather than cyclopentene. We observe rapid Co−H to Co−D exchange upon addition of deuterated MMA to the reaction mixture.



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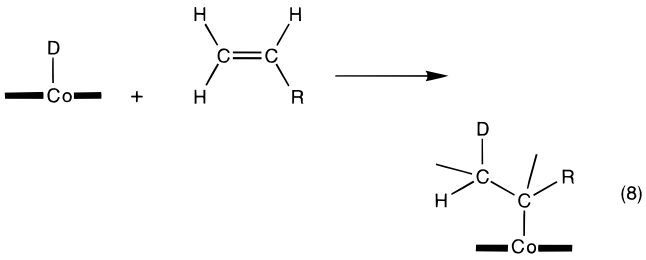
The resulting Co−D can then be trapped with olefins which undergo slower H−D exchange but which form more stable Co(III) alkyls.



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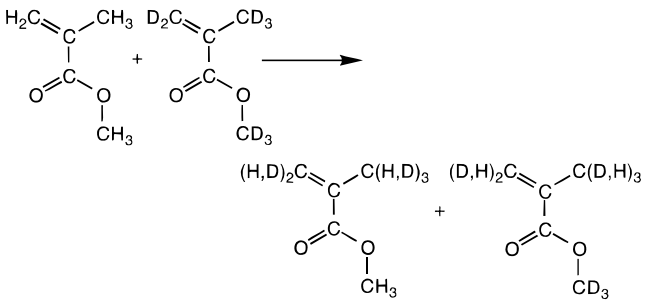
Because the protio initiators are present in concentrations lower than the MMA-d_8, they do not contribute significantly to the Co(III) hydride/deuteride pool.

Another demonstration of this process results from the mixing of MMA and MMA-d_8 under chain transfer conditions involving very high levels of cobalt. The course of the reaction can be followed mass spectrometrically. Over a period of hours, the peaks at mass 100 and 108 (MMA and MMA-d_8, respectively) are redistributed to a complex mixture of isomer containing all masses in between. The pattern is not a normal distribution because the three hydrogen atoms of the methyl group are not involved in the exchange process.



Conveniently, by electron impact mass spectroscopy, the base peak of the spectrum is MMA minus OMe. In that case, the initial spectrum displays peaks at 79 and 84 and at the end of the reaction the peaks are distributed statistically between those two numbers. Thus, the trace concentrations of cobalt hydride generated under these conditions are reacting with both the MMA and MMA-d_8 to exchange the five protons which are associated with the ethylene or methyl, while the three methoxy protons do not exchange.

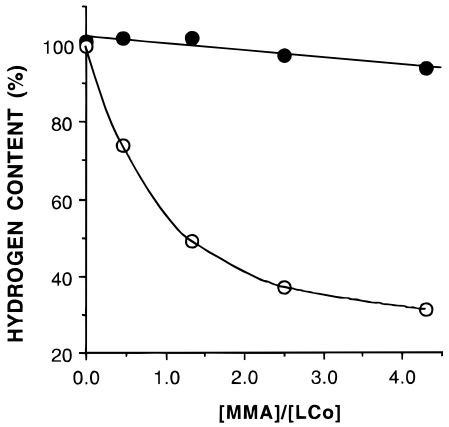


Figure 3. Dependence of hydrogen content at the tetrahydrofuranyl β-carbon atom of (TAP)Co−3-tetrahydrofuranyl on the relative concentration of MMA-d_8. Conditions: $CDCl_3$, 23 °C, 150 min, [V-70] = 6.5×10^{-2} M, [(TAP)Co] = 9.4×10^{-3} M, [2,5-dihydrofuran] = 0.9 M. Key: ●, trans; ○, cis β-hydrogen. (The measurement was relative to the integration of the other methylene hydrogen atoms; hence, the slight increase above 100% indicates the accuracy of the experiment.)

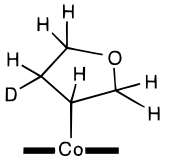
Deuterium exchange with MMA is sufficiently rapid that stoichiometric quantities seem to be sufficient. As demonstrated by the relative proton integrations of the cis and trans hydrogen atoms of a dihydrofuran adduct to Co−H/Co−D, a concentration of MMA-d_8 equimolar to that of the porphyrin exchanges almost half of the hydride to deuteride (Figure 3). One could assume that the isotope effect of the $(CH_3)_2(CN)C^{\bullet}$ radical is similar to that of PMMA-derived radical, or about 3.5. Once MMA-d_8 has received a hydrogen atom from Co−H the proportion of deuterium atoms to hydrogen atoms in the intermediate radical species is 5:1, so it is clear that the observed deuterium incorporation of about 50% into the organocobalt chelate when the [(TAP)Co]/[MMA-d_8] ratio is approximately one approaches its theoretical limit. One of the limitations of the MMA-d_8 method to generate Co−D is that high concentrations of MMA can decrease the yield of the organometallic products; thus, in H/D exchange experiments the lowest practical concentrations of MMA are generally preferred.

