with the ground-state bleach, we observe a new absorption centered at 2110 cm^{-1}, which decays with $\tau < 0.5$ ps. Subsequently, we observe a broad feature extending from 1950 to 2040 cm^{-1}. Shown in Figure 1 are three kinetic traces taken throughout the region 1950–2040 cm^{-1}. While the rise times of the transients at the low-energy end of the band are instrument limited, they become progressively slower when moving to the high-energy side of the band and in fact correspond to the *decay* times found for the lower energy transients (Table I). Additionally, the decay times of the transients change from <1 ps at 1954 cm^{-1} to 6 ps at 2034 cm^{-1}, matching the recovery time of the ground-state band (6 ± 1 ps).[8]

MMCT excitation should lead to a complex in which the ruthenium cyanide center has formally changed from a 2+ to a 3+ oxidation state, resulting in a shift of the RuC≡N stretch from the ground-state value of 2053 cm^{-1} to ca. 2120 cm^{-1}.[9] We can thus unambiguously assign the short-lived transient at 2110 cm^{-1} to the MMCT excited state. The features between 1950 and 2040 cm^{-1} are consistent with vibrationally hot ground-state molecules formed following the back electron transfer. Metal–cyanide stretches exhibit anharmonicities of ca. 14 cm^{-1},[10] leading to vibrationally excited states that are shifted to lower energy from the ground-state band. The frequencies observed correspond to population of the vibrationally excited states $v = 1$–7.[11]

Data taken throughout the band from 1950 to 2040 cm^{-1} show that there is a steady progression of rate constants, with the higher vibrational states relaxing more quickly (see Table I). This is consistent with the expectation based on existing evidence[12] that higher vibrational states typically have larger cross sections for energy transfer. In the present case, relaxation can take place either through an intramolecular mechanism (i.e., IVR) or through transfer of the excess energy to the surrounding solvent molecules. Little is known about IVR rates in inorganic molecules; the available evidence suggests that such rates may be slower than observed in organic systems (typically <1 ps) due to large frequency mismatches, which lead to poor coupling between modes, particularly across M–L linkages.[13] Transfer of energy to the solvent from excited inorganic molecules is generally found to be much slower than we observe[14] and is typically solvent dependent. We are presently preparing to perform picosecond Raman experiments to directly observe low-frequency modes to address this question.

These findings demonstrate that the back electron transfer[15] from the MMCT state is ultrafast ($\tau < 0.5$ ps). The infrared frequency observed for the MMCT state suggests that nearly a full charge transfer occurs. More intriguing, however, is that upon return to the ground electronic state large amounts of energy (up to 14 000 cm^{-1}) are placed into a single vibration: the terminal RuC≡N stretching mode.[16] The large energy difference[2] (ca. 8000 cm^{-1}) between the Ru^{II}–Ru^{III} and the Ru^{III}–Ru^{II} species potentially allows the deposition of large amounts of energy into selected vibrational modes of the product of the thermal back electron transfer. The efficiency and selectivity of this process in the present case is, however, quite remarkable.[17] Vibrationally excited products following electron transfer have been observed in the gas phase, but to our knowledge this is the first direct observation in the solution phase.[18] Moreover, the relative rates observed for electronic and vibrational relaxation in $[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^{1-}$ suggest that activated modes in the excited state remain so on the time scale of electron transfer, holding important consequences for electron-transfer theories and for fast electron-transfer processes such as charge separation in photosynthesis. Studies of related systems are in progress in our laboratories in order to discern how modifications to the system may affect electron transfer and energy relaxation dynamics.

Acknowledgment. Support of this work by NIH Grant GM45807 and by LANL Laboratory Directed Research Grants X15D (W.H.W.) and X15B (R.B.D.) is gratefully acknowledged. In addition, we thank Professor Joseph Hupp and Ms. Yuhua Dong for providing samples of Na^+ $[(NC)_5Ru^{II}CNRu^{III}(NH_3)_5]^{1-}$ and Dr. Laura Worl and Dr. Keith Gordon for helpful discussions. This work was performed at Los Alamos National Laboratory under the auspices of the U. S. Department of Energy.

(8) No differences were seen when the solvent was changed from D_2O to H_2O.

(9) We base this on comparison to model compounds, for example $[(NC)_6Fe^{III}]^{3-}$ (2118 cm^{-1}) and $[(NC)_6Fe^{II}]^{4-}$ (2044 cm^{-1}); similar behavior is expected for the analogous ruthenium complexes. See: Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 273.

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(11) We do not expect to be able to resolve the individual states as the ground-state band itself is broad (FWHM = 23 cm^{-1}) and the spectral width of our infrared probe pulse is ca. 8 cm^{-1} FWHM.

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(13) See, for example: (a) Rogers, P. J.; Selco, J. I.; Rowland, F. S. *Chem. Phys. Lett.* **1983**, *97*, 313. (b) Rogers, P.; Montague, D. C.; Frank, J. P.; Tyler, S. C.; Rowland, F. S. *Chem. Phys. Lett.* **1982**, *89*, 9. (c) Angel, S. A.; Hansen, P. A.; Stephