is quite similar to those of $Ru(bpy)_3^{2+}$ [1-3] and $Ru(bpy)_2(CN)_2$[25] except for a smaller integrated intensity of the d-π^* transition. The spectrum exhibits an extremely pronounced solvatochromic behavior, with solvent shifts that are twice as large as observed for $Ru(bpy)_2(CN)_2$.[25,26] This strengthens previous proposals[26-28] that in this class of complexes the relevant interactions with the solvent involve the cyanides, being presumably of the donor-acceptor type.[29]

The complex emits in fluid solution at room temperature with solvent-dependent energy and lifetime (Table I). In deaerated water, the emission quantum yield[30] is 0.0068, corresponding to a radiative rate constant of 7.1×10^4 s^{-1}, practically coincident with the values found for $Ru(bpy)_3^{2+}$ and $Ru(bpy)_2(CN)_2$.[31] The smaller solvent dependence of emission relative to absorption is consistent with the expected lower basicity of the cyanides in the d-π^* excited state. In low-temperature glasses, the emission is substantially blue shifted with respect to room temperature and depends to a smaller extent on the matrix (Table I). The minor dependence of the lifetime observed in these conditions probably arises from energy-gap-law effects.[20,32] The comparison between the low-temperature and room-temperature lifetimes indicates that the solvent has a large influence on the rate of the main thermally activated excited-state decay process, most probably the conversion between the d-π^* state and a d-d state.[20,32,33]

The excited-state absorption (ESA) spectrum[34,35] of $Ru(bpy)(CN)_4^{2-}$ is shown in Figure 2. It is quite similar to that reported for $Ru(bpy)_3^{2+}$[9,35-38] except for a greater sharpness and lower intensity of most bands, consistent with the greater simplicity of the chromophoric unit of the mono-bpy complex.

The complex is reversibly oxidized in cyclic voltammetry,[39] with potentials that are remarkably dependent on the solvent: $E_{1/2}$[Ru(III)/Ru(II)] = 0.78 V vs. SCE in H_2O, and $E_{1/2}$[Ru(III)/Ru(II)] = 0.20 V vs. SCE in DMF. The observed potential shift is comparable to the spectral shifts (Table I) and provides further, direct evidence for the importance of second-sphere donor-acceptor interactions[29] between the cyanide ligands and the solvent. In DMF, the complex is reversibly reduced in cyclic voltammetry[39] with $E_{1/2}$[Ru(II)/Ru(I)] = -1.95 V vs. SCE.

For systems, such as $Ru(bpy)(CN)_4^{2-}$, in which the emission energy is strongly dependent on solvent *and* physical state, the usual procedures[4,40] for estimating the excited-state redox potentials involve large uncertainties.[26] Taking 77 and 298 K emission maxima as upper and lower limits, respectively, for the zero-zero excited state energy, the following estimates can be made for the redox potential $^*E°$ (V vs. SCE) of the $Ru(bpy)(CN)_4^-/^*Ru(bpy)(CN)_4^{2-}$ couple: $-1.60 < {}^*E° < -1.28$ in water and $-1.83 < {}^*E° < -1.32$ in DMF. Within these uncertainties, the excited state of $Ru(bpy)(CN)_4^{2-}$ is expected to be a very strong reductant. In fact, in 3:1 water/acetonitrile the emission is quenched at diffusion-controlled rate ($k_q = 7.5 \times 10^9$ M^{-1} s^{-1}) by nitrobenzene (reduction potential, -1.15 V vs. SCE). For comparison purposes, it may be recalled that nitrobenzene does not quench $^*Ru(bpy)_3^{2+}$ ($k_q < 2 \times 10^5$ M^{-1} s^{-1}).[41]

Work is in progress toward a more complete characterization of $Ru(bpy)(CN)_4^{2-}$, with particular regard to solvent and temperature dependence of the photophysical behavior, ground- and excited-state acid-base equilibria, electron-transfer quenching, and metalation via cyanide bridges.

