

Figure 1. The structure of adenosylcobalamin (Coenzyme B₁₂) and the abbreviation for the coenzyme that is used throughout the text.

homolysis^{6d,10,11} and H[•] transfer steps¹² have appeared, but the question of the subsequent steps and of cobalt participation or nonparticipation has remained unanswered. In particular, neither studies of the enzymes¹³ nor recent theoretical,¹⁴ pulse radiolysis,¹⁵ Co(III) π -complex,¹⁶ or other model studies¹² have been able to provide a consistent or convincing picture of the rearrangement step. It is important to note that the starting point for many of the previous studies is the *assumption* that the B_{12(r)}, Co(II), and RCH(OH)CHOH radicals of Scheme I combine to form Co-

(10) Although photochemical Co-C bond homolysis in models is very well-known, *quantitative* studies of the thermal homolysis of this bond have only recently appeared. (a) Halpern, J. *Acc. Chem. Res.* **1982**, *15*, 238. (See also: ref 3b, Chapter 14.) (b) Halpern, J.; Ng, F. T. T.; Rempel, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 7124. (c) Schrauzer, G. N.; Grate, J. H. *Ibid.* **1981**, *103*, 541. (d) Ng, F. T. T.; Rempel, G. L.; Halpern, J. *Ibid.* **1982**, *104*, 621. (e) Tsou, T. T.; Loots, M.; Halpern, J. *Ibid.* **1982**, *104*, 623. (f) Gjerde, H. B.; Espenson, J. H. *Organometallics* **1982**, *1*, 435. (g) Reference 6d.

(11) For structural model studies related to the homolysis step see: (a) Marzilli, L. G. *Prog. Inorg. Chem.*, in press. (b) Randaccio, L.; Bresciani-Pahor, N.; Toscano, P. J.; Marzilli, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 6347. (c) *Ibid.* **1980**, *102*, 7372. (d) Marzilli, L. G.; Toscano, P. J.; Randaccio, L.; Bresciani-Pahor, N.; Calligaris, M. *J. Am. Chem. Soc.* **1979**, *101*, 6754. (e) Marzilli, L. G.; Toscano, P. J.; Ramsden, J. H.; Randaccio, L.; Bresciani-Pahor, N. In "Catalytic Aspects of Metal Phosphine Chemistry"; Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, DC, 1982; Adv. Chem. Ser. No. 196. (f) Chemaly, S. M.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2259 (part 17); 2267 (part 18); 2274 (part 19).

(12) (a) Golding, B. T.; Sell, C. S.; Sellars, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 961. (b) Golding, B. T.; Kemp, T. J.; Sell, C. S.; Sellars, P. J.; Watson, W. P. *Ibid.* **1978**, 839. (c) Rudakova, I. P.; Ershova, T. E.; Belikov, A. B.; Yurkevich, A. M. *J. Chem. Soc., Chem. Commun.* **1978**, 592. (d) Breslow, R.; Khanna, P. L. *J. Am. Chem. Soc.* **1976**, *98*, 1297.

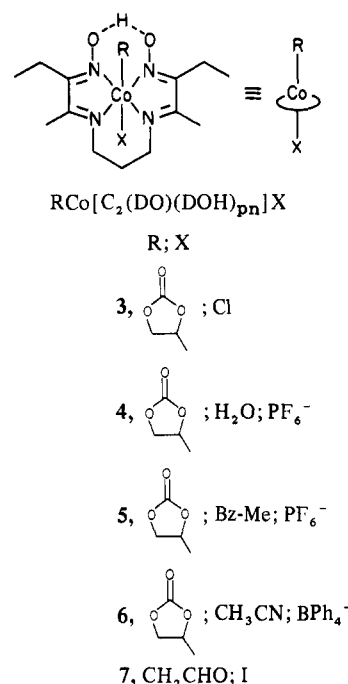
(13) (a) Woodward, R. B., in ref 3a, p 73. (b) Reference 4b, p 105. (c) Boas, J. F.; Hicks, P. R.; Pilbrow, J. R.; Smith, T. D. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 417. (d) In ribonucleotide reductase, similar ESR signals are observed, including both kinetically competent^{13f,g} and noncompetent ones. See also this discussion, ref 3a (p 502) and ref 4b (p 65). (e) Coffman, R. E.; Ishikawa, Y.; Blakley, R. L.; Beinert, H.; Orme-Johnson, W. H. *Biochim. Biophys. Acta* **1976**, *444*, 307. (f) Blakley, R. L.; Orme-Johnson, W. H.; Bozdeck, J. M. *Biochemistry* **1979**, *18*, 2335. (g) Hamilton, J. A.; Tamao, Y.; Blakley, R. L.; Coffman, R. E. *Ibid.* **1972**, *11*, 4696. (h) Buettner, G. R.; Coffman, R. E. *Biochim. Biophys. Acta* **1977**, *480*, 495.

(14) (a) Salem, L.; Eisenstein, O.; Anh, N. T.; Burgi, H. B.; Davaquet, A.; Segal, G.; Veillard, A. *Nouv. J. Chim.* **1979**, *1*, 335. (b) Golding, B. T.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 6331. (c) Russell, J. J.; Rzepa, H. S.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 625.

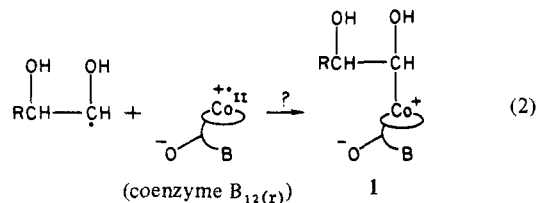
(15) (a) Mulac, W. A.; Meyerstein, D. *J. Am. Chem. Soc.* **1982**, *104*, 4124. We thank Professor Meyerstein for providing us with a copy of this work prior to publication. (b) Elroi, H.; Meyerstein, D. *Ibid.* **1978**, *100*, 5540. (c) Blackburn, R.; Kyaw, M.; Phillips, G. O. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2277.

(16) (a) Silverman, R. B.; Dolphin, D. *J. Am. Chem. Soc.* **1976**, *98*, 4626; **1974**, *96*, 7094; **1973**, *95*, 1686; **1975**, *97*, 2924. (b) Silverman, R. B.; Dolphin, D. *J. Organomet. Chem.* **1975**, *101*, C14. (c) Silverman, R. B.; Dolphin, D.; Babior, B. M. *J. Am. Chem. Soc.* **1972**, *94*, 4028. (d) Silverman, R. B.; Dolphin, D.; Carty, T. J.; Krodell, E. K.; Abeles, R. H. *Ibid.* **1974**, *96*, 7096. (e) Vickrey, T. M.; Katz, R. N.; Schrauzer, G. N. *Ibid.* **1975**, *97*, 7248. (f) Schrauzer, G. N.; Michaely, W. J.; Holland, R. J. *Ibid.* **1973**, *95*, 2024. (g) Michaely, W. J.; Schrauzer, G. N. *Ibid.* **1973**, *95*, 5771.

Chart I



CH(OH)CHROH (**1**, eq 2), a postulated, key intermediate in the overall rearrangement shown in eq 1 and Scheme I.



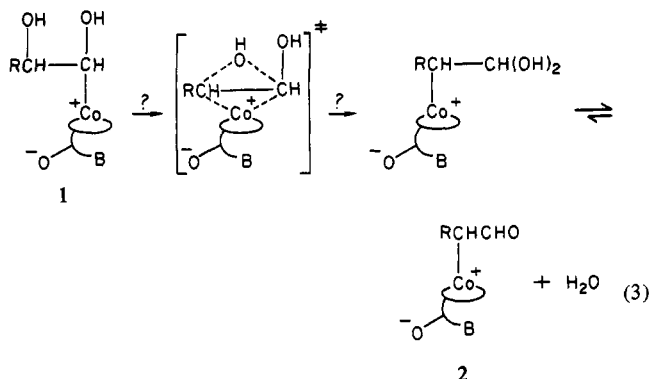
There is no convincing evidence for **1**. In fact, all attempts to detect this intermediate with the enzyme have failed,¹³ and the available ESR experiments argue against **1**, the data being fully consistent with a Co(II)[•] and substrate R[•] influencing each other at distances $>10 \text{ \AA}$.^{13c,d} The only *suggestive* evidence for **1** was that its formation was apparently needed to explain the early diol dehydratase ¹⁸O labeling and stereochemical studies.^{17a,b} More recent ¹⁸O labeling and stereochemical studies^{17c} have greatly changed this picture, however, with some mechanism (such as a protein-bound radical mechanism)^{17c} other than the stereospecific formation and stereospecific further reaction of **1** now being required. In fact, **1** is not even necessary to explain the early stereochemical results, and the interested reader is referred elsewhere⁷ for a discussion of this point. Furthermore, the formation of **1** from B_{12(r)}, Co(II)[•], and RCH(OH)CHOH should be hindered by a redox side reaction to give B_{12(s)}, Co(I) + RCH(OH)CHO + H⁺, known to occur at $k = 4 \pm 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the related α -hydroxy radical, (CH₃)₂CHO[•], with B_{12(r)}.¹⁸ Disproportionation (H[•] atom transfer) to yield Co-H and HOC-

(17) (a) Rétey, J.; Umani-Ronchi, A.; Arigoni, D. *Experientia* **1966**, *22*, 72. (b) Rétey, J.; Umani-Ronchi, A.; Seibl, J.; Arigoni, D. *Ibid.* **1966**, *22*, 502. (c) Arigoni, D., in ref 3a, p 389. (d) Zagalak, B.; Frey, P. A.; Karabatsos, G. L.; Abeles, R. H. *J. Biol. Chem.* **1966**, *241*, 3028.

(18) (a) Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979**, *101*, 4000. (b) Tait, A. M.; Hoffman, M. Z.; Hayon, G. *Ibid.* **1976**, *98*, 86. (c) Ryan, D. A.; Espenson, J. H.; Meyerstein, D.; Mulac, W. A. *Inorg. Chem.* **1978**, *17*, 3725. (d) Even simple Co(diamine)³⁺ complexes are reduced at rates $\sim 10^5 \text{ M}^{-1} \text{ s}^{-1}$ by (CH₃)₂C(OH)[•] at 25.0 °C. Espenson, J. H.; Shimura, M.; Bakay, A., submitted for publication. An additional interesting part of this work (that is somewhat relevant to the present work although it uses Co(III) and not Co(II)) is Espenson's mechanistic study of Co(NH₃)₆³⁺ reduction in H₂O formulated as consisting of three pathways: (1) outer-sphere reduction by (CH₃)₂CHOH at pH 0–3, (2) outer-sphere reduction by (CH₃)₂CO[•] at pH >10 , and (3) reversible formation and then decomposition of a covalent intermediate at pH 5–9, (NH₃)₅CoNH₂C(CH₃)₂OH³⁺.

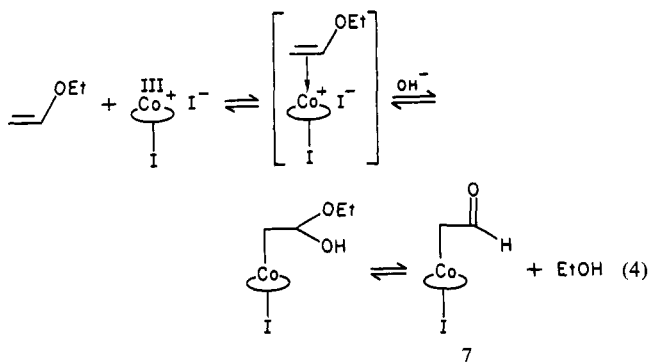
$\text{H}=\text{CHOH}$ ($\equiv \text{HOCH}_2\text{CHO}$) also has some precedent^{10,15a} and, therefore, could be a rearrangement-inhibiting side reaction.

If, however, one ignores for the moment the evidence against the formation of **1** and assumes, as is often done, that it does form, the literature^{12,14-16} strongly suggests that it is generally accepted that rearrangement of **1** proceeds via a Co(III) π -complex (eq 3). One immediate problem with this mechanism is that the



$\text{Co}-\text{CH}_2\text{CHO}$ formylmethyl product¹⁹ (**2**) has been prepared and is too stable²⁰ to be a catalytic intermediate, in the absence of significant enzyme effects.

The acceptance of the π -complex mechanism is surprising, since a Co-assisted, OH migration (i.e., a Co, OH 1,2-interchange, eq 3) has never been experimentally demonstrated. The existence of Co(III) π -complexes must be considered as firmly established, on the basis of numerous synthetic¹⁶ and labeling and stereochemical studies,²¹ as well as Brown's recent direct NMR observation²² of a π -complex. We have even used Co(III) π -complex chemistry (eq 4) to prepare the formylmethyl complex (**7**, Chart



I) in the B_{12} model system employed in the present work. However, existing Co(III) π -complex studies only suggest, somewhat indirectly, the Co(III) π -complex mechanism shown in eq 3, since these studies generally consist of β -OH (or OR) addition or loss,

(19) For references to formylmethyl transition-metal complexes in B_{12} , cobaloximes, $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{CH}_2\text{CHO})$, and $\text{HfCl}(\text{PMe}_3)_3(\text{CH}_2\text{CHO})$ see a-g: (a) Reference 16. (b) Silverman, R. B.; Dolphin, D. J. *Am. Chem. Soc.* **1976**, *98*, 4633. (c) Vickery, T. M.; Wright, E. E.; Kok, R. A. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 317. (d) Curzon, E. H.; Golding, B. T.; Wong, A. K. J. *Chem. Soc., Chem. Commun.* **1982**, 63. (e) Bodnar, T.; Coman, G.; La Croce, S.; Lambert, C.; Menard, K.; Cutler, A. J. *Am. Chem. Soc.* **1981**, *103*, 2471. (f) Milstein, D.; Calabrese, J. C. *Ibid.* **1982**, *104*, 3773. (g) Milstein, D. *Ibid.* **1982**, *104*, 5227.

(20) (a) $\sigma-\pi$ hyperconjugation (vertical stabilization) appears to be responsible for the so-called β -effect^{19f,20b} and $\nu_{\text{CO}} \sim 1635-1665 \text{ cm}^{-1}$ in these complexes. (b) Brown, K. L.; Zahonyi-Budo, E. J. *Am. Chem. Soc.* **1982**, *104*, 4117.