(e) Other Olefins. Preliminary testing of the above approach with cyclopentene and maleic anhydride yielded results analogous to those observed with their deuterium-labeled counterparts, though slight deuterium kinetic isotope effects would be expected to affect the selectivities. For instance, the reaction with maleic anhydride, V-70, (TAP)Co, and MMA-d_8 at 6 and 23 °C resulted in a product **10-d_1** with resonances at −3.51 and −2.72 ppm; the resonance at −5.32 ppm for H_b was missing as expected.

The yield of the reaction of (TAP)Co with 2,5-dihydrofuran was relatively insensitive to the presence of added MMA. Concentrations of MMA-d_8 comparable to those of (TAP)Co do not significantly reduce the yield

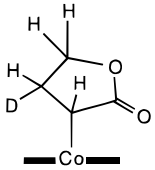
(21) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1996**, *15* (1), 222.

of the (TAP)Co−3-tetrahydrofuranyl product



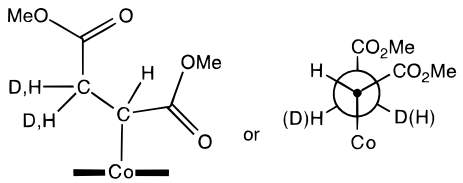
and clearly indicates a preference for cis-addition of (TAP)CoD to the double bond of 2,5-dihydrofuran (cis/trans is approximately 2.5).

Completing the series between maleic anhydride and dihydrofuran, reactions with 2(5*H*)-furanone in the presence of MMA-d_8 gave the product



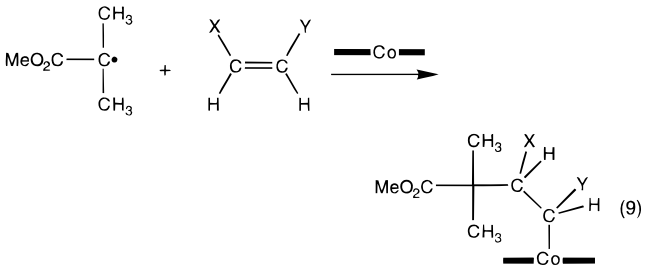
The addition was predominently cis (probably greater than 93%), but overlaps in the NMR spectra of the resulting products resulted in a relatively high uncertainty (±7%) for these measurements.

Experiments with the isomeric acyclic esters dimethyl maleate and dimethyl fumarate (V-70, (TAP)Co, and MMA-d_8 at 6 and 23 °C) resulted in identical products. Equal population of the two β-hydrogen atoms (−4.6 and −3.2 ppm) with hydrogen and deuterium indicated no selectivity in the reaction, as did the inability to differentiate between the addition products of dimethyl maleate and dimethyl fumarate.



The spectroscopic differentiation between the two β-hydrogen atoms in the organocobalt porphyrin was particularly notable. The chiral center at the α-carbon center produces a strong diastereotopic effect in the two β-hydrogen atoms. The two β-hydrogen atoms had distinctly different coupling constants, indicating a significant barrier to free rotation of the second carbon atom. Similar, strong diastereotopic splittings of the β-hydrogen atoms were found in the case of fumaronitrile (CH + CH_2(A), bm, −3.9; CH_2(B), dd, −3.45, J_1 = 17, J_2 = 9) and methyl crotonate (CH, dd, −3.62, J_1 = 11.8, J_2 = 3; CH_2(trans), m, −4.02; CH_2(cis-), bm, −5.75; CH_3, t, −1.57). (Also note Figure 1S.)