Acknowledgment. This work was supported by the Consiglio Nazionale delle Ricerche (P. S. "Dinamica Molecolare e Catalisi") and by the Ministero della Pubblica Istruzione. We are indebted to Professor V. Balzani for suggesting the photochemical synthetic route.

(24) Measurements in nonaqueous solvents were carried out by using the tetrabutylammonium salt of the complex. This salt (deep violet when dry) was obtained from the potassium salt by ion exchange on a cationic CM Sephadex C-25 resin in aqueous solution, followed by evaporation to dryness. Notice that small amounts of water left in this step can substantially affect the results in nonaqueous solutions.

(25) Demas, J. N.; Addington, J. W.; Peterson, S. H.; Harris, E. W. *J. Phys. Chem.* **1977**, *81*, 1039.
(26) Bignozzi, C. A.; Scandola, F. *Inorg. Chem.* **1984**, *23*, 1540.
(27) Belser, P.; von Zelewsky, A.; Juris, A.; Barigelletti, F.; Balzani, V. *Gazz. Chim. Ital.* **1985**, *115*, 723.
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(29) Balzani, V.; Sabbatini, N.; Scandola, F. *Chem. Rev.* **1986**, *86*, 319.
(30) The quantum yield was obtained by using a corrected emission spectrum (Rhodamine B quantum counter), by comparison with $Ru(bpy)_3^{2+}$.[2]
(31) Demas, J. N.; Crosby, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 2841.
(32) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583.
(33) Allen, G. H.; White, R. P.; Rillema, D. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 2613.
(34) The ESA spectrum was taken in laser photolysis 50 ns after the shot, allowing for a 30% correction in intensity due to the finite laser flash duration. The spectrum was put on a molar absorptivity scale by using triplet benzophenone as a laser actinometer.[26,35]
(35) Bensasson, R.; Salet, C.; Balzani, V. *J. Am. Chem. Soc.* **1976**, *98*, 3722.
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(38) Milder, S. J.; Gold, J. S.; Kliger, D. S. *J. Phys. Chem.* **1986**, *90*, 548.
(39) Working platinum electrode (oxidation) or HME (reduction), SCE reference electrode, sweep rates in the range 0.04-0.4 V s^{-1}, 0.1 M TEAP.
(40) Balzani, V.; Scandola, F. In *Energy Resources through Photochemistry and Catalysis*; Graetzel, M., Ed.; Academic Press: New York, 1983; p 1.
(41) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909.

π-Facially Controlled Nucleophilic Additions of Chiral Vinylorganometallics to Chiral β,γ-Unsaturated Ketones. 1. Double Diastereoselection Studies Involving 7,7-Dimethoxy-5-norbornen-2-one

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A wealth of information exists concerning methods for achieving relative asymmetric induction in nucleophilic additions to optically active acyclic carbonyl compounds.[1] Transition state models based on steric considerations,[2] stereoelectronic factors,[3] and σ-orbital interactions involving the α-substituents[4] abound. Much less well understood is the extent to which stereochemistry can be controlled, both in a relative and absolute sense, when the carbonyl group is only remotely perturbed.[5]

To our mind, the oxy-Cope rearrangement holds considerable synthetic promise, much of which is yet untapped. Importantly,