(21) (a) Reference 19d. (b) Brown, K. L.; Ingraham, L. L. J. *Am. Chem. Soc.* **1974**, *96*, 7681. (c) Golding, B. T.; Holland, H. L.; Horn, U.; Sakrikar, S. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 959. (d) There are at least 25 papers in the literature on such π -complexes; additional references can be found in the lead references provided.^{16,21} (e) A Pt- π -vinyl alcohol complex has been studied by crystallography: Hillis, J.; Francis, J.; Ori, M.; Tsutsui, M. J. *Am. Chem. Soc.* **1974**, *96*, 4800. Cotton, F. A.; Francis, J. N.; Frenz, B. A.; Tsutsui, M. *Ibid.* **1973**, *95*, 2483. (f) Ag^+ -olefin complexes are also well known: Fueno, T.; Kajimoto, O.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 782.

(22) Brown, K. L.; Ramamurthy, S. *Organometallics* **1982**, *1*, 413.

the reversible second step of eq 4, but not OH migration. They also do not demonstrate the kinetic dominance of the β -OH cleavage over simple homolytic cleavage¹⁰ of the Co-C (α -OH) bond in **1**, since the models used prior to the present study contained only β -OH but not both β -OH and α -OH groups. Since recent work has shown that Co-C bonds in B_{12} models are generally weak¹⁰ and that metal-C (α -OH) bonds are even weaker,²³ due to the significant influence of the α -OH group on the stability of the radical, $\text{RCH}(\text{OH})\dot{\text{C}}\text{HOH}$, one can argue that the absence of both α - and β -OH groups in previous studies is a significant omission. Thus, neither the kinetic competence of the established Co(III) π -complex mechanism nor an OH-migration- π -complex mechanism have been experimentally established.

An important approach to the key intermediate **1** and its reactions is Meyerstein's most recent pulse radiolysis study^{15a} that generates $\text{HOCH}_2\dot{\text{C}}\text{HOH}$ in the presence of Co(II), $\text{B}_{12(\text{r})}$. Although reaching essentially the opposite conclusion relative to Blackburn's earlier, apparently incorrect work^{15c} concluding **1** did not form, Meyerstein's study appears to provide evidence for the formation of metastable **1** at pH 7, but no rearrangement to Co- CH_2CHO (**2**) or CH_3CHO . Instead, only an apparent side reaction to Co(I) and HOCH_2CHO was observed, although just UV-visible characterization of the cobalt products was reported, the pulse radiolysis technique providing too little organic products for traditional methods of characterization.

Finally, it should be mentioned, and we note it has been stressed by Golding,^{4a,14b,12a} that nine studies²⁴ of $\text{HOCH}_2\dot{\text{C}}\text{HOH}$ (a) show that such α -hydroxy radicals are up to 10^5 more acidic, $\text{p}K_a \sim 10-12$,²⁴ than the parent alcohol (cf. the significant effect of the α -OH on the radical stability mentioned earlier), (b) provide ample precedent for a free radical fragmentation reaction without cobalt participation, $\text{HOCH}_2\dot{\text{C}}\text{HOH} \rightarrow \cdot\text{CH}_2\text{CHO} + \text{H}_2\text{O}$, that occurs with base or acid catalysis at 24°C $3 \times 10^6 \text{ s}^{-1}$ and 24°C $8 \times 10^5 \text{ s}^{-1}$, respectively, $\text{HOCH}_2\dot{\text{C}}\text{HOH} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{HOCH}_2\text{CHO}^- \rightarrow \cdot\text{CH}_2\text{CHO} + \text{OH}^-$, $\text{HOCH}_2\dot{\text{C}}\text{HOH} + \text{H}^+ \rightleftharpoons \text{H}_3\text{O}^+ + \cdot\text{CH}_2\text{CHO}$, and (c) show that α -hydroxy radicals and especially their conjugate bases are strong reductants, $\text{R}_2\dot{\text{C}}\text{OH}$, $E_{1/2}$ ca. -1.3 V vs. SCE.²⁵

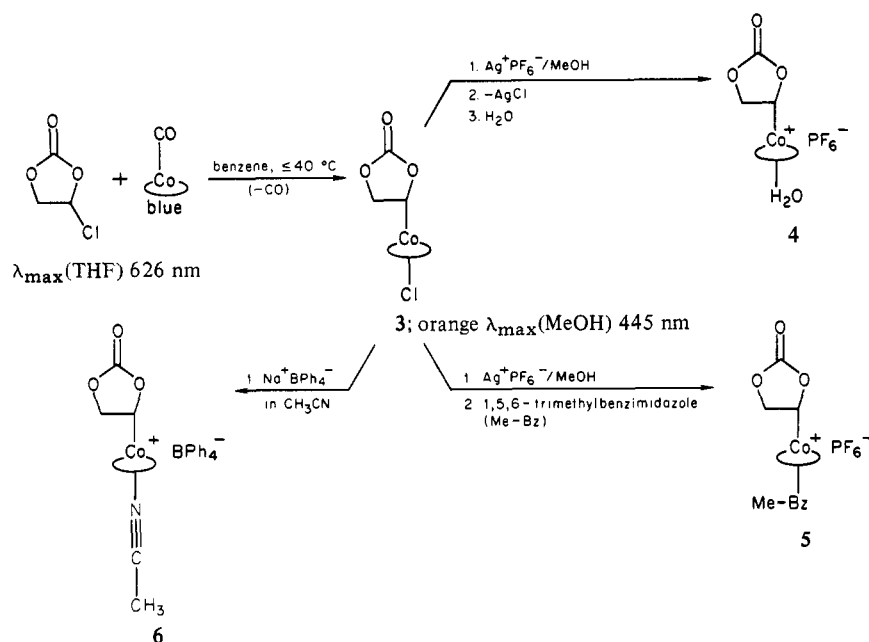
It is hoped that this relatively brief presentation of a much more voluminous, sometimes conflicting and confusing literature will help place in perspective the question of cobalt participation or nonparticipation. In our opinion, the interest and emphasis on this question and **1** are justified due to the possible finding, in the

(23) (a) Although several stable α -hydroxy/metal complexes are now known,^{23a-b} $(\text{OC})_5\text{MnCH}(\text{OH})\text{Ph}$ is unstable even at -50°C and yields $\text{HMn}(\text{CO})_5$ and PhCHO ,^{23b} a result that may be relevant since $\cdot\text{Mn}(\text{CO})_5$ is isoelectronic and isostructural with d^7 , 5-coordinate, square-pyramidal, base-on Co(II). Recent work^{23c} is consistent with Gladysz's work, and the studies presented herein suggesting that α -hydroxy alkyl complexes of the first transition-metal series will be rare due to weak M-C bonds. (b) Gladysz, J. A.; Selover, J. C.; Strouse, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 6766. (c) Vaughn, G. D.; Gladysz, J. A. *Ibid.* **1981**, *103*, 5608. (d) Casey, C. P.; Jones, W. D. *Ibid.* **1980**, *102*, 6154 and reference 1 therein. (e) Espenson, J. H.; Bakač, A. *Ibid.* **1980**, *102*, 2488; **1981**, *103*, 2721; **1981**, *103*, 2728. (f) Brown, K. L.; Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *Ibid.* **1979**, *101*, 503. (g) Wayland, B. B.; Woods, B. A.; Minda, V. M. *J. Chem. Soc., Chem. Commun.* **1982**, 634. (h) Kirker, G. W.; Bakac, A.; Espenson, J. J. *Am. Chem. Soc.* **1982**, *104*, 1249.

(24) (a) Pikaev, A. K.; Kartasheva, L. I. *Int. J. Radiat. Phys. Chem.* **1975**, *7*, 395. (b) Buley, A. L.; Norman, R. O. C.; Pritchett, R. J. *J. Chem. Soc. B* **1966**, 849. (c) Livingston, R.; Zeldes, H. *J. Am. Chem. Soc.* **1966**, *88*, 4333. (d) Gilbert, B. C.; Larkin, J. P.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 794. (e) Bansal, K. M.; Grätzel, M.; Henglein, A.; Janata, E. *J. Phys. Chem.* **1973**, *77*, 16. (f) Venter, P. J.; van der Linde, H. J.; Basson, R. A. *J. Chem. Soc., Chem. Commun.* **1972**, 187. (g) Burchill, C. E.; Perron, K. M. *Can. J. Chem.* **1971**, *49*, 2382. (h) Steenken, S.; Schulte-Frohlinde, D. *Tetrahedron Lett.* **1973**, 653. (i) Steenken, S. *J. Phys. Chem.* **1979**, *83*, 595. See also ref 24e.

(25) The value -1.3 V (SCE) is for $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$,^{25a} and differs slightly from the value quoted in a review of this area.^{25b} The experimental value for $\text{HOCH}_2\dot{\text{C}}\text{HOH}$, ca. -1.0 V (SCE), is a peak potential, E_p , containing kinetic effects and referring to the couple R/ROH and not R/R^+ as previously noted^{15a}. It is, however, similar to $\text{R}/\text{R}^+ E_{1/2}$ values measured by others.^{25c} (a) Lilie, V. J.; Beck, G.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1971**, *75*, 458. (b) Endicott, J. F. In "Concepts in Inorganic Photochemistry"; Adamson, A. W.; Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; pp 88-92. (c) Jaun, B.; Schwartz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

Scheme II



case of cobalt participation, of a novel role for cobalt or, in the case of nonparticipation, the *significant, resultant simplification* of the controversial area of mechanistic B₁₂ chemistry with, in the case of diol dehydratase at least, the Co-C bond of the cofactor simply serving as Nature's C(5') radical source following homolysis with the *protein* and not the cofactor serving to bind, control, and direct the (protein) "bound radicals".

In a preliminary communication^{1a} in 1980, we described our "protected intermediate" approach to the synthesis of **1**, where it was prepared in a carbonate-protected form **3** (Chart I) due to the anticipated instability of the α -hydroxyalkyl-cobalt bond in **1**. The approach was to preform the Co-C bond, thereby removing the assumption of Co-C bond formation and "inviting" cobalt participation. The model employed was our modification⁶ of Costa's B₁₂ model, which we have shown^{6a,b} is the closest electrochemical mimic from among simple Schiff base, B₁₂ model systems. Herein we provide (a) the full details of the preparation, characterization, and physical properties of **3-6**, the carbonate-protected forms of **1**, (b) product studies demonstrating the catalytic MeO^- in MeOH deprotection of **3** and resultant products, including $95 \pm 4\%$ CH_3CHO , and (c) the synthesis, after numerous unsuccessful routes, of the Co- CH_2CHO formylmethyl complex, **7**, its characterization, and conditions of stability and instability.

In the accompanying paper,^{1b} a kinetic and mechanistic study of the CH_3CHO forming methanolysis of **3** is reported, evidence which we believe argues effectively against the participation of cobalt. In a third manuscript,⁷ the relevance or nonrelevance of these model studies and of the known α -hydroxy radical chemistry to diol dehydratase is presented, considerations which lead to a single, simplified and unified mechanism of action that has been, at least in part, previously suggested and that we prefer to call the "bound-radical mechanism".⁷

Results and Discussion

Synthesis and Characterization of 3-6. A reasonably large-scale, efficient, and clean synthesis of **3** and its derivatives was required. We have used approximately 750 g of the $\text{ICo}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{I}$ model system in all of our mechanistic studies⁶ over the last 5 years.² This provides a good justification for the initial use of the model system, since the equivalent cost of cyanocobalamin is considerable at current prices. Although somewhat unusual, but quite reasonable on the basis of our oxidative-addition studies^{6c} to $\text{OC-Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]$, it seemed likely that the oxidative addition of chloroethylene carbonate to the blue cobalt(I) carbonyl complex would provide a clean route to **3**. Oxidative

addition in benzene of chloroethylene carbonate to the $\text{Co}^{\text{I}}\text{CO}$ complex does in fact provide **3** in 80% yield in 0.5 g (to 1.0 g) quantities as shown in Scheme II, with small amounts of Co(II) , $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}$ (or Co(III) , $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}_2$ in O_2) as the major side products. The analogous reaction with $\text{Rh}^{\text{I}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]$ is of interest due to the greater stability of $\text{Rh-C}(\alpha\text{-OH})$ bonds^{23g} and is currently under study.¹¹ Desired derivatives of **3, 4-6**, were prepared by the unexceptional chemistry shown in Scheme II.^{6c}

Determining the exact structure of **3** proved to be more of a problem. The repeatedly good elemental analysis and characteristic IR band expected for a cyclic carbonate, $\nu_{\text{CO}}(\text{3, KBr}) = 1778\text{ cm}^{-1}$, were very suggestive from the start as was the observation of two diastereotopic ligand CH_3 singlets, δ 2.4 in the 100-MHz ^1H NMR (Figure 2A). However, much of the rest of the 100-MHz NMR (Figure 2A) was nearly uninterpretable, and to make matters worse, when **3** was placed in CH_3OH , the solvent that proved optimum for further studies, the ^1H NMR broadened (Figure 2B) as if decomposition were occurring to a paramagnetic product such as Co(II) .

A breakthrough was provided by a higher field, 360-MHz ^1H NMR (Figure 3). The now well-known spectral simplification is still striking (Figure 2A vs. 3A), and with the aid of five decoupling experiments, the spectrum was fully assigned to the structure and labeling scheme given in the inset on Figure 3. A tabulation of the numerical data for Figure 3A and the five decoupling experiments are provided in the Experimental Section and as supplementary material. The important diagnostic feature in the ^1H NMR is the numerous sets of diastereotopic and thus chemical shift nonequivalent hydrogens due to, and proving the presence of, the chiral carbon attached directly to cobalt. The difference in chemical shift observed between, for example, the diastereotopic CH_3 groups d and k, Figure 3 inset, is $\Delta\delta = 0.06$, similar to that observed for analogous R-Co cobaloxime complexes,²⁶ $\Delta\delta$ (CH_3 groups) = 0.01–0.07, depending upon the alkyl.

The reason for the unexplained, more complicated ^1H NMR in CD_3OD was also uncovered with the aid of 360-MHz and other experiments. The possibility of paramagnetic Co(II) broadening in **3** in the CD_3OD spectrum (Figure 2B) was ruled out by showing that the CH_3 group of added toluene remained sharp and the fact that O_2 , added to the solution to oxidize any Co(II) , did not affect the spectrum. The 360-MHz NMR (Figure 3B) spectrum showed

(26) (a) Naumberg, M.; Duong, K. N. V.; Gaudemer, F.; Gaudemer, A. C. *R. Hebd. Seances Acad. Sci., Ser. C* **1970**, 270, 1301. (b) Gaudemer, A.; Gaudemer, F.; Diep, L. *Bull. Soc. Chim. Fr.* **1972**, 884.