The use of MMA-d_8 to generate (TAP)CoD is not without complications. The addition reaction of the MMA radicals [$(CH_3)_2(CO_2CH_3)C^{\bullet}$] with the target olefin followed by addition of the radical adduct to the cobalt porphyrin (reaction 9) can yield more complicated products. Reaction 9 has been observed as an important side reaction with substrates such as vinylene carbonate, and maleic anhydride, as mentioned above. It is especially important in the reaction with succinonitrile in the presence of MMA. The reaction may at first appear to be putting an NMR-silent deuterium atom



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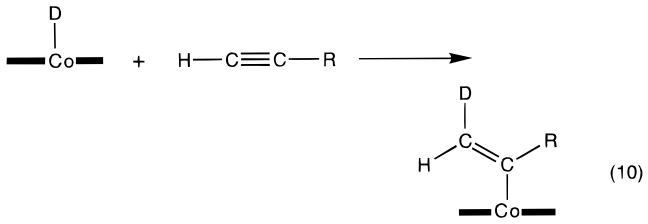
into the resulting complex because the MMA-d_8 moiety is similarly NMR-silent, but the observed NMR spectrum is not the same as would be expected in the absence of MMA-d_8. Reference experiments with nondeuterated MMA allow the MMA incorporation to be monitored by the characteristic singlet (or pair of singlets for optically active axial ligands) at approximately −0.65 ppm (similar to those shown in Figures 1S and 2S). Incorporation of the bulky dimethylmethoxycarbonyl methyl substituent instead of hydrogen usually causes a slight upfield shift of the signal of the trans-β-hydrogen, making it possible to spectroscopically differentiate the two organometallic species obtained.

Reaction of Co−D with Acetylenes. As noted in one of the early papers in this series,[5b] acetylenes form rather stable vinylic organocobalt complexes under free radical conditions. To determine the stereochemistry of the reaction, reaction 6 can once again be utilized to provide the Co−D intermediate which is then trapped in the vinyl complex by reaction 10.



(10)

The reaction proceeds well even in the presence of a 100-fold excess of MMA-d_8 to generate the label. The addition of the cobalt deuteride to 1-hexyne or 5-hexynenitrile is found to display Markovnikov regioselectivity and trans (anti) stereoselectivity. (See Figure 4S in the Supporting Information. The top of Figure 4S is the protio reaction and the reaction in the bottom portion includes MMA-d_8. The resonance marked (a) is the trans-vinylic proton resonance while (b) is the cis-vinylic proton signal. It is clear that the trans signal disappears while the cis proton becomes a singlet.)

Because the addition of acetylenes gives such high conversion of the Co(II) to vinylcobalt(III) porphyrins, it was felt that it should be possible to carry out the labeling study using AIBN-d_{12} as a source of (TAP)CoD. Unexpectedly, it was found that incorporation of deuterium into the axial vinyl substituent on cobalt was dependent on the concentration of the acetylene. Comparison of trans-vinyl hydrogen signal with that of cis-vinyl and other CH_2-hydrogen atoms in the products showed incorporation of only 40 atom % of D when the 1-hexyne concentration was 0.04 M. The percent deuterium incorporation increased systematically to 90 atom % in the trans-vinylic site at a 1 M concentration of 1-hexyne (Figure 4). The deuterium content of the

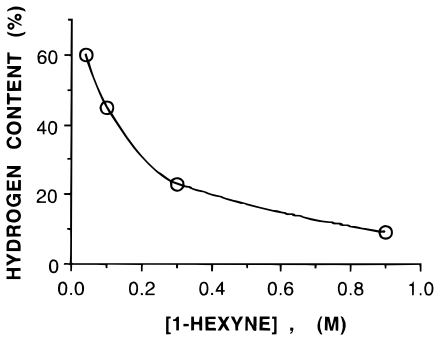
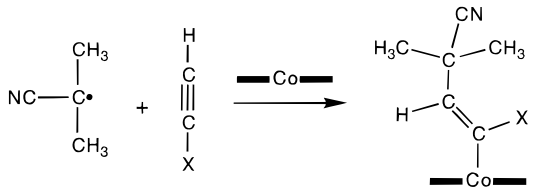


Figure 4. Hydrogen content at the trans-vinylic site of (TAP)Co−C(=CH_2)(CH_2)$_3CH_3$ as a function of the concentration of 1-hexyne. Conditions: $CDCl_3$, [AIBN-d_{12}] = 0.07 M, 60 °C, 40 min, [(TAP)Co] = 9.4×10^{-3} M.

product was also found to increase during the course of a reaction when run at a fixed acetylene concentration. For instance, the deuterium content increases from 40 atom % at 40 min or about 20% conversion of (TAP)Co to 57 atom % at 160 min or about 80% conversion. It should be stressed that there was no deuterium incorporation at cis-vinylic site occurred during these experiments; the deuterium was simply being lost to an unknown side reaction. Presumably, some impurity partially exchanges deuterium in (TAP)CoD back to hydrogen before the acetylene traps the deuteride/hydride. Carrying out the reaction in the presence of a very large excess of MMA-d_8 thereby assuring multiple exchanges of the hydrogen or deuterium atom overcomes the unknown reaction and provides a practically quantitative level of deuterium incorporation in the trans vinyl position. Similar results were obtained employing 5-hexynenitrile.

As in the case of olefins, the nature of hydride addition to acetylenes is dependent on the structure of the acetylene. Thus, methyl propiolate in the presence of MMA-d_8 and V-70 as a radical source produces an organometallic at 23 °C with cis-/trans-addition ratio of approximately one. This ratio cannot be explained by thermal isomerization because once again, the Co−C bond energy of these vinylic compounds should be too high to allow isomerization on the time scale of these experiments, especially at the temperatures employed.

As in the use of MMA-d_8 to generate (TAP)CoD for reactions with olefins, the addition reaction of the MMA radicals [$(CH_3)_2(COOCH_3)C^\bullet$] with acetylenes followed by addition of the radical adduct to the cobalt porphyrin is an important side reaction.



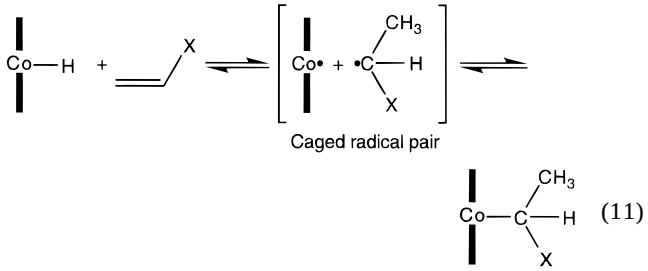
This type of product has been observed with substrates such as methyl propiolate and phenylacetylene.

Discussion

The kinetic isotope effect observed in the process of chain transfer catalysis indicates that hydrogen atom transfer is involved in the rate determining step of the chain transfer process. The particular reaction involves transfer of the hydrogen atom from carbon to a metal center. It is difficult to conclude more from this single line of experimentation, though the observation clearly points toward a fruitful area of investigation which we will encourage and aid others to pursue.

Under conditions of interest for CTC (reactions 1 and 2) in free radical methacrylate polymerizations the concentration of Co(III) alkyls is an order of magnitude less than the concentration of free Co(II) and the concentration of Co(III)−H must be at least another order of magnitude lower.[2b,3f,22] Hence, the rate-limiting step of CTC must be reaction 1 and the observed lowering of the average molecular weight of the resulting PMMA reflects the rate of reaction 1 rather than that of reaction 2.

Isotopic investigation of reactions in which observable levels of organometallic products are formed provides additional information about the reactions of olefins with Co(II) species under free radical conditions. We conclude that olefins react with Co−H in a stereoselective insertion to give preferentially cis products, but that there are often opportunities to loose this stereoselectivity. The intermediacy of the caged radical pair [LCo• + •R] which is formed as the initial product upon reaction of CoH and olefin probably determines the selectivity of the reaction. If the radical pair collapses immediately to product, then stereoselectivity is retained and the reaction is difficult to differentiate from a concerted addition. If the lifetime of the radical pair is as long as a rotation of the radical or if the radical leaves the caged pair, then the stereoselectivity of the reaction is compromised. However, if the radical pair has a lifetime on the order of a molecular rotation, then intermediate levels of stereoselectivity are expected.



(11)

Because vitamin B_{12} chemistry played such an important role in the early development of organocobalt(III) chelate chemistry, it has become *de rigueur* to consider all results from that point of view. Commercial interest in application of cobalt chelates in processes like living radical polymerization[17,23] and CTC[24] are leading to renewed interest in this area and are requiring a fresh look at the important steps in this chemistry. Cobalamine is several orders of magnitude less reactive in chain transfer catalysis than are cobalt porphyrins and especially cobaloximes.[8] The steric hindrance of the active center in cobalamine is not sufficient to rationalize the difference because (TMP)Co has a catalytic site

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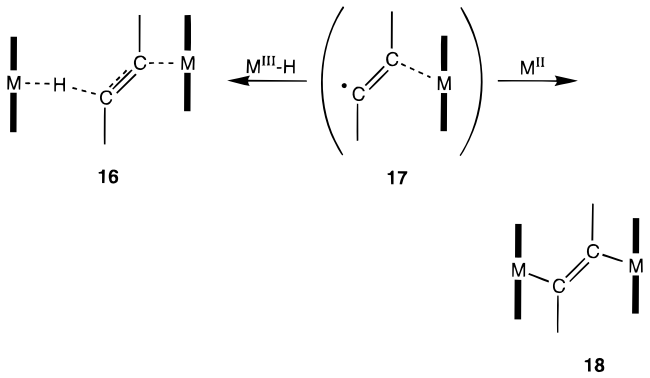
which is more restricted than that in cobalamine, yet it is almost as reactive as cobalt tetraphenylporphyrin.[7h] The significant difference in reactivity between cobalamine and cobaloximes is likely due to the inherent difference between their ligand structures. It is probable that some basic aspects of the free-radical chemistry of cobaloximes and cobalamines are different, making uncritical extrapolation of conclusions obtained in vitamin-B_{12} chemistry to other cobalt chelates risky. There are a number of mechanism which are possible alternatives to the one presented here; we considered only radical-type, single-step processes not involving the ligands. The possibility of H−D exchange through protic intermediates was recognized even in the very earliest work on hydridocobalt(III) chelate reactions.[25,26] The work described here demonstrates that olefinic impurities can lead to very rapid *aprotic* exchange which must also be considered in labeling experiments. These alternative mechanisms are considered in more detail in the Supporting Information.