(1) (a) Eliel, E. L. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2, Chapter 5. (b) Solladié, G. *Ibid.*, Chapter 6. (c) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, Chapter 2. (d) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1.
(2) (a) Cram, D. J.; Wilson, D. R. *J. Am. Chem. Soc.* **1963**, *85*, 1245. (b) Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112. (c) Karabatsos, G. J. *J. Am. Chem. Soc.* **1967**, *89*, 1367. (d) Chêrest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (e) Arjona, O.; Pêrez-Ossorio, R.; Pêrez-Rubalcaba, A.; Quiroga, M. L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 597.
(3) (a) Giddings, M. R.; Hudec, J. *Can. J. Chem.* **1981**, *59*, 459. (b) Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540 and pertinent references cited in these papers.
(4) (a) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162. (b) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703. (c) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. (d) Fukui, K.; Fujimoto, H.; Inagaki, S. *J. Am. Chem. Soc.* **1976**, *98*, 4054. (e) See also: Cheung, C. K.; Tseng, L. T.; Lin, H.-H.; Srivastava, S.; leNoble, W. J. *Ibid.* **1986**, *108*, 1598.
(5) Consult, for example: (a) Brown, H. C.; Muzzio, J. *J. Am. Chem. Soc.* **1966**, *88*, 2811. (b) Solladié, G.; Greck, C.; Demailly, G.; Solladié-Cavallo, A. *Tetrahedron Lett.* **1982**, 5047. (c) Tramontini, M. *Synthesis* **1982**, 605. (d) Zwick, J.-C.; Vogel, P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 787.

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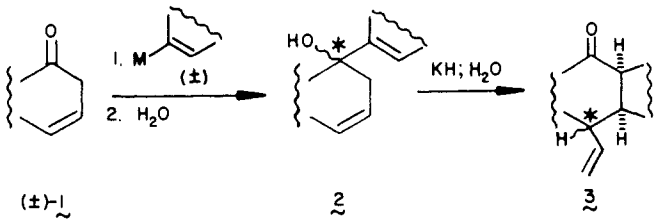
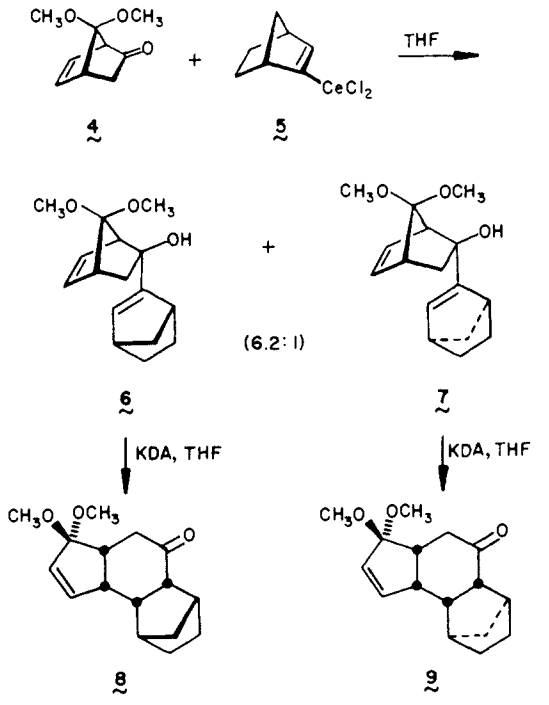
Scheme I



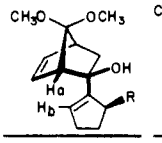
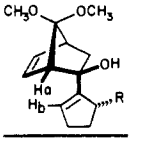
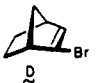
Scheme II



Scheme I represents one of the few processes that can be strictly classified as a *carbonyl regenerative sequence*. In view of the pivotal role of the carbonyl group in synthesis, this particular consideration holds special synthetic appeal and importance. In this connection, it is striking to recognize that no example of this transformation has been documented where *both reaction partners* are chiral! There is good reason. If a minimum of one chiral element is present in each reactant, the process must give rise to *eight* diastereomeric products since a new stereogenic center is created. As a consequence of the stereocontrolled course of the ensuing oxy-Cope reaction, the product mixture at this more advanced stage is no less complex. On the other hand, *if* facial stereoselectivity were sterically regulated and *if* respectable levels of diastereoselectivity were realizable during the initial coupling step, kinetic resolution could become eminently feasible. In this paper, we demonstrate the workability of these concepts in the case of 7,7-dimethoxy-5-norbornen-2-one (**4**),[6] where exo attack is strictly precluded.