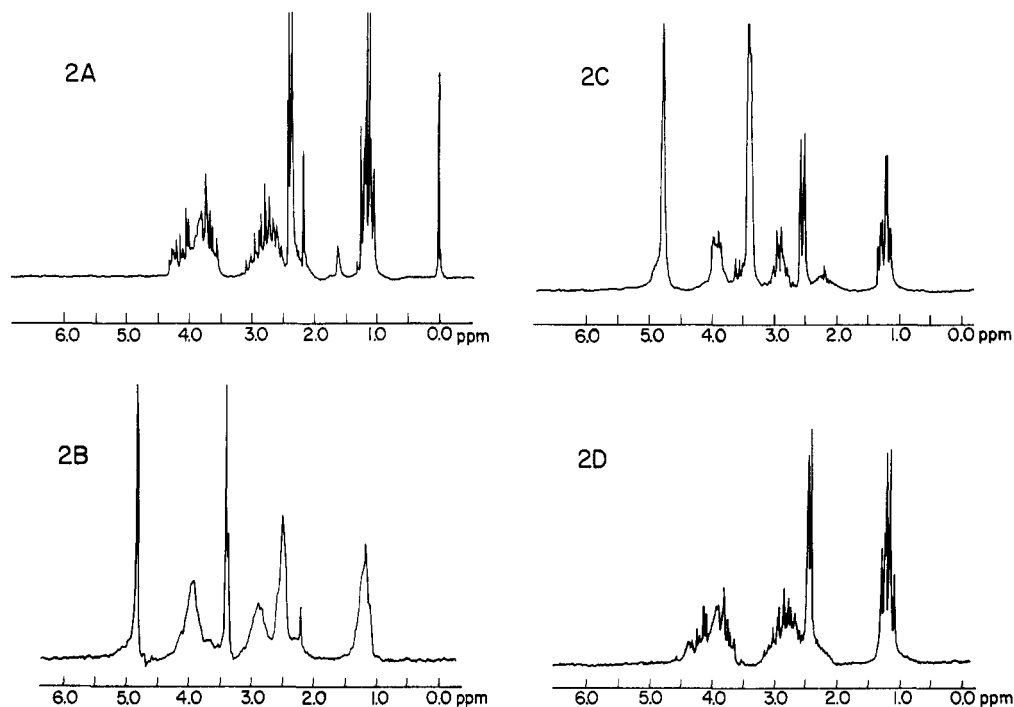


Figure 2. 100-MHz ^1H NMR spectra of **3** in CDCl_3 (A), in CD_3OD (B), in CD_3OD after treatment with Ag^+PF_6^- (C), and after removal of the CD_3OD under vacuum from the sample used for spectrum B, followed by redissolving the solid in CDCl_3 (D).

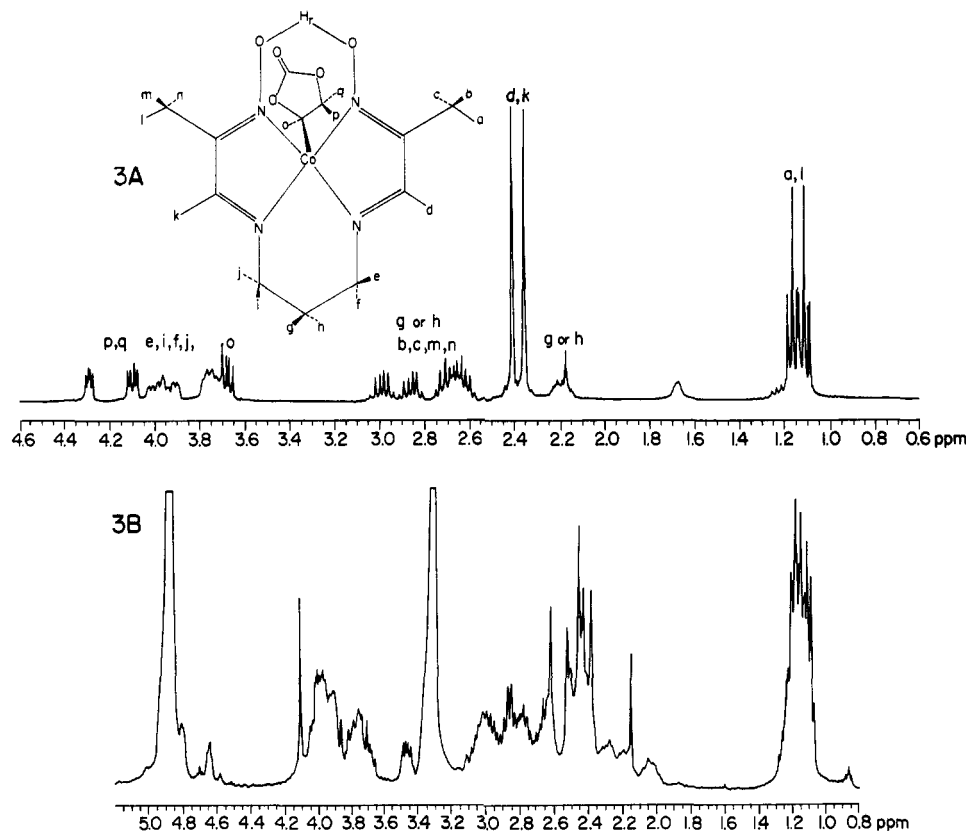


Figure 3. 360-MHz ^1H NMR spectra of **3** in CDCl_3 (A) and in CD_3OD (B). The assignments given in (A) refer to the labeling scheme given on the structure shown in the inset.

that the 100-MHz NMR spectrum in Figure 2B really contains considerable fine structure, and suggested that the observed 100-MHz spectrum was probably a composite of several, possibly three, forms of **3** in solution. Since conductivity measurements demonstrated that the axial Cl^- in **3** is ionized in CH_3OH (see Experimental Section), it seemed likely that the several forms of **3** differed in their average positions, on the NMR time scale, of the Cl^- , i.e., that ion pairing²⁷ was responsible for the complex

NMR spectrum observed in CD_3OD . This explanation is fortified by the 100-MHz NMR experiments shown in Figure 2C,D. An

(27) (a) Szwarc, M., Ed. "Ions and Ion Pairs in Organic Reactions"; Wiley-Interscience: New York, 1972; Vol. 1, pp 289, 311. (b) Goering, H. L.; Silversmith, E. F. *J. Am. Chem. Soc.* **1955**, *77*, 6249. This work shows that in *cis*- or *trans*-5-methyl-2-cyclohexyl *p*-nitrobenzoates, ion-pair formation does not lead to *cis,trans* isomerization.

aliquot of the same solution used for the spectrum in Figure 2B was treated with AgPF₆, the AgCl removed, and the spectrum of the resultant solution obtained (Figure 2C). This spectrum demonstrates that removal of the Cl⁻ yields a single solution species as its PF₆⁻ salt, i.e., that the presence of an anion like Cl⁻ is required to generate the complex NMR spectrum observed in CD₃OD. Figure 2D shows the NMR spectrum of an aliquot of the original CH₃OH solution used for spectrum 2B in which the CH₃OH was removed under vacuum and the sample was redissolved in CDCl₃. The NMR spectrum obtained (Figure 2D) is identical with that of freshly prepared 3 in CDCl₃ (Figure 2A) except for some presently unexplained change in the multiplet at δ 2.19. This NMR experiment demonstrates that no major irreversible changes in 3, such as its decomposition, occur over about an hour in CD₃OD at 25 °C and is consistent with the ion-pairing explanation, since the Cl⁻ in 3 is not ionized in CDCl₃ by conductivity. The exact nature of the ion pairs, such as whether tight and/or solvent-separated forms are present, cannot be deduced from the present data. The fact that CH₃OH solutions of 3 conduct requires that dissociated ions be present in solution, a result verified by the addition of Bu₄N⁺Cl⁻, which causes a considerable sharpening of the CH₃OH ¹H NMR spectrum of 3 due to the Cl⁻ common ion effect. The NMR results require that the several forms interconvert slowly on the NMR time scale, a result seemingly inconsistent with the postulated interconversion of simple tight and solvent-separated ion pairs. A more likely but unproven possibility, based on the ion-pairing literature,²⁷ is that the NMR distinct species differ by having a Cl⁻ above and below the plane of the equatorial tetradentate macrocycle in tight and/or solvent-separated ion pair form.

The ν_{CO} IR data for 3 is also somewhat interesting and deserves a brief examination. It is characteristic of a carbonate as noted earlier, $\nu_{\text{CO}}(\text{KBr}) = 1778 \text{ cm}^{-1}$, but especially reminiscent of ethylene carbonate, $\text{OCH}_2\text{CH}_2\text{OC}=\text{O}$ where two bands are observed in the carbonyl region.²⁸ These two bands arise from the interaction (Fermi resonance) of a ν_{CO} in the region of 1810–1870 cm^{-1} and the overtone $2\nu_7 = 2(890) = 1780 \text{ cm}^{-1}$. The result is that two bands are observed, $\nu(\text{CHCl}_3) = 1812, 1785 \text{ cm}^{-1}$, whose exact positions and relative intensities are quite solvent dependent. For 3, one to two bands depending upon the solvent are observed in the carbonyl region, $\nu(\text{pyridine}) = 1974 \text{ cm}^{-1}$, $\nu(\text{CH}_3\text{CN}) = 1794 \text{ cm}^{-1}$, $\nu(\text{CH}_3\text{OH}) = 1805, 1780 \text{ cm}^{-1}$. Clearly, these IR data demonstrate the presence of a cyclic carbonate carbonyl in 3.

The single-crystal, X-ray diffraction structural analysis of 3 was of interest, especially the Co–C bond length in such a compound with an oxygen atom α to the Co–C bond. Repeated attempts with different crystals failed to produce a high-precision X-ray structure of 3. The best results, significantly better than the earlier $R_f = 13.6\%$ structure,¹ were obtained as the BPh₄⁻ salt (compound 6, Chart I). A large crystal was found to belong to the monoclinic crystal system, space group $P2_1/n$, with a unit cell of dimensions $a = 12.133(3) \text{ \AA}$, $b = 24.027(5) \text{ \AA}$, $c = 13.876(3) \text{ \AA}$, $\beta = 92.91(3)^\circ$, and $Z = 4$. The crystals diffracted weakly, often a sign of disorder, and of 4153 independent reflections, only 1326 were observed to have intensities greater than $3\sigma(I)$. Some additional data, the source of the disorder problem, and an ORTEP plot are provided as supplementary material, the final discrepancy indices being $R_f = 0.086$ and $R_{\text{wf}} = 0.091$. The data served primarily to confirm the structure deduced from the spectroscopic data, with average Co–N (ring) lengths being $1.880(9) \text{ \AA}$, Co–N (axial CH₃CN) = $1.979(10) \text{ \AA}$, and Co–C (ethylene carbonate) = $2.034(27) \text{ \AA}$, values consistent with other, related structures.²⁹

Some additional physical properties, including its light and thermal stability, its solubility, and axial 1,5,6-trimethylbenzimidazole binding constant, were determined, properties necessary to understand how to optimally conduct the methanolysis (carbonate protecting group removal) experiments. The most im-

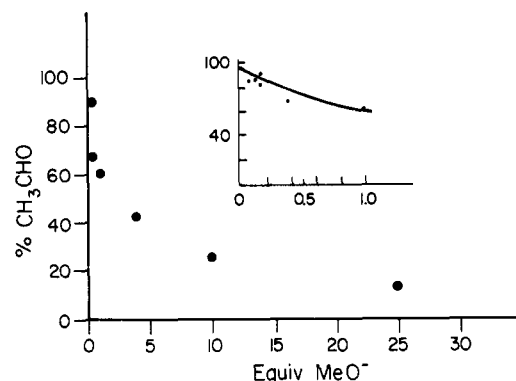
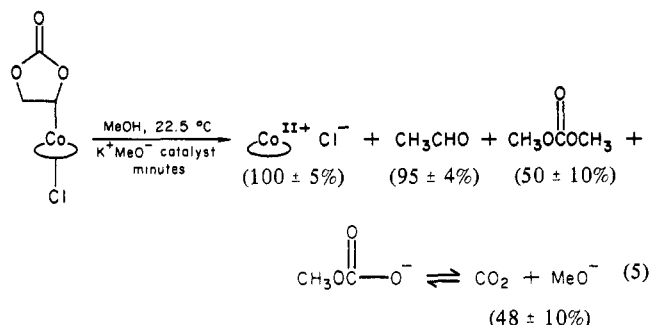


Figure 4. Acetaldehyde yield vs. equivalent of added CH₃O⁻. The inset shows the data at ≤ 1 equiv of CH₃O⁻.

portant measurement was the axial 1,5,6-trimethylbenzimidazole binding in methanol to 4, $K_{\text{assoc}} = 90 \pm 20 \text{ M}^{-1}$. As will be seen in the accompanying mechanistic paper, added axial 1,5,6-trimethylbenzimidazole has an important, inhibiting effect upon the CH₃CHO-forming, methanolysis reaction.

Methanolysis Stoichiometry. The most significant feature of 3 is its catalytic deprotection by K⁺MeO⁻ in MeOH, methanol being chosen after a survey of solvent systems, and the resultant stoichiometry eq 5), where $95 \pm 4\%$ of CH₃CHO and $100 \pm 5\%$



of Co^{II}[C₂(DO)(DOH)_{pn}]Cl are produced along with carbonate deprotection products, MeOCO₂Me and MeOCO₂⁻. Early control experiments revealed that KOH/MeOH, [MeO⁻]/[HO⁻] = 4000/1 under the reaction conditions,³⁰ gave an identical stoichiometry to anhydrous K⁺OMe⁻ prepared from potassium and dry MeOH, and that the PF₆⁻ salt, 4, free from possible Cl⁻ ion-pairing effects, gave identical results (eq 5) in comparison to Cl⁻ containing 3. Subsequent experiments were therefore performed with the more easily prepared 3 + KOH/MeOH. We also note that the stoichiometry (eq 5) has been repeatedly obeyed over a minimum of 25 experiments by several of us over the course of this study.

The reaction (eq 5) is easily followed by the orange to burgundy-red color change over a few minutes, characteristic of Co^{II}[C₂(DO)(DOH)_{pn}]Cl formation. This Co(II) product was characterized and quantified by its visible and ESR spectra in comparison to authentic samples prepared by $1/2[\text{Cr}(\text{acac})_2]$ atom abstraction reduction of Co^{III}[C₂(DO)(DOH)_{pn}]Cl₂ ($\rightarrow \text{Cl}-\text{Cr}(\text{acac})_2 + \text{Co}^{\text{II}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}$) or, more easily, a Co(I) and Co(III) $\rightleftharpoons 2 \text{Co(II)}$ disproportionation reaction ($\text{OC}-\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}] + \text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}_2 \rightarrow \text{CO} + 2\text{Co}^{\text{II}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}$).

Acetaldehyde was identified by GC and GC/MS and was isolated as its 2,4-DNP derivative, unequivocally confirming its presence. At 1 equiv of MeO⁻, $61 \pm 6\%$ of CH₃CHO is observed by GLC as previously reported,¹ but when the % CH₃CHO vs. MeO⁻ is studied (Figure 4), the % CH₃CHO rises to $95 \pm 4\%$

(28) Angell, C. L. *Trans. Faraday Soc.* **1956**, *52*, 1178.

(29) Glusker, J. In "X-Ray Crystallography of B₁₂ and Cobaloximes, Vitamin B₁₂", Dolphin, D., Ed.; Wiley: New York, 1981; Chapter 3.

(30) (a) One equivalent of 0.9 M KOH·XH₂O (85% KOH, 15% H₂O) in dry CH₃OH ($\text{p}K_a = 15.5$)^{30b} added to a $1.1 \times 10^{-2} \text{ M}$ solution of 3 in CH₃OH yields 0.50 M H₂O ($\text{p}K_a = 15.7$) and a $[\text{CH}_3\text{O}^-]/[\text{HO}^-] = 4 \times 10^3$. (b) Streitwieser, A., Jr.; Heathcock, C. H. "Introduction to Organic Chemistry", 2nd ed.; MacMillan: New York, 1981; p 238.

CH₃CHO. Control experiments using authentic CH₃CHO and the MeO⁻/MeOH reaction conditions demonstrated that the major part of the CH₃CHO losses at higher MeO⁻ concentrations are due to the well-known facile aldol chemistry of acetaldehyde.³¹ In MeOH, NMR experiments demonstrated that CH₃CHO is present largely as its hemiacetal, CH₃CH(OH)(OMe).

The remaining carbonate-deprotection products of eq 5 were identified and quantified by IR in comparison to authentic samples, CH₃OCO₂CH₃ ($\nu_{\text{CO}}(\text{MeOH}) = 1755 \text{ cm}^{-1}$) and CH₃OCO₂⁻K⁺ ($\nu_{\text{CO}}(\text{MeOH}) = 1655 \text{ cm}^{-1}$). The MeO⁻-consuming formation of CH₃OCO₂⁻ decreases at <1 equiv of MeO⁻, as it must if the reaction is catalytic in MeO⁻, with MeOCO₂⁻ being undetectable at ≤0.1 equiv of MeO⁻. Under these latter conditions, the product is CO₂ and a facile CH₃OCO₂⁻ = CO₂ + MeO⁻ equilibrium³² is present, as demonstrated by the addition of ≥0.5 equiv of MeO⁻ to the reaction products and IR detection of the ca. 50% CH₃OCO₂⁻, $\nu_{\text{CO}} = 1655 \text{ cm}^{-1}$, that is generated. The observation of both CH₃OCO₂CH₃ and CH₃OCO₂⁻ is interesting and has proven to be a very useful feature of the carbonate protected intermediate, 3. Simple ethylene carbonate yields only CH₃OCO₂CH₃ as expected, OCH₂CH₂OC=O + MeO⁻ (catalytic)/MeOH → HOCH₂CHOH + CH₃OCO₂CH₃. These results are those expected for the formation of the well-known tetrahedral intermediate by MeO⁻ attack at the carbonyl carbon of 3, followed by its near statistical opening each of the two possible ways and eventual formation of 50% each of CH₃OCO₂⁻ and CH₃OCO₂CH₃. Additional evidence for initial MeO⁻ attack at the carbonyl carbon and the intermediates shown in Scheme III will be presented in the following mechanistic paper.^{1b}

The H[•] Source Question. The stoichiometry (eq 5) is complete except for the H[•] source required for CH₃CHO formation. Restated, the stoichiometry (eq 5), mass, and charge balance strongly suggest, although they do not prove, the formation of ·CH₂CHO³³ prior to CH₃CHO formation. There are only two possible sources of the required H[•], the ligand or the CH₃OH solvent. The visible and ESR characterization of the Co(II)⁺ Cl⁻ product appeared to rule out the ligand as a H[•] source, in spite of precedent for this process,³⁴ and this was confirmed by I₂ (0.5 ± 0.05 equiv) or BrCCl₃ oxidation of the Co(II) product and visible, TLC, and 360-MHz NMR characterization and 100 ± 5% quantification of the resultant product as authentic, ligand intact, Co[C₂(DO)(DOH)_{pn}]₂X₂.

Demonstration that CH₃OH was the H[•] source proved elusive under these basic conditions, however. There are numerous literature citations³⁵ that the CH₃OH methyl group (vs. the OH group) is the preferential H[•] source with the resultant ·CH₂OH expected to give combination, HOCH₂CH₂OH, and disproportionation products, 0.5CH₃OH + 0.5 H₂CO, although these products are almost never adequately characterized, if at all.³⁵ Thermodynamic and kinetic considerations furthermore confirm that the reaction ·CH₂CHO + CH₃OH → CH₃CHO + ·CH₂OH should occur, $\Delta H_{\text{(est)}}^{36a-f} = -3 \text{ to } -5 \text{ kcal/mol}$, $75 \text{ M}^{-1} \text{ s}^{-1} < k_{\text{(est)}}$

$< 10^5 \text{ M}^{-1} \text{ s}^{-1}$.^{36g,h} For the more exothermic reaction, Ph· + CH₃OH → PhH + ·CH₂OH, $\Delta H_{\text{(est)}}^{36a-f} = -12 \text{ kcal/mol}$ and $k_{\text{obsd}}^{36h} = 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Under basic conditions, ·CH₂OH, $pK_a = 10.7$,²⁴ would be fully deprotonated by MeO⁻, yielding ·CH₂O⁻, and one might expect the resultant negative charge to inhibit dimerization to HOCH₂CH₂OH (after protonation) relative to H₂CO formation.

Direct ¹H NMR experiments in CD₃OD demonstrated that no HOCH₂CH₂OH was present under conditions where a control showed that ≥10% was detectable and also showed that no H₂CO or H₂C(OH)(OMe) were present. The use of ¹³CH₃OH and ¹³C NMR or dimedon, 2,4-DNP, or chromotropic acid tests³⁷ to detect H₂CO similarly failed, the expected result since control experiments demonstrated that even added H₂CO was not detectable due to the well-known, rapid consumption of formaldehyde under basic conditions.³⁸ A labeling experiment using CD₃OH to produce DCH₂CHO was precluded by a control experiment that demonstrated, as expected, rapid H/D exchange with the solvent hydroxyl and the methyl hydrogens of CH₃CHO. Given these control experiments demonstrating that H₂CO detection or labeling experiments were essentially impossible under the reaction conditions, other solvents were examined with the hope of observing their radical-derived oxidation products (solvent/product): ((CH₃)₂CHOH/(CH₃)₂CO; HOCH₂CH₂OH/HOCH₂CHO; CH₃CH₂OH/CH₃CHO; PhCH₂OH/PhCHO). One could reasonably expect ethanol or ethylene glycol to be the best solvents, where 0.5 equiv of CH₃CHO, catalytic CH₃CHO formation,³⁹ and stoichiometric (0.5 equiv) HOCH₂CHO formation, respectively, are the anticipated products. In practice, slower rates of alcoholysis, competing aldol chemistry, and other problems hinder experiments in these solvents. The desired participation by solvent was finally obtained by using carefully purified, PhCHO-free (negative 2,4-DNP test) PhCH₂OH as a solvent. The aldehyde, PhCHO, was isolated and characterized as its 2,4-DNP in ca. 40% (52 ± 15% by GC) yield, results that are difficult to explain by any process other than R· + PhCH₂OH → RH + PhCHOH and then under basic conditions PhCHOH → 0.5PhCHO + 0.5PhCH₂OH.

The Putative (Formylmethyl)cobalt Intermediate, 7. A π -complex mechanism (eq 3) should produce the Co-CH₂CHO, formylmethyl intermediate, 7, as should all other Co-participation mechanisms that we are aware of. Given the stability of all known formylmethyl complexes,^{19,20} the lack of observation of this product and the observation of Co(II) instead (eq 5) are significant results that strongly argue against cobalt participation. An independent preparation and characterization of Co-CH₂CHO, 7, in the present model system and a verification of its stability were clearly required, however.

Following the investigation of five unsuccessful routes, involving (i) Co(I) + ClCH₂CHO, (ii) 2Co(II) + ClCH₂CHO, (iii) Co(III) + CH₂=CHOSiMe₃ + F⁻, (iv) Co(III) + R₃SnCH₂CHO, and (v) Co(III) + LiCH₂CHO (details are provided as supplementary materials), the formylmethyl complex 7 was successfully prepared in ≥90% yield in a slow reaction, 20% conversion in 6 days, by Dolphin's method by using Co^{III}[C₂(DO)(DOH)_{pn}]₂, ethylvinyl ether and moist, basic ethanol (the previous eq 4, which is repeated below). The product, 7, was unambiguously characterized by 360-MHz ¹H NMR ($\delta(\text{CDCl}_3)$ 8.97 (t, 1 H, J = 5.2 Hz, Co-CH₂CHO), 1.56 (d, 2 H, J = 5.2 Hz, Co-CH₂CHO) and IR

(31) Nielsen, A. T.; Houlihan, W. J. *Org. React. (N.Y.)* **1968**, *16*.

(32) Pocker, Y.; Davison, B. L.; Deits, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 3564 and references therein.

(33) (a) Zimmerman, A. H.; Reed, K. J.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 7203. (b) Huyser, E. S.; Feller, D.; Borden, W. T.; Davidson, E. R. *Ibid.* **1982**, *104*, 2956.

(34) Hydrogen atom abstraction from the cobaloxime ligand is known: (a) Brown, K. L. *J. Am. Chem. Soc.* **1979**, *101*, 6600. (b) Brown, K. L. *J. Chem. Soc., Chem. Commun.* **1981**, 598. (c) Brown, K. L.; Hessley, R. K. *Inorg. Chim. Acta* **1981**, *53*, L115. (d) Brown, K. L. *Ibid.* **1978**, *31*, L401. (e) Brown, K. L.; Hessley, R. K. *Inorg. Chem.* **1980**, *19*, 2410. (f) See also ref 12b.

(35) (a) Cher, M. J. *Phys. Chem.* **1963**, *67*, 605. (b) Elson, I. H.; Kochi, J. K. *J. Org. Chem.* **1974**, *39*, 2091. (c) Costa, G.; Mestroni, G.; Pellizer, G. *J. Organomet. Chem.* **1968**, *15*, 187. (d) Armstead, J. A.; Cox, D. J.; Davis, R. *Ibid.* **1982**, *236*, 213. See the statement, p 215, following eq 1.

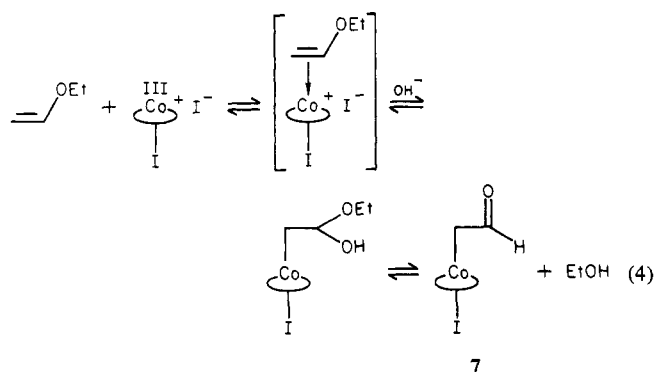
(36) (a) McKean, D. C. *Spectrochim. Acta, Part A* **1975**, *A31*, 861. (b) McKean, D. C.; Duncan, J. L.; Batt, L. *Ibid.* **1973**, *A29*, 1039. (c) Kerr, J. *Chem. Rev.* **1966**, 497. (d) Cruickshank, F. R.; Benson, S. W. *J. Phys. Chem.* **1969**, *73*, 733. (e) Buckley, E.; White, E. *Trans. Faraday Soc.* **1962**, *58*, 536. (f) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516. (g) Reference 24g. (h) Ingold, K. N. In "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 76.

(37) Rosin, J. "Reagent Chemicals as Standards"; Van Nostrand: Princeton, NJ, 1967; p 135.

(38) Geissman, T. A. *Org. React. (N.Y.)* **1944**, *2*, Chapter 3.

(39) Reference 24f. Other than this pulse radiolysis paper, the chemical generation of HOCH₂CHOH in HOCH₂CH₂OH, with or without added Co(II), does not appear to give catalytic CH₃CHO formation.^{12c,24}

(40) (a) Sargent, F. P.; Gardy, E. M. *Can. J. Chem.* **1975**, *53*, 3128. (b) Brown, O. R.; Chandra, S.; Harrison, J. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *38*, 185. (c) Bansel, K. M.; Henglein, A. *J. Phys. Chem.* **1974**, *78*, 160. (d) Ayscough, P. B.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1402. (e) For *t*-BuO· + PhCH₂OH → *t*-BuOH + PhCHOH (λ_{max} 535 nm), $k = 6.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, with a lifetime for PhCHOH = $5.7 \times 10^5 \text{ s}^{-1}$. Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.



($\nu_{\text{CO}}(\text{CHCl}_3 \text{ or } \text{CH}_3\text{OH}) = 1650 \text{ cm}^{-1}$) in comparison to literature formylmethyl complexes.¹⁹ The diagnostically low, $\nu_{\text{CO}} = 1635\text{--}1665 \text{ cm}^{-1}$, carbonyl band is due to the so-called β -effect, in this case explained as $\sigma\text{--}\pi$ hyperconjugation.²⁰ Significantly, **7** was relatively stable in MeO^-/MeOH (no decomposition by IR or ^1H NMR for 1 h), or in MeO^-/MeOH with added 1,5,6-trimethylbenzimidazole (ca. 10% loss by IR, a slight upfield shift in the ^1H NMR, δ 8.82 (t, $J = 5 \text{ Hz}$, 1 H), 1.40 (d, $J = 5 \text{ Hz}$, 2 H), and decrease by 20 cm^{-1} in the IR, $\nu_{\text{CO}}(\text{CH}_3\text{OH}) = 1630 \text{ cm}^{-1}$. Additional studies of **7** are provided in the Experimental Section. Although other mechanistic experiments with the $\text{Co}-\text{CH}_2\text{CHO}$ complex, **7**, will be presented in the following paper,^{1b} the present results with **7** would appear to rule out the π -complex mechanism (eq 3), any other cobalt-participation mechanism that should produce **7**, and the participation of **7** in Scheme III.

Discussion and Conclusions

The goal of this first stage of the present work was (a) the high yield preparation and unambiguous characterization of a protected form of the postulated intermediate **1** (eq 2), (b) establishment of the conditions required for the deprotection of the protected intermediate, (c) establishment of the complete stoichiometry of any resultant "rearrangement"⁴¹ reaction, and (d) the preparation, characterization, and stability/instability studies of the second, often postulated diol dehydratase intermediate, the formylmethyl complex, using the $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]$ model system.

These goals were met by the 80% yield and full characterization of carbonate-protected intermediate, **3**, its MeO^- -catalyzed deprotection in MeOH to yield near quantitative CH_3CHO , 1 equiv of $\text{Co}^{\text{II}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}$ and ca. 0.5 equiv each of MeOCO_2Me and MeOCO_2^- , and the synthesis and study of the relatively stable formylmethyl complex, **7**. In principle, the ideal protecting group or collection of protecting groups would undergo deprotection at acidic, neutral, and basic pH. In the early phases of this work, seven other protecting groups (PG) that can be removed at different pH values were examined in an effort to prepare $\text{OCH}_2\text{CH}(\text{Cl})\text{O-PG}$ for oxidative addition to $\text{Co}(\text{I})$ analogous to our successful synthesis of **3**. In particular, the following protecting groups were examined: *tert*-butoxyboronate ($\text{PG} = -\text{B}(\text{O}i\text{Bu})_2$), phenylboronate ($\text{PG} = \text{BPh}$), ortho ester ($\text{PG} = -\text{C}(\text{CH}_3)_2\text{OCH}_3$), bis(trimethylsilyl) ($\text{PG} = -\text{SiMe}_3$), diphenyl ketal ($\text{PG} = -\text{CPh}_2$), phosphate ester ($\text{PG} = \text{P}(\text{O})(\text{OPh})_2$), and thionocarbonate ($\text{PG} = >\text{C}=\text{S}$). Other than the thionocarbonate, which is still under investigation as part of the extension of these studies to cobalamins and cobinamides,⁴² these protecting groups failed or proved far less satisfactory than the carbonate in **3**. (The investigation of the other protecting groups is documented in the supplementary material for the interested reader.) The major disadvantage of **3** is that its deprotection is limited to basic pH values. We note, however, that the optimum pH range for diol dehydratase is 6–10, not far from the pH range of 10–12 generally

studied herein. Although the pH at the active site of diol dehydratase is unknown, we have argued elsewhere⁷ for basic binding, $\text{HOCH}_2\text{CHOH}\cdots\text{base}$ (protein), of the α -hydroxy radical. If correct, studies under basic conditions may prove most important.

Advantages of the carbonate-protected **3** include its easy, high-yield preparation, its ready deprotection with catalytic MeO^- in MeOH , its record 95% CH_3CHO formation, and the IR (MeOCO_2Me , MeOCO_2^-), GLC (CH_3CHO), and visible spectroscopy ($\text{Co}(\text{II})$) handles provided by its subsequent, clean "rearrangement" reaction, eq 5. In the following mechanistic study, kinetic and nitroxide radical trapping experiments, the dramatic CH_3CHO -inhibiting effect of axial 1,5,6-trimethylbenzimidazole, and other mechanistic experiments are presented.^{1b}

Experimental Section

(A) General. (i) **Methods of Handling Air-Sensitive Compounds.** All manipulations involving air-sensitive materials were handled by using standard Schlenk-tube techniques, an inert-atmosphere (N_2) Vacuum Atmospheres Inc. drybox, gas-tight syringes or stainless steel cannula for air-free transfers, and purified N_2 , all as previously described.^{6c}

(ii) **Equipment.** NMR spectra were obtained on a Varian XL-100 (100 MHz) and a Nicolet NT-360 FT NMR spectrometer (360 MHz). Early 360-MHz NMR spectra were obtained at the Stanford Magnetic Resonance Laboratory with the expert assistance of Dr. Lois Durham. IR spectra were recorded on a Beckman IR-10 and a Sargent-Welch 3-200 infrared spectrophotometer, using a matched pair of CaF_2 solution cells (International Crystals Inc.). UV-visible spectra were run on a Cary 15 spectrophotometer equipped with a Neslabs Inc. Exacal 100 and Endocal 350 temperature control unit, circulating 1:1 water/ethylene glycol through a jacketed cuvette holder, using either standard 1.0-cm quartz rectangular UV-visible cuvettes or a cylindrical 0.1-mm path-length cell (Markson Scientific Inc.). ESR measurements were made on a Varian E-3 spectrometer. Gas chromatography was performed on a Hewlett-Packard Model 700 laboratory chromatograph, utilizing a flame ionization detector. Acetaldehyde was detected by GC by using a 21-ft 10% Carbowax 20M on 80–100 mesh Chromosorb W-HP column run isothermally at 70°C . GC-mass spectra were recorded on a Hewlett-Packard 7620A GC interfaced to a Model 15930A mass spectrometer. Conductivity measurements were made with a Radiometer (Copenhagen) CDM 2e conductivity meter, a type CDC 114 cell (cell constant = 1.69 cm^{-1}), and a Yellow Springs Instruments Model 31 conductivity bridge and No. 3403 cell (cell constant = 1.00 cm^{-1}). Elemental analyses were obtained from the University of Oregon microanalytical laboratory.

(iii) **Solvents.** All solvents were distilled under nitrogen. Benzene (Baker) was distilled from CaH_2 , methanol (Baker) from $\text{Mg}(\text{OMe})_2$, ethanol (U.S.I.) from $\text{Mg}(\text{OEt})_2$, pyridine (Fischer) from BaO , ethylene glycol (Aldrich) from Linde 4-Å molecular sieves, acetonitrile (Baker) from CaH_2 , and isopropyl alcohol (Baker) from MgSO_4 . Solvents were stored in 1-L brown bottles in the drybox, after being bubbled with N_2 in the box for at least 15 min. Deuterated NMR solvents, CDCl_3 (Aldrich), CD_3OD (KOR Isotope Chemicals), and CD_3CN (Aldrich), were used without further purification.

(iv) **Other Chemicals.** Commercially available chemicals that were used without purification include: ethylene carbonate, dimethyl carbonate, bromotrichloromethane, and vinylene carbonate (Aldrich), CO and CO_2 (Matheson), AgPF_6 , AgBF_4 , NaBPh_4 , $(\text{CH}_3)_4\text{NCl}$, $(n\text{-C}_4\text{H}_9)_4\text{NI}$, and $[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]^+\text{Cl}^-$ (Alfa), and ^{13}C -methanol (KOR Isotope Chemicals). Ethyl vinyl ether and triethylamine (Aldrich) were distilled immediately prior to use. 1,5,6-Trimethylbenzimidazole was prepared by the literature method.⁴³ The 2,4-dinitrophenylhydrazine (2,4-DN-P),⁴⁴ dimedon,⁴⁵ and chromotropic acid³⁷ test reagents were prepared according to published methods. Chromium(II) acetoacetonate was a gift from Dr. Thomas Sorrell and was prepared by the published procedure.⁴⁶

Neither repeated fractional distillations nor treatment with base and ether extraction followed by fractional distillation⁴⁷ proved effective in

(43) Simonov, A. M.; Pozharskii, A. T.; Mavianovskii, V. M. *Indian J. Chem.* **1967**, *5*, 81.

(44) Roberts, R. M.; Gilbert, J. L.; Rodewald, C. B.; Wingrove, A. S. "An Introduction to Modern Experimental Organic Chemistry"; Holt, Rinehart and Winston: New York, 1974; p 270.

(45) Pasto, D. J.; Johnson, C. R. "Organic Structure Determination"; Prentice-Hall: Englewood Cliffs, NJ, 1969; p 385.

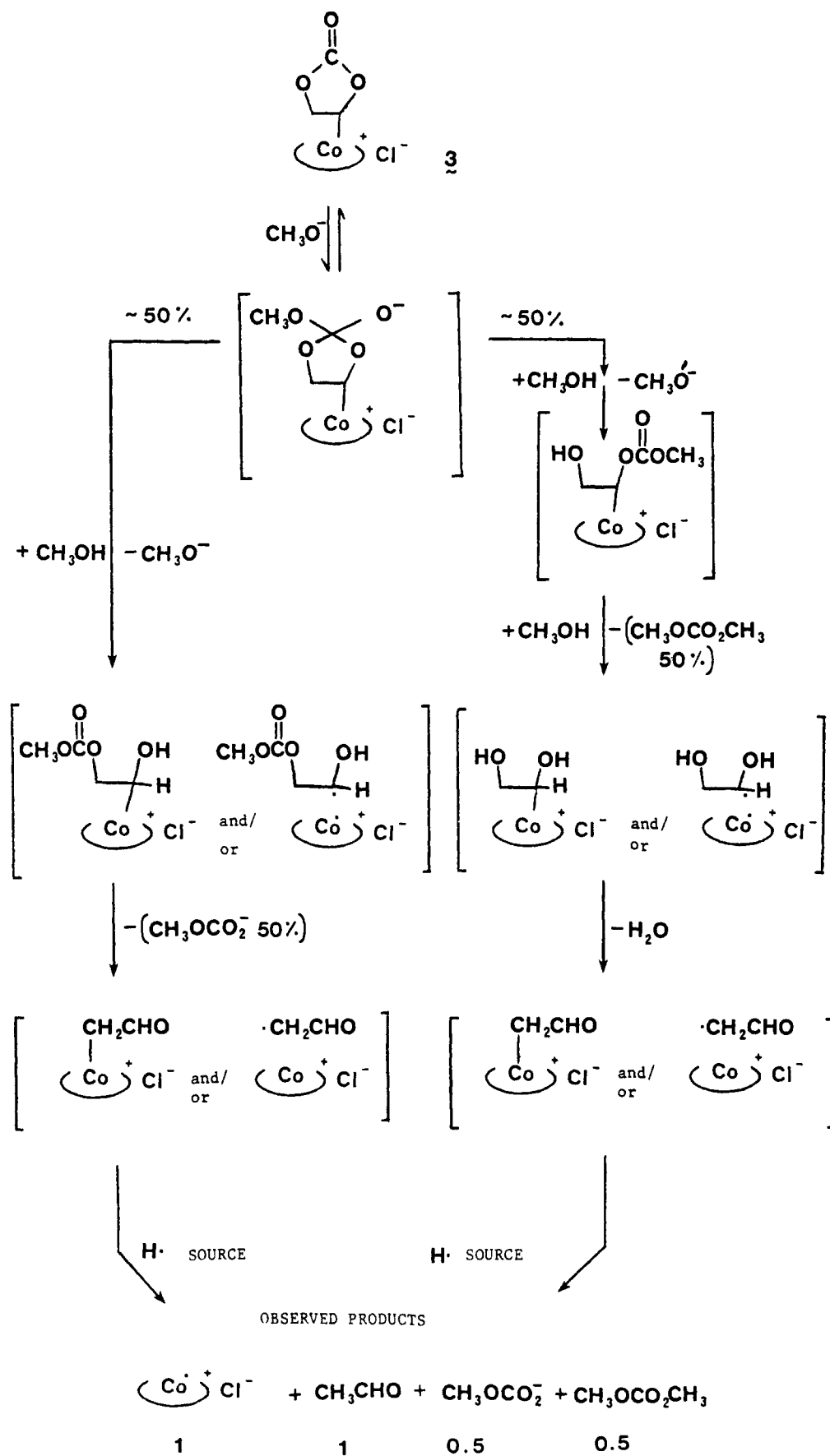
(46) Ocone, L. R.; Block, B. P. *Inorg. Synth.* **1966**, *8*, 130.

(47) Perrin, D. D.; Armavego, W. C. F.; Perrin, D. R. "Purification of Laboratory Chemicals"; Pergamon Press: Oxford, 1966.

(41) Strictly speaking, if the reaction $\text{HOCH}_2\text{CHOH} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{O}$ is involved, this reaction is not a rearrangement reaction since HOCH_2CHOH and CH_2CHO are not isomers, i.e., do not have the same molecular formula.

(42) Finke, R. G.; Sweet, M., unpublished results.

Scheme III



our hands at quantitatively removing benzaldehyde impurities from commercial benzyl alcohol. Treatment with the 2,4-DNP reagent was much more effective. To 10 mL of benzyl alcohol (Fischer) was added

5 mL of the 2,4-DNP reagent. The solution was filtered, and the filtrate gave a negative 2,4-DNP test. The organic fraction of the filtrate was mixed with 30 mL of diethyl ether, washed with 2×30 mL of water,

and dried (MgSO₄), and the ether was removed by rotary evaporation. Fractional distillation at 69–71 °C (2 torr) yielded 4 mL of colorless PhCH₂OH, which gave a negative 2,4-DNP test and was then stored under nitrogen.

(v) **Preparation of 4-Chloro-2-dioxolanone (Chloroethylene Carbonate).** (1) The preparation of 4-chloro-2-dioxolanone was accomplished by the photochemical chlorination of ethylene carbonate, in CCl₄, after the literature method failed in our hands.⁴⁸

A solution of 161 g (1.83 mol) of ethylene carbonate in 250 mL of CCl₄ was irradiated with a 350-W sunlamp. Chlorine was passed into the reaction flask at a rate sufficient to maintain a pale yellow color in solution. After 130 min, excess Cl₂ was removed by bubbling the solution with N₂ for 15 min. Carbon tetrachloride was removed by a flask-to-flask distillation. Vacuum distillation gave 148 g (66%) of colorless chloroethylene carbonate: bp 130–139 °C (39 torr); IR ν_{CO} (neat film) 1825 cm⁻¹; ¹H NMR (CDCl₃, Me₄Si as an external reference) δ 4.8 (2 H), 6.6 (ABX pattern, 1 H); ¹³C NMR (CDCl₃, Me₄Si as an external reference) δ 152.9, 86.2, 74.4; n_D^{25} 1.4513 (lit.⁴⁸ n_D^{25} 1.4530). The 4-chloro-2-dioxolanone was protected from light and was stored at -10 °C under nitrogen in sealed ampules. At room temperature, the liquid slowly yellows, but is easily repurified by redistillation.

(B) **Syntheses.** The cobalt complexes Co[C₂(DO)(DOH)_{pn}]₂, Co[C₂(DO)(DOH)_{pn}]₂, and (CO)Co[C₂(DO)(DOH)_{pn}] were all prepared and characterized as previously detailed.^{6c}

(i) **Synthesis of 3, Chloro(2-oxo-1,3-dioxolan-4-yl)(2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraene-1,1-diol)cobalt(III), CH₂O(C=O)OCHCo[C₂(DO)(DOH)_{pn}]Cl.** This synthesis was accomplished by using the general oxidative-addition chemistry to (CO)Co[C₂(DO)(DOH)_{pn}] we previously reported.^{6c}

In the drybox, protecting the reaction vessel from light, 25 mL of benzene, 530 mg (1.28 mmol) of (CO)Co[C₂(DO)(DOH)_{pn}], and 1.0 mL (13 mmol) of 4-chloro-2-dioxolanone were combined to give a deep blue solution. The reaction mixture was stirred at ≤ 40 °C for 6 h to give a red-orange solution. The flask was removed from the drybox and filtered to give 330 mg (48%) of an orange solid, which was collected and washed with 5 mL of benzene. The filtrate was evaporated to dryness to give an orange-brown solid, which was chromatographed on two 1000- μ m SiO₂ plates with acetone. Three bands resulted on the TLC plates, green Co[C₂(DO)(DOH)_{pn}]₂ (R_f 0.85), the orange chloroethylene carbonate adduct (R_f 0.60) and brown decomposition product(s) (R_f 0). The orange band was collected with acetone, evaporated to dryness, and combined with the previous orange solid to give a total of 550 mg of product (crude yield = 80%). Recrystallization from ethanol/acetone at -10 °C gave 412 mg (60%) of analytically pure orange solid after vacuum drying at room temperature (Anal. (C₁₆H₂₆N₄O₅CoCl) C, H, N); visible λ_{max} (MeOH) 450 nm; IR (KBr) ν_{CO} 1778 cm⁻¹, (MeOH) ν_{CO} 1805, 1780 cm⁻¹; ¹H NMR (CDCl₃, Me₄Si as an external reference) δ 1.12 (dd, J = 7.5 Hz, 3 H), 1.17 (dd, J = 7.5 Hz, 3 H), 2.19 (m, 1 H), 2.36 (s, 3 H), 2.67 (m, 3 H), 2.86 (ABC₃ type, 1 H), 2.99 (ABC₃ type, 1 H), 3.67 (dd, J = 10, 7 Hz, 1 H), 3.74 (m, 2 H), 3.96 (m, 2 H), 4.19 (dd, J = 10, 7 Hz, 1 H), 4.28 (dd, J = 7.5 Hz, 1 H), and 18.75 (s, 1 H, O-H-O). The ¹H NMR assignments were supported by five decoupling experiments, the results of which are provided as supplementary material.

(ii) **Synthesis of 4, the (Aquo) Hexafluorophosphate Complex.** A 100-mg (0.22-mmol) sample of the chloroethylene carbonate oxidative-addition product 3, prepared as in (i) above, was added to 55 mg (0.22 mmol) AgPF₆ in MeOH. After removal of the AgCl, crystallization was accomplished at -22 °C. With H₂O addition to the methanol, crystals formed overnight (without the H₂O, no crystals formed over 1 week). The 73 mg (57%) of dark orange analytically pure crystals were collected, washed with 5:1 H₂O-MeOH, and dried at 25 °C under vacuum. (Anal. (C₁₆H₂₆N₄O₅CoPF₆H₂O) C, H, N.) (In related R[Co](OH₂)]⁺PF₆⁻ complexes,^{6c} the H₂O was confirmed by a Karl Fischer titration.) The ¹H NMR spectrum appeared very similar to that shown in Figure 2A, but with (-CH₂CH₃) at δ 1.10 (t, 3 H) and 1.11 (t, 3 H), and (-CH₃) at 2.47 (s, 3 H) and 2.56 (s, 3 H) (vs. Me₄Si) in d₆-acetone.

(iii) **Preparation and Attempted Isolation of 5, the 1,5,6-Trimethylbenzimidazole Hexafluorophosphate Complex.** Complex 5 was cleanly generated in situ by treating a solution of 100 mg (0.22 mmol) of the chloroethylene carbonate oxidative addition product 3 in 10 mL of methanol with 39 mg (0.24 mmol) of 1,5,6-trimethylbenzimidazole and then 56 mg (0.22 mmol) of AgPF₆. Complex 5 was characterized by its spectral properties: visible λ_{max} (MeOH) 405 nm; ¹H NMR ((CD₃)₂CO, Me₄Si as an external reference) δ 1.03 (br t, 6 H), 2.29 (s, 3 H), 2.30 (s, 3 H), 2.50 (s, 3 H), 2.59 (s, 3 H), 2.60 (m, 2 H), 2.78 (br q, 4 H), 2.80 (m, 2 H), 3.81 (s, 3 H), 4.08 (m, 4 H), 4.75 (m, 1 H), 7.08 (s, 1 H), 7.35 (s, 1 H), 7.64 (s, 1 H).

Attempts to isolate 5 in nonprotic solvents gave at least some of the correct material (IR, NMR), but an analytically pure sample was never obtained. It is likely that trace amounts of H₂O are present that, with the benzimidazole base, give OH⁻, which attacks the carbonate moiety in 5.

(iv) **Synthesis of 6, the (Acetonitrile) Tetraphenylborate Complex for X-ray Crystallography.** The cobalt(III) carbonate complex 3 was converted into the tetraphenylborate salt as follows. To a solution of 130 mg (0.29 mmol) of 3 in 25 mL of methanol was added dropwise a solution of 150 mg (0.44 mmol) of NaB(Ph)₄ in 5 mL of water. Methanol (10 mL) was added, and the solution was filtered to remove NaCl. The volume of the filtrate was reduced by rotary evaporation until a bright orange powder precipitated. This powder was collected by filtration and crystallized from hot aqueous methanol. Subsequent crystallization from acetonitrile by methylene chloride vapor diffusion gave crystals that were adequate for X-ray analysis.

A summary of the X-ray crystallographic data, results, and GC ORTEP plot are provided as supplementary material.

(v) **Successful Synthesis of the Formylmethyl Complex 7, OHCH₂Co[C₂(DO)(DOH)_{pn}].** Following the method of Dolphin,^{16a-d} Co[C₂(DO)(DOH)_{pn}]₂ (5.0 g, 8.6 mmol), Et₃N (1.38 g, 14 mmol, freshly distilled), CH₂Cl₂ (165 mL), 95% ethanol (22 g), and ethyl vinyl ether (34 g, 0.47 mol, freshly distilled) were combined in a 1-L Erlenmeyer flask. The flask was stoppered and stored in the dark for 6 days. Rotary evaporation gave a black solid, which was purified on four 1000- μ m silica plates. Elution with acetone gave two bands, green starting cobalt(III) diiodide (R_f 0.85), and an orange-brown substance (R_f 0.70). The orange-brown band was collected with acetone and evaporated to dryness to give dark orange, solid (OHCH₂)Co[C₂(DO)(DOH)_{pn}]₂ (0.84 g, 20% conversion of >95% yield, 80% recovered starting material): visible λ_{max} (CHCl₃) 392 nm; IR (CHCl₃) 1650, 1491 cm⁻¹; ¹H NMR (CDCl₃, vs. Me₄Si) δ 1.50 (t, J = 7.5 Hz, 6 H), 1.56 (d, J = 5.2 Hz, 2 H), 2.25 (br, 1 H), 2.38 (s, 6 H), 2.80 (br, 1 H), 2.90 (m, 4 H), 3.67 (br dd, 2 H), 4.14 (br dd, 2 H), 8.97 (t, J = 5.2 Hz, 1 H), 19.30 (s, 1 H). Anal. Calcd: C, 36.31; H, 5.28; N, 11.29. Found: C, 35.43; H, 4.75; N, 10.99. Ratios C:H:N, calcd 3.22:0.47:1.00; found, 3.22:0.43:1.00. Repeat analysis on an independently prepared sample gave C, 33.54; H, 4.93; N, 10.44. Recrystallization was attempted in ethanol/diethyl ether, ethanol/acetone, and carbon tetrachloride, all resulting in decomposition of the formylmethyl complex due to the heating required to overcome its relative insolubility. Care is necessary when working with solutions of 7 as it appears to be especially light sensitive. Repeating the synthesis using the dichloride, Co[C₂(DO)(DOH)_{pn}]₂, led to a cleaner sample where a Cl⁻ replaced the I⁻ in 7. Anal. Calcd. for OHCH₂Co[C₂(DO)(DOH)_{pn}]Cl: C, 44.51; H, 6.47; N, 13.84. Found: C, 44.60; H, 6.57; N, 12.03.

Unsuccessful routes to 7 are provided as supplementary material.

(C) **Physical Properties of 3.** (i) **Solubility.** With gentle warming and stirring to overcome any possible kinetic insolubility, 3 was found to have a maximum solubility of ca. 11 mg/1.0 mL of methanol as well as reasonable solubility in acetonitrile, pyridine, 2-propanol, benzyl alcohol, and chloroform. Compound 3 was soluble to a lesser extent in ethanol, ethylene glycol, and THF.

(ii) **Conductivity Determination of the Extent of Axial Chloride Dissociation in Methanol.** Methanol solutions (5.5 $\times 10^{-4}$ M) of 3, Co[C₂(DO)(DOH)_{pn}]₂, Et₃NH⁺Cl⁻, and [Ph₃P=N=PPh₃]⁺Cl⁻ were prepared and their molar conductivities at 25 °C were found to be 6.2 $\times 10^{-3}$, 8.5 $\times 10^{-3}$, 8.5 $\times 10^{-3}$, and 5.6 $\times 10^{-3}$ Ω^{-1} cm⁻¹ M⁻¹, respectively, demonstrating that 3 is largely dissociated in methanol at 25 °C.

(iii) **Axial 1,5,6-Trimethylbenzimidazole Binding Constant.** A 1.60 $\times 10^{-4}$ M anhydrous methanol solution of the aquo PF₆⁻ complex (5) was prepared and the decrease in the λ_{max} 445 peak was monitored (an isosbestic point at 430 nm was observed) as 0, 50, 100, 150, 200, 400, 600, 800, and 1000 equiv of 1,5,6-trimethylbenzimidazole were added by use of a solution of 2.5 M 1,5,6-trimethylbenzimidazole in methanol. The data were graphically analyzed and the error bar was estimated by using Drago's method,⁴⁹ $K_{\text{assoc}} = 90 \pm 20$ M⁻¹.

(iv) **Axial Chloride, Ion Pairing Effects in the ¹H NMR of 3 in CD₃OD.** 3 (10 mg, 0.022 mmol) was dissolved in 1.0 mL of CD₃OD under N₂ and the 100-MHz ¹H NMR spectrum of the resulting solution was obtained (Figure 2B). In the drybox, 0.5 mL of the above solution was treated with a slight excess of Ag⁺BF₄⁻, the resulting AgCl was removed by filtration, and the 100-MHz ¹H NMR spectrum was recorded (Figure 2C). The remaining 0.5-mL CD₃OD solution used for the first ¹H NMR spectrum, but which was not treated with Ag⁺BF₄⁻, was evaporated to dryness under vacuum and redissolved in CDCl₃. The ¹H NMR spectrum (Figure 2D) was then obtained. This material also showed a single

(48) Newman, M. S.; Addor, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 1263.

(49) Drago, R. S. "Physical Methods in Chemistry"; Saunders: Philadelphia, 1977; p 90.

TLC spot (SiO₂, acetone) identical with a fresh sample of 3.

The lack of any detectable effect of Co(II) or other paramagnetic impurities on the ¹H NMR spectrum of 3 in CD₃OD was demonstrated by showing O₂ did not affect the ¹H NMR spectrum of 3 and that added toluene showed the usual sharp singlet for its methyl group.

(v) **Thermal Stability of 3 in CD₃OD.** A 0.022 M solution of 3 in CD₃OD was prepared, the ¹H NMR spectrum was recorded, and this material was left at room temperature in the dark. After 40 h, roughly 30% of the starting material remained. Similar experiments at 5 and -22 °C in the dark showed 3 also reacts or decomposes at these temperatures, often with the formation of a small amount of gray-green crystals. A more detailed study of the thermolysis of this complex is under investigation.⁵⁰

(vi) **Photochemical Stability of 3.** No photochemical decomposition in the solid state of 3 was ever detected. However, like all analogous cobalt alkyls, it is quite sensitive in solution, especially at the concentrations used for UV-visible experiments. Since a knowledge of the photochemical stability of 3 was necessary prior to a study of its other reactions, it was briefly investigated with the following experiments (in CD₃CN rather than CD₃OD due to the more easily interpreted ¹H NMR spectrum of 3 in the former solvent).

A 0.22 M CD₃CN solution of 3 was prepared in a Pyrex ¹H NMR tube in the drybox. After an initial ¹H NMR spectrum was obtained, it was exposed for 10 min to diffuse fluorescent room lighting and then a second ¹H NMR spectrum was obtained that showed no detectable change. After 2 h more of room light, the intensities of the peaks due to starting material had decreased slightly and there was the appearance of a small singlet at δ (CD₃CN) 7.3 that was superimposable with the NMR spectrum of authentic vinylene carbonate. Within 24 h, about 50% of the starting material had decomposed, as estimated by the ¹H NMR spectrum. After 5 days in the drybox in the diffuse light, the solution was noticeably darker. The ¹H NMR spectrum showed that, relative to the HCD₂CN residuals, ca. 80% of the starting 3 had decomposed with the appearance of an intense δ 7.3 (s) peak, as well as the appearance of peaks at δ 3.45 (q, J = 7 Hz) and δ 1.1 (t, J = 7 Hz). These new peaks were not superimposable with the CH₃CH₂ group in free C₂(DOH)₂pn ligand in CD₃CN. In a separate experiment, a 0.44 M NMR tube solution of 3 in CD₃CN was completely decomposed after 11 h of irradiation with a 275-W UV lamp and showed predominantly a broad, intense singlet, δ 7.7, and the sharp, δ 7.3, singlet attributed to vinylene carbonate.

(D) **Physical Properties and Stability of the Formylmethyl Complex 7.** (i) **Conductivity Determination of the Extent of Axial Iodide Dissociation in Methanol.** A 2.02×10^{-3} M anhydrous methanol solution of the formylmethyl complex 7 was prepared, and its molar conductivity at 26 °C was found to be $1.8 \times 10^{-2} \Omega^{-1} \text{cm}^{-1} \text{M}^{-1}$. Comparison of this value with those in part ii of section C clearly demonstrates that 7 is largely dissociated in methanol at 26 °C.

(ii) **Solution Stability of 7.** (a) **Stability in Basic Methanol.** A solution of 8.0 mg of the formylmethyl complex 7 in 1.0 mL of CD₃OD (1.6×10^{-2} M) was examined by ¹H NMR both before and 1 h after treatment with 0.6 equiv of KOH/CD₃OD. This was repeated for a 2.0×10^{-2} M solution in CD₃OD (10 mg/1.0 mL) and 1.0 equiv of KOH/CD₃OD. In both cases no loss of the formylmethyl signals (δ 8.97, 1.56) was observed.

(b) **Stability toward 1,5,6-Trimethylbenzimidazole.** A solution of 10 mg of the formylmethyl complex 7 in 1.0 mL of CD₃OD (2.0×10^{-2} M) was treated with 5.0 mg (1.0 equiv) of AgPF₆. After removal of AgI by filtering through glass wool, 20 equiv of 1,5,6-trimethylbenzimidazole and 1 equiv of KOH/CD₃OD were added. The ¹H NMR spectrum, taken after 1 h, showed >90% of 7 remaining, and a slight upfield shift in the formylmethyl signal (δ 8.82 (t, J = 5 Hz, 1H), 1.40 (d, J = 5 Hz, 2H)).

(c) **Stability toward Cobalt(II).** To 1.0 mL of a 1.1×10^{-2} M solution of Co[C₂(DO)(DOH)_{pn}]Cl in methanol containing 1 equiv of KOH 5 mg (0.92 equiv) of the formylmethyl complex 7 was added. The formylmethyl complex was shown to be completely stable under these conditions for at least 10 min (by visible and IR spectroscopy).

(E) **Methanolysis of 3 and Resultant Stoichiometry.** (i) **General.** The methanolyses of 3 were generally performed at a concentration of 5.0 mg of 3 per 1.0 mL of dry (Mg(OMe)₂), degassed methanol (1.1×10^{-2} M), well below the maximum solubility of 3 in methanol of approximately 2.2×10^{-2} M. Samples of 2a were weighed (± 0.3 mg) into 2-dram vials, brought into the drybox, and dissolved in methanol. Solution vials were septum capped to exclude air, aluminum foil wrapped to exclude light, and were removed from the drybox along with septum-capped vials containing the base catalyst.

Standard KOH/methanol solutions were prepared from 1.50 g of KOH·X(H₂O) (85% KOH, 15% H₂O) and 25 mL of degassed methanol. The addition of a known amount of acid followed by base back-titration

to a phenolphthalein end point confirmed the base molarity was 0.92 M. Under the usual conditions of 5.0 mg of 3 in 1.0 mL of CH₃OH, 12 μ L of the 0.92 M KOH/MeOH solution corresponds to 1.0 equiv of base. The CH₃O⁻/HO⁻ ratio is 4000:1 under these conditions (calculated by using pK_w = 15.7, pK_a (CH₃OH) = 15.5).⁵¹

(ii) **The Methanolysis of Ethylene Carbonate $\text{OCH}_2\text{CH}_2\text{OC}=\text{O}$, as a Control Reaction.** To establish the conditions and rate at which carbonate methanolysis of the carbonate group occurs, ethylene carbonate was examined in a model reaction. A 2.2×10^{-3} M ethylene carbonate solution in CH₃OH was prepared. Within 1 min of the addition of 1.0 equiv of the standard KOH/MeOH solution at 22 °C, the starting IR bands at 1805 and 1780 cm⁻¹ had almost completely disappeared, and a new band at 1755 cm⁻¹, that superimposed with that of authentic CH₃OCO₂CH₃, had appeared. In a similar experiment, 0.2 equiv of KOH/MeOH catalytically removed ca. 90% (IR) of the carbonate group in ethylene carbonate in 2 min.

The presence of DOCH₂CH₂OD was established in a ¹H NMR experiment where 25 mg (0.28 mmol) of ethylene carbonate in 1.0 mL of CD₃OD treated with 1.0 equiv of KOH/CD₃OD gave a singlet at δ 3.58, superimposable with that of authentic HOCH₂CH₂OH in CD₃OD.

(iii) **Methanolysis of 3 with Anhydrous KOCH₃, as a Control Reaction.** In the drybox, an anhydrous KOCH₃/CH₃OH solution was prepared by cautiously combining 852 mg of elemental potassium and 25.0 mL of CH₃OH. One equivalent of this KOCH₃/CH₃OH solution was used to initiate a 10 mg of 3/1.0 mL of CH₃OH reaction. The burgundy-red color appeared with the usual, ca. 0.5 min, half-life, and the product analysis with the usual, ca. 0.5 min, half-life, and the product analysis as described below showed 56% CH₃CHO, 98% Co(II), and 50% each of CH₃OCO₂⁻ and CH₃OCO₂CH₃; i.e., the normal methanolysis reaction was observed.

(iv) **Methanolysis of the (Aquo) Hexafluorophosphate Complex, 4, and of 3 in the Presence of Excess Cl⁻ or I⁻.** A Control Probing the Effect of Ion Pairing. Since Cl⁻ ion pairing in 3 was shown to affect the ¹H NMR spectrum of 3 in MeOH, a control reaction using 4 was done to show that 3 and 4 gave identical methanolysis stoichiometries.

A solution of 12.8 mg (0.022 mmol) of analytically pure 4 in 1.0 mL of degassed CH₃OH was treated with 24 μ L (1.0 equiv) of the standard KOH/CH₃OH solution. The usual orange to burgundy-red color change was observed, and product analysis showed 100% Co(II), 51% CH₃CHO, and ca. 50% each of CH₃OCO₂CH₃ and CH₃OCO₂⁻.

To 1.0-mL aliquots of a solution of 10.0 mg of 3 in 2.0 mL of MeOH were added (CH₃)₄NCl (122 mg, 100 equiv), and (*n*-C₄H₉)₄Ni (113 mg, 20 equiv). Deprotection with 12 μ L (1.0 equiv) of standard KOH/MeOH and product analysis showed 100% Co(II), 55% CH₃CHO, and ca. 50% each of CH₃OCO₂CH₃ and CH₃OCO₂⁻ in both cases.

(v) **CH₃CHO Identification and Yield.** Twenty standard (5 mg of 3/1.0 mL of degassed CH₃OH) solutions were prepared as above. Each orange solution was, in turn, treated with 1.0 equiv (12 μ L) of the standard KOH/CH₃OH solution and the burgundy-red product mixture was analyzed after 2 min by GC on a 21-ft 10% Carbowax 20 M on 80–100 mesh Chromosorb W-Hp column run isothermally at 70 °C. A sharp peak was observed which coincided with authentic CH₃CHO in CH₃OH or in THF. This and the GC-MS experiment (vide infra) show that the compound detected is CH₃CHO, even though a ¹H NMR experiment in CD₃OD showed that (0.011 M CH₃CHO in CD₃OD exists completely, as expected, as its hemiacetal: δ 1.37 (d, J = 7 Hz, CH₃CH(OD)(OCD₃)), 4.8 (q, J = 7 Hz, CH₃CH(OD)(OCD₃)). Rapid methanol loss from the hemiacetal to yield CH₃CHO must be occurring on the GC injector port or column. The observed yield of CH₃CHO, and its standard deviation, $61 \pm 6\%$, was obtained from cut-and-weigh quantification in comparison to an equal number of injections of independently prepared 1.1×10^{-2} M CH₃CHO (freshly distilled)/CH₃OH solutions. In a control experiment where 1.0 mL of the standard CH₃CHO/CH₃OH solution was placed in a septum-capped, 2-dram vial with a large N₂ volume above the solution and then injected into the GC, it was shown that the volatile CH₃CHO is not lost to vaporization. In an experiment performed in CD₃OD, the CH₃CHO was found to be identical with that in CH₃OH.

The identity of the volatile product as CH₃CHO was confirmed in a GC-MS experiment, and by isolation of a 2,4-dinitrophenylhydrazone derivative. In the GC-MS experiment, a solution of 5.0 mg of 3 in 1.0 mL of CH₃OH was treated with 12 μ L of standard KOH/CH₃OH and injected after 2 min. The following *m/e* values, % of the base peak, and (literature % of the base peak) were observed: 44, 70% (77%); 43, 40% (42%); 42, 12% (12%); 41, 7% (5%); 29, 100% (100%). Rapid H/D

(51) Reference 30b, p 62.

(52) "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds"; Graselli, J. G., Ritchey, W. M., Eds.; CRC Press: Cleveland, 1975; Vol. II, p 3.

exchange between basic methanol and acetaldehyde rendered GC-MS experiments with deuterium-labeled methanol useless.

In the 2,4-DNP experiment, a solution of 400 mg of **3** in 40 mL of methanol was treated with 160 μ L (0.17 equiv) of standard KOH/CH₃OH. After 15 min the burgundy-red solution was poured into 16 mL of freshly prepared 2,4-DNP reagent, and the reaction mixture was evaporated to dryness. Possible products were separated by TLC (1000 μ m of silica, repeatedly eluted with 90% CCl₄/10% pyridine)⁵³ to give five distinct bands (*R_f* values): orange (0.95); red-orange (0.80); yellow (0.55); red-orange (0.2); purple (0.1), turned colorless over 1 h. Only the yellow band (*R_f* 0.55) was unambiguously identified, and was shown to be identical with authentic acetaldehyde 2,4-dinitrophenylhydrazine by TLC and ¹H NMR (δ 1.50 (br s, 1H), 2.04 (d, *J* = 6 Hz, 3H), 7.45 (m, 1H), 7.84 (d, *J* = 9 Hz, 1H), 8.20 (m, 1H), 9.01 (d, *J* = 3 Hz, 1H).

(vi) **CH₃OCO₂CH₃ and CH₃OCO₂⁻ Identification and Yields.** Using ten 5.0 mg of 3/1.0 mL of CH₃OH solutions, each treated with 12 μ L (1.0 equiv) of KOH/CH₃OH, the IR yield and standard deviation of CH₃OCO₂CH₃ (ν_{CO} 1755 cm⁻¹, ϵ 2.5 \pm 0.1 \times 10² M⁻¹ cm⁻¹) was 50 \pm 10% in comparison to authentic material. Similarly, CH₃OCO₂⁻ (ν_{CO} 1655 cm⁻¹, ϵ 3.4 \pm 0.3 \times 10² M⁻¹ cm⁻¹) was detected in 48 \pm 10% yield by IR. The IR standards of CH₃OCO₂⁻ were prepared by the addition of 1.0 equiv of CO₂ via gas tight syringe to 0.022 M KOH/CH₃OH solutions to give samples with reproducible IR spectra. A simple control showed that the addition of 1 equiv of KOH/CH₃OH to a 0.022 M dimethylcarbonate in CH₃OH solution gave no reaction, i.e., that CH₃OCO₂⁻ is not formed from the dimethylcarbonate product and OH⁻ present in the reaction.

(vii) **Co^{II}[C₂(DO)(DOH)_{pn}]Cl Identification and Yield.** The treatment of orange CH₃OH solution of **3** with base causes the rapid formation of a burgundy-red, air-sensitive solution of Co^{II}[C₂(DO)(DOH)_{pn}]Cl. This cobalt(II) material was independently prepared by the Cl atom transfer reduction of 122 mg (0.3 mmol) of Co[C₂(DO)(DOH)_{pn}]Cl₂ with 80 mg (0.31 mmol) of [Cr(acac)₃]₂ in 100 mL of CH₃OH. Alternatively, the cobalt(II) complex was prepared by a Co(I) + Co(III) \rightarrow 2Co(II) redox reaction. Fifty milligrams (0.13 mmol) of Co[C₂(DO)(DOH)_{pn}]Cl₂ and 44.5 mg (0.13 mmol) of (CO)Co[C₂(DO)(DOH)_{pn}] were combined in 25 mL of CH₃OH to give the desired burgundy-red product. The product showed a λ_{max} (CH₃OH) of 520 nm, obeyed Beer's law with an ϵ_{max} (CH₃OH) of 3.6 \pm 0.2 \times 10³ M⁻¹ cm⁻¹, and exhibited the expected⁵⁴ eight-line (*I*(Co) = 7/2) ESR spectrum under N₂, identical with that observed for the Co(II) methanolysis product of a 2.2 \times 10⁻² M solution of **3**. The yield and standard deviation of Co^{II}[C₂(DO)(DOH)_{pn}]Cl, 100 \pm 5%, were determined from 20 methanolysis experiments using the measured extinction coefficient. In the drybox, solutions of 5.0 mg of 3/1.0 mL of CH₃OH were treated with 12 μ L (1.0 equiv) of standard KOH/CH₃OH, and the products were analyzed and quantified by visible spectroscopy in a septum-capped, 0.10-mm pathlength quartz cell.

(viii) **Methanolysis Product Yields vs. Equivalents of KOMe.** Aliquots (1.0 mL) of a 1.1 \times 10⁻² M **3**/CH₃OH solution were treated with 25, 10, 3.8, 1.0, 0.4, 0.17, 0.13, and 0.08 equiv of the standard KOH/CH₃OH solution and the products were identified as above. For \geq 1 equiv of base, analyses were performed 2 min after addition of base. For < 1 equiv of base, analyses were performed after a period of time inversely proportional to the amount of base added. Cobalt(II) yields of 100 \pm 5% were determined for each of the base concentrations. Yields of 50% each for CH₃OCO₂CH₃ and CH₃OCO₂⁻ were observed in each case, except for < 1 equiv of base, where only trace CH₃OCO₂⁻ and 50% CH₃OCO₂CH₃ were detected. In the samples giving < 50% CH₃OCO₂⁻, addition of 1 equiv of KOH/CH₃OH after completion of the methanolysis regenerated 50% CH₃OCO₂⁻, consistent with the equilibrium CH₃O⁻ + CO₂ \rightleftharpoons CH₃OCO₂⁻. Observed acetaldehyde yields (equiv of base) were the following: 13% (25), 25% (10), 42% (3.8), 60% (1), 67% (0.4), 80–88% (0.17), 84% (0.13), 84% (0.08). That the base-dependent acetaldehyde yields were a consequence of base-catalyzed decomposition of acetaldehyde was supported by a control experiment. A freshly prepared 1.1 \times 10⁻² M solution of acetaldehyde in methanol was divided into 1.0-mL aliquots in septum-capped 2-dram vials. To the aliquots 0, 0.08, 0.13, 0.17, 0.40, 1.0, 3.8, 10, and 25 equiv of KOH/CH₃OH were added and the solutions were examined by GLC after a period of time analogous to that used for the methanolysis reaction. The number of equivalents of base used, observed % acetaldehyde remaining (and corrected 3 methanolysis yields) are the following: 25, 15% (87%); 10, 35% (70%); 3.8, 65% (65%); 1.0, 80% (75%); 0.4, 80% (85%); 0.17, 90% (89–98%); 0.13, 95% (90%); 0.08, 95% (90%); 0, 100% (95% by extrapolation).

(F) **The H⁻ Source.** (i) **Oxidation of the Co^{II}[C₂(DO)(DOH)_{pn}]Cl Product and Its Characterization as Intact Co^{III}[C₂(DO)(DOH)_{pn}]X₂.** Although the identical visible and ESR spectra of the Co(II) methanolysis product, in comparison to authentic Co^{II}[C₂(DO)(DOH)_{pn}]Cl (section E, (vii)), seemed to rule out the macrocyclic ligand as the H⁻ source, this was confirmed by I₂ or BrCCl₃ oxidation to Co^{III}[C₂(DO)(DOH)_{pn}]X₂, followed by visible, TLC, and 360-MHz ¹H NMR analysis.

A solution of 5.0 mg of 3/1.0 mL of CH₃OH was treated with 12 μ L (1 equiv) of standard KOH/CH₃OH, and after 2 min was titrated with a solution of 200 mg of I₂/4.0 mL of CH₃OH (0.20 M), monitoring loss of λ_{max} 520 nm in the visible spectrum. To completely consume the Co(II) 27 μ L of the I₂ solution (0.50 \pm 0.05 equiv of I₂) was required. The resultant orange Co(III) solution was evaporated to dryness, and the ¹H NMR spectrum of the residue (CDCl₃) showed 100 \pm 10% of each of the ligand positions to be intact and identical with those of authentic Co^{III}[C₂(DO)(DOH)_{pn}]X₂: δ 1.2 (t, 6H), 2.6 (s, 6H), 2.7 (m, 2H), 3.1 (q, 4H), 4.2 (m, 4H), 19.4 (s, 1H, O---H---O). In addition to the NMR signals assigned to the ligand system, several small, unidentified peaks at δ 9.63 (s), 4.69 (s), 3.85 (d), and 3.79 (s) were observed. These peaks were not generated in control reactions of 1.1 \times 10⁻² M solutions of CH₃CHO and/or H₂CO in methanol with I₂ or BrCCl₃.

A solution of 5.0 mg of 3/1.0 mL of CH₃OH was oxidized with 5 μ L of BrCCl₃, and the reaction mixture was evaporated to dryness. Purification of the residue by TLC (silica/acetone) gave one major band which cospotted with authentic Co(III) dihalides. The ¹H NMR spectrum (CDCl₃) of the green Co(III) product was similar to that obtained in the I₂ oxidation above, showed 100 \pm 10% of all ligand positions to be intact, and also included the same small, unidentified peaks.

(ii) **Attempted Detection of -CH₂OH Derived Products H₂CO and HOCH₂CH₂OH.** The potential -CH₂OH derived products, H₂CO and HOCH₂CH₂OH, were searched for among the methanolysis products of **3**. Control experiments were also done to determine the reported levels of detectability of these substances under the reaction conditions.

(a) **HOCH₂CH₂OH.** A solution of 34 mg of HOCH₂CH₂OH/10 mL of CH₃OH was prepared (5.5 \times 10⁻³ M), a 1.0-mL aliquot of this solution was treated with 12 μ L (2 equiv) of the standard KOH/CH₃OH, and the solution was evaporated to dryness. The ¹H NMR spectrum of the residue (CD₃OD) showed DOCH₂CH₂OD, δ 3.56, to be detectable at concentrations as low as 5.5 \times 10⁻⁴ M in the reaction mixture.

A solution of 5.0 mg of 3/1.0 mL of CH₃OH was treated with 12 μ L (1 equiv) of the standard KOH/CH₃OH, air oxidized to Co(III) after 2 min, and evaporated to dryness. The ¹H NMR spectrum (CD₃OD) of the residue showed no (< 5%) HOCH₂CH₂OH.

(b) **H₂CO.** Solutions of H₂CO (5.5 \times 10⁻³ M, generated from either paraformaldehyde or aqueous solutions) in CH₃OH were used in control experiments. While H₂CO could be detected in 1.0-mL aliquots of these solutions by the chromotropic acid test (detectability level 10%) and by isolation of the dimedon and 2,4-DNP derivatives, treatment of the H₂CO/CH₃OH solution with 0.25–1.0 equiv of standard KOH/CH₃OH resulted in solutions which gave negative results to all three tests. These results suggest that a 50% yield of H₂CO in the methanolysis of **3** would not be detectable.

In keeping with the control experiments, methanolysis products from solutions of 5.0 mg 3/1.0 mL CH₃OH and 3 μ L (0.25 equiv) of standard KOH/CH₃OH gave a negative chromotropic acid test and failed to give dimedon or 2,4-DNP derivatives of H₂CO.

(c) **¹³CH₃OH Methanolysis of **3**.** In an attempt to observe solvent derived products, the methanolysis of **3** in ¹³C-labeled CH₃OH was performed.

In a mixture of 0.5 mL of ¹³CH₃OH, 1.0 mL of CD₃OD, and 1.5 mL of CH₃OH was dissolved 17 mg of **3**, and 12 μ L (0.4 equiv) of standard KOH/CH₃OH was added. After 10 min the Co(II) solution was air oxidized and the ¹³C NMR spectrum of the products was obtained. After 18 000 transients, only methanol was observed in the ¹³C NMR spectrum.

(iii) **PhCH₂OH Solvent.** Using carefully prepared PhCH₂OH solvent, which gave a negative PhCHO test (section A (iv)), PhCHO produced in the deprotection of **3** was detected as its 2,4-DNP derivative.

To a solution of 5 mg of 3/0.9 mL of PhCH₂OH was added 12 μ L (1 equiv) of standard KOH/CH₃OH. After 5 min the deep red-brown, air-sensitive solution was examined by GC (21-ft 10% Carbowax on 80–100 mesh Chromosorb W-HP run isothermally at 150 $^{\circ}$ C) and the amount of PhCHO produced was determined to be 52 \pm 15%. Air oxidation of the Co(II) solution gave an orange solution, but no change in the GC-observed PhCHO concentration. (The PhCHO yields determined by GC are suspect, as a background concentration corresponding to 180 \pm 10% (based on **3**) was generated from PhCH₂OH by, apparently, an injection port phenomenon. For this reason, the PhCHO yield was independently determined by a 2,4-DNP experiment). The Co(III) solution was added to 10 mL of the 2,4-DNP reagent and evaporated to

(53) Seifert, B.; Kolbe, M. Z. *Anal. Chem.* **1974**, *271*, 337.

(54) (a) Endicott, J. F.; Lilie, J., Jr.; Kusza, J. M.; Ramaswathy, B. S.; Schmonsees, W. G.; Simic, M. G.; Glick, M. D.; Rillema, D. P. *J. Am. Chem. Soc.* **1977**, *99*, 429. (b) Daul, C.; Schapfer, C. W.; Von Zelewsky, A. *Struct. Bonding (Berlin)* **1979**, *36*, 129.

dryness, and the ^1H NMR spectrum of the residue dissolved in CDCl_3 showed ca. 40% PhCHO, DNP derivative: δ 9.05 (d, 1 H), 8.66 (br s, 1 H), 8.28 (m, 1 H), 8.06 (m, 2 H), 7.68 (m, 2 H), 7.39 (m, 3 H), identical with authentic material.

(iv) **Other Solvents.** (a) **Ethanol.** To a heterogeneous mixture of 5.0 mg of **3** and 1.0 mL of ethanol was added 5 μL (0.5 equiv) of 1.1 M sodium ethoxide in ethanol. After 4 min the acetaldehyde yield was measured by GC ($55 \pm 10\%$, corrected for base-catalyzed decomposition).

In a 0.1-mm pathlength visible cell, 1.0 mL of a solution of 5 mg of **3** in 5.0 mL of ethanol was treated with 1.0 equiv of NaOEt/EtOH, and growth of cobalt(II), λ_{max} 520 nm, was followed vs. time. The reaction required 4800 s to go to completion, and after 5300 s the reaction products were examined by visible and IR spectroscopy and by GC. The observed products were the following: cobalt(II), $95 \pm 5\%$; diethyl carbonate, IR 1760 cm^{-1} , assigned by analogy to dimethyl carbonate (1755 cm^{-1}); acetaldehyde $60 \pm 20\%$, after correction for base-catalyzed decomposition over 5300 s.

Solutions of 5 mg of **3** in 1.0 mL of MeOH/EtOH (7:3 and 3:7) were prepared and 0.5 equiv of standard base was added. The acetaldehyde yields were determined by GC to be 63 ± 10 and $66 \pm 10\%$, after 5 and 6 min, respectively.

(b) **Isopropyl Alcohol.** In the manner described above, 5 mg of **3** in 1.0 mL of MeOH/*i*-PrOH (7:3 and 3:7) were prepared and deprotected with 0.5 equiv of base. The acetaldehyde yields were determined by GC to be $47 \pm 10\%$ and $36 \pm 5\%$ after 5 and 45 min, respectively. No acetone was detected among the products.

This procedure was repeated in 7:3 *i*-PrOH/ CD_3OD . After 10 min the acetaldehyde yield was determined to be $50 \pm 5\%$. Again, no acetone was detected among the products (by GC).

(c) **Ethylene Glycol.** To a solution of 5 mg of **3**/1.0 mL of ethylene glycol was added 22 μL (1.0 equiv) of a 0.5 M KOH/ethylene glycol solution, and the products were analyzed after 3 min. The burgundy-red solution was determined to contain 80% Co(II) (λ_{max} 520 nm) and 40% CH_3CHO (GC). Acidification of the solution with 4 μL (4.3 equiv) of concentrated HCl resulted in the conversion of acetaldehyde and ethylene glycol into 2-methyl-1,3-dioxolane (40% yield based upon starting **3**, determined by GC by comparison to a standard solution; δ (CDCl_3) 1.25 (d, $J = 5\text{ Hz}$, 3 H), 3.8 (m, 4 H), 4.82 (q, $J = 5\text{ Hz}$, 1 H) (lit.⁵⁵ δ 1.26, 3.8) by the well-known⁵⁶ dehydration reaction. The acetaldehyde yields were not greatly increased by reducing the amount of base catalyst used

in the deprotection of ethylene glycol solutions of **3**. When 0.17 equiv of KOH/ethylene glycol was used, an acetaldehyde yield of ca. 45% was detected. In order to confirm the structure of the Co(II) product in the above reactions, a BrCCl_3 oxidation of the solvolysis product followed by ^1H NMR analysis was used. A solution of 5 mg of **3**/1.0 mL of ethylene glycol was treated with 22 μL (1.0 equiv) of 0.5 M KOH/ethylene glycol. After 15 min, the burgundy-red solution was treated with 5 μL (4.6 equiv) of BrCCl_3 , and the resultant orange solution was evaporated to dryness. The ^1H NMR (CDCl_3) spectrum of the residue, δ 1.2 (t, 6H), 2.6 (s, 6H), 3.1 (q, 4 H), was identical with that of authentic $\text{Co}^{\text{III}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{X}_2$ added to the solution. Clearly, catalytic CH_3CHO formation or H- abstraction from the ligand are not taking place.

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Registry No. **3**, 75504-42-6; **3** (PG = $-\text{B}(\text{O}i\text{Bu})_2$), 87728-43-6; **3** (PG = BPh), 87738-96-3; **3** (PG = $-\text{C}(\text{CH}_3)\text{OCH}_3$), 87728-44-7; **3** (PG = $-(\text{SiMe}_3)_2$), 87728-45-8; **3** (PG = $-\text{CPh}_2$), 87728-46-9; **3** (PG = $\text{P}(\text{O})\text{OPh}$), 87728-47-0; **4**, 87728-37-8; **5**, 87728-39-0; **6**, 87728-41-4; **7**, 87728-42-5; $(\text{CO})\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]$, 75504-41-5; $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}_2$, 75962-19-5; $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{I}_2$, 75962-04-8; $\text{Co}^{\text{II}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Cl}$, 75504-43-7; $\text{Co}^{\text{II}}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{Br}$, 75962-16-2; $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}]\text{I}(\text{PF}_6)$, 87728-35-6; Bz-Me, 1128-27-4; $\text{OCH}_2\text{CH}_2\text{OC}=\text{O}$, 96-49-1; CH_3CHO , 75-07-0; $\text{CH}_3\text{OCO}_2\text{CH}_3$, 616-38-6; $\text{CH}_3\text{OCO}_2\text{H}$, 7456-87-3; ClCH_2CHO , 107-20-0; $\text{CH}_2\text{CHO}^-\text{Li}^+$, 67285-39-6; $\text{CH}_2=\text{CHOSn}(n\text{-Bu})_3$, 66031-94-5; ethyl vinyl ether, 109-92-2; trimethylsilyl vinyl ether, 6213-94-1; diol dehydratase, 9026-90-8; 4-chloro-2-dioxolanone, 3967-54-2.

Supplementary Material Available: A tabulation of the data from the five decoupling experiments on **3**, details and ORTEP plot from the X-ray diffraction structural study of **3**, experimental details on the unsuccessful routes to the formylmethyl complex **7**, and a summary on other diol protecting groups for analogs of **3** that were examined (12 pages). Ordering information is given on any current masthead page.

(55) Story, P. R.; Saunders, M. *J. Am. Chem. Soc.* **1962**, *84*, 4876.

(56) van der Linde, H. V. *Tetrahedron Lett.* **1973**, *29*, 3925.