Acetylenes. It is unclear why the stereoselectivity of Co−H addition reactions to olefins are generally cis while the additions of acetylene are trans. There are a number of both cis[27] and trans[28] additions of acetylenes known in platinum chemistry and it has been suggested that radical intermediates can play a role in these insertions.[29] Cis additions are thought to indicate concerted insertion reactions while trans additions are indicative of radical pathways. In cases of acetylenes with sterically demanding substituents, the regio- and stereo-chemistry of the addition was reversed.[5c]

The trans addition of cobalt hydride to acetylene might proceed through the intermediacy of species like **16** and **17**.



Structures of the type shown for **18** are well documented in rhodium porphyrin chemistry.[30] They are presumed to form through association of an acetylene with one metal centered radical and the resulting organic radical is trapped by addition of a second metal-centered radical. The lower bond dissociation energy of cobalt relative to rhodium might disfavor species like **18** relative to rhodium chemistry, thereby favoring the reaction with metal−hydride intermediates. Any species like **17** would ultimately be trapped by the reactive Co−H through **16** to form a trans product.

Conclusions

The process of cobalt porphyrin catalyzed chain transfer in methacrylate free radical polymerizations shows a deuterium kinetic isotope effect greater than 3, indicating that hydrogen atom transfer occurs in the rate-limiting step of the catalytic cycle. This step involves formation of a transient hydridocobalt(III) complex by a reversible hydrogen atom abstraction from an incoming radical; the other product is an olefin. For methacrylates and methacrylonitrile, this process is reversible and rapid. This rapid reversibility is manifested by the isotopic exchange between unlabeled and deuterium labeled methacrylates through the intermediacy of a cobalt porphyrin hydride/deuteride under free radical conditions.

This exchange reactions has implications for the catalytic chain transfer process. Under conditions of high catalyst levels, it had normally been thought that the dimer was the lowest oligomer product formed, but it is now clear that the most prevalent "product" would be monomer which has been converted to monomer radical and then traped by the catalyst before it could react with monomer to yield dimer radical. The kinetic implications of this process are detailed elsewhere.[31]

In reactions with olefins which would form secondary rather than tertiary alkyls, the resulting radical can be trapped as a stable alkylcobalt(III) product. The use of labeled cyclic olefins indicates that the formation of the alkylcobalt(III) species can be at least partially stereoselective in some cases and when it is, the addition is cis. The exchange reaction of deuterated vinylidene olefins such as methyl methacrylate-d_8 provides a convenient new method for deuterium labeling experiments under mild conditions. The transient cobalt deuterides are similarly trapped by addition of pro-

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tioolefins, again yielding cis adducts when stereoselectivity is evident.

The stability of the resulting Co(III) alkyls is related to both steric and electronic factors. Tertiary alkyls are marginally stable largely for steric reasons—cyanoisopropyl Co(III) is observable at room temperature while the larger Co(III) carbomethoxyisopropyl is not. Increasing the size of one methyl on the cyanoisopropyl group renders the resulting complex unobservable at room temperature. Secondary alkyls are much more stable, with electron-withdrawing groups increasing the stability.

Thermal isomerization of the labeled products with time results in gradual loss of stereoselectivity, but observation of the initial stereoselectivity of this reaction indicates an underlying limit to the reaction selectivity with selected olefins. The ready availability of radical homolysis products will always limit the selectivity of the products.

Similar experiments with acetylenes result in trans-vinyl products except when steric effects dominate. This shift from cis products with olefins to trans products for acetylenes is unexplained, but may indicate a role for a second cobalt complex in the transition state.

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Supporting Information Available: NMR spectra, text and a figure providing preliminary crystallographic information, and text containing a discussion of possible alternative mechanisms (20 pages). Ordering information is given on any current masthead page.

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