Because our initial attempts to couple **4** with vinyllithium reagents were unpromising due to excessive enolization, recourse was made to cerium reagents such as **5**.[7] In a prototypical procedure, vacuum-dried $CeCl_3 \cdot 7H_2O$ (140 °C, 0.5 torr, 2.5 h) was slurried in dry tetrahydrofuran, cooled to −78 °C, and treated with the vinyllithium reagent (0.94 equiv). After 30 min, an equimolar amount of **4** was introduced (−78 °C), followed by saturated NH_4Cl solution 2 h later. Product ratios were determined by analytical HPLC techniques.

Table I. Diastereoselectivity Ratios for the Addition of Vinylcerium Reagents to **4** and Key ^1H NMR Chemical Shift Data (300 MHz, C_6D_6 Solution)

vinyl bromide	yield,[a] %	diastereoselectivity ratio	 H_a	H_b	 H_a	H_b
 A	50 (92)	16:1 (94%)	3.63	5.13	3.20	5.36
 B	38 (76)	10.4:1 (91%)	3.80	5.37	3.38	5.38
 C	43 (86)	2.1:1 (68%)	2.97	4.91	2.84	5.15
 D	41 (73)	6.2:1 (86%)	3.52	5.51	3.10	5.57
 E	61 (90)	10.4:1 (91%)	3.14	5.25	2.83	5.39
 F	43 (99)	4.2:1 (81%)	2.88	5.20	2.85	5.30
 G	24 (~80)	2.3:1 (70%)	3.23	5.49	2.95	5.62

[a] The values in parentheses take account of the amount of unreacted **4** that was recovered.

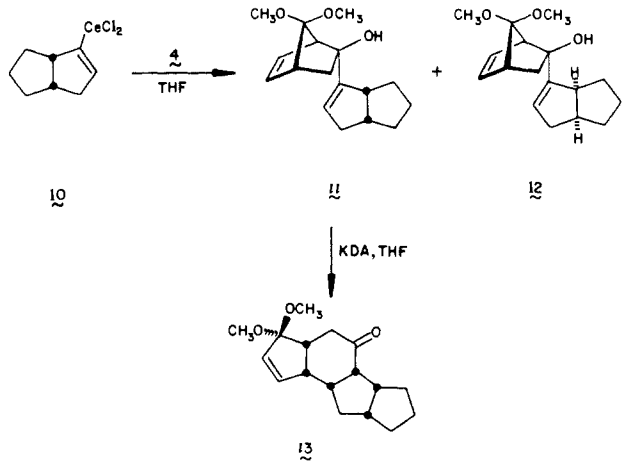
In the specific case of **5**, a 6.2:1 mixture of **6** and **7** was produced in good yield (Scheme II). Following chromatographic separation of these diastereomers, the crystalline major product (mp 70 °C) was subjected to X-ray analysis for structural confirmation.[8] Subsequently to unfold was recognition that the chemical shifts of those protons labeled H_a and H_b in these alcohols exhibit an ordering pattern in C_6D_6 solution that correlates strictly with the relative configuration of the cyclopentenyl R substituent (Table I). Independent anionic oxy-Cope rearrangement[9] of **6** and **7** readily gave rise to **8** and **9**, respectively.[10] From this series of experiments, a methodology is seen to emerge for the stereochemically controlled introduction of chiral centers (in this example, the methano bridge of the norbornane unit) that reside at sites remote from chemically modifiable functionality.

While the level of diastereoselectivity encountered with **5** is only modest (86%), improved discrimination is unquestionably feasible as witnessed by the conversion of **4** to coupled products **11** and **12** in a 16:1 ratio (Scheme III). As before, these alcohols were easily separated and **11** was subsequently rearranged to the tricyclopentanoid **13**.

The structural features of **10** reveal no need to incorporate high levels of steric imbalance to achieve a respectable energetic gap between the pair of diastereomeric transition states associated with nucleophilic capture by **4**. Our investigation of the additional examples listed in Table I[11] has shown all of the alcohol mixtures

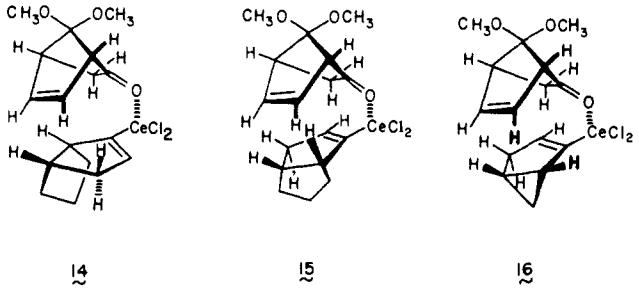
(6) Jung, M. E.; Hudspeth, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 5508; **1978**, *100*, 4309.
(7) (a) Imamoto, T.; Sugiura, Y.; Takiyama, N. *Tetrahedron Lett.* **1984**, 4233. (b) Imamoto, T.; Sugiura, Y. *J. Organomet. Chem.* **1985**, *285*, C21. (c) Imamoto, T.; Takiyama, N.; Nakamura, K. *Tetrahedron Lett.* **1985**, 4763.
(8) Jones, N. D.; Swartzendruber, J. K.; Deeter, J. B., private communication.
(9) (a) Evans, D. A.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *Ibid.* **1978**, *100*, 2242.
(10) All new compounds described herein gave correct elemental analysis and/or accurate mass spectral data. All ^1H NMR, ^{13}C NMR, and IR spectra are also in accord with the assigned structures.

Scheme III



to be chromatographically separable. Furthermore, since 7,7-disubstituted 2-norbornenones are available in optically pure condition,[12] the preparation of **8**, **13**, and related ketones in high enantiomeric purity can potentially be easily realized.

The reasons for this synthetically useful[13] intermolecular recognition have not yet been fully elucidated. The methoxyl oxygens do not appear to play a significant coordinative role, since other functionality at C-7 leads to roughly comparable results.[14] Solvation factors are quite important,[15] and one-electron processes cannot be dismissed. If the Dunitz trajectory model[16] is assumed, with resultant stacking of the reactants as in **14**–**16**, then the



product ratios can be *satisfactorily* attributed to steric factors. On this basis, **15** (the combination leading to **12**) is disfavored because of nonbonded interactions not present in **14** (that culminating in production of **11**). Particularly intriguing is the triad of organocerium reagents derived from vinyl bromides A, B, and C, for which an appreciable falloff in diastereoselectivity is observed. Perhaps the increasing outward splaying brought on by small-ring annulation (see **16**) is responsible. Although this working hypothesis has predictive capability,[13] stereoelectronic effects are not accommodated and further exploration is highly desirable. Experiments aimed at elucidating some of these questions are in progress.[17]

(11) All of the vinyl bromides were prepared by application of the Shapiro reaction to the appropriate ketone tosylhydrazone precursor and condensation of the resulting vinyllithium reagent with cyanogen bromide. Compare: Barth, W.; Paquette, L. A. *J. Org. Chem.* **1985**, *50*, 2438.

(12) See, for example: (a) Grieco, P. A.; Takigawa, T.; Moore, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 4380. (b) Grieco, P. A.; Owens, W.; Wang, C.-L. J.; Williams, E.; Schillinger, W. J.; Hirotsu, K.; Clardy, J. *J. Med. Chem.* **1980**, *23*, 1072.

(13) For an application to the synthesis of the tricyclic segment of the antibiotic ikarugamycin, see: Paquette, L. A.; Romine, J.; Lin, H.-S. *Tetrahedron Lett.*, in press.

(14) Romine, J., unpublished observations.

(15) Tetrahydrofuran is superior. Our findings on solvent effects will be discussed in the full paper.

(16) (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153 and pertinent references cited therein.

(17) This research was supported by the National Institutes of Health (Grant GM-28468).

Structure of Factor S3, a Metabolite of *Propionibacterium shermanii* Derived from Uroporphyrinogen I

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During the last decade's research on the biosynthesis of vitamin B_{12}, three partially methylated intermediates have been isolated, viz. factors I (**2**), II (**3**), and III (**4**) corresponding to the introduction of one, two, and three methyl groups, respectively, from S-adenosylmethionine (SAM) into the reduced type III porphyrin template (**1**).[1] Recent studies on the sequence of methylation have revealed that eight methyl groups from SAM are inserted into uro'gen III (**1**) in the order C_2 (≡factor I) > C_7 (≡factor II) > C_{20} (≡factor III) > C_{17} > $C_{12\alpha}$ > C_1 followed by C_5/C_{15}[2,3] on the way to cobyrinic acid (**7**) (Scheme I). However, no intermediates beyond factor III have yet been discovered. In this paper we describe the isolation and structure of the zinc complex of a novel *tetramethylated* derivative of the porphyrinogen family whose UV/visible spectrum is closely related to that of the corresponding zinc corphinate (**8**).[4] The latter type of structure is unknown as a natural product but has been the subject of extensive synthetic studies by Eschenmoser.[4] It has been suggested[3,5] that both a corphin (such as **6**) and an isomeric pyrrocorphin (**5**)[2,3] may be intermediates in the biosynthesis of cobyrinic acid (**7**) from uro'gen III[3] (**1**).

Incubation of cobalt-deficient cell-free extracts of *Propionibacterium shermanii* with δ-aminolevulinic acid (ALA) in the presence of SAM followed by esterification ($MeOH/H_2SO_4$) and extensive preparative TLC afforded *four isomeric compounds* (factors S1–S4), each containing a UV/vis chromophore reminiscent of the synthetic model zinc corphinate (**8**).[4] The most abundant of these isomers, factor S3 (300 μg), was chosen for structural studies. FD- and FAB-MS revealed a molecular weight *m/z* 1102 ($C_{52}H_{67}O_{16}N_4ZnCl$) ($\xrightarrow{-Cl}$ 1067 $\xrightarrow{-Zn}$ 1004). Factor S3 is an octacarboxylic acid (FD-MS *m/z* octaethyl ester − octamethyl ester = 112 mass units) containing *four* methionine-derived methyl groups ($^{14}C/^{3}H$ ratios of factors derived from [$^{14}CH_3$]SAM + [2,3-$^{3}H_2$]ALA: F II:F III:F S3, **2** (0.29):**3** (0.44):**4** (0.58); FD-MS on a sample derived from CD_3-SAM showed addition

(1) Reviews: Scott, A. I. *Pure Appl. Chem.* **1981**, *53*, 1215; **1986**, *58*, 753; *Ann. N.Y. Acad. Sci.* **1986**, *471*, 174.

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(3) Uzar, H.; Battersby, A. R. *J. Chem. Soc., Chem. Commun.* **1985**, 585. We have been unable to confirm the suggestion by these authors that methylation at C-5 and C-15 can be distinguished as $C_{15} > C_5$.

(4) Johnson, A. P.; Wehrli, P.; Fletcher, R.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 623. Müller, P. M. *ETH Dissertation No. 5135*, 1973, Zurich. Eschenmoser, A. *Ann. N.Y. Acad. Sci.* **1986**, *471*, 108.

(5) Scott, A. I. *Proceedings of The Robert A. Welch Conferences on Chemical Research XXVIII. Chemistry in Texas: The 30th Year of The Welch Foundation*; Houston, TX, Nov, 1984. A corphin intermediate (cf. **9**) in B_{12} biosynthesis was invoked as early as 1973 (Scott, A. I.; Townsend, C. A.; Okada, K.; Kajiwara, M. *Trans. N.Y. Acad. Sci.* **1973**, *35*, 72).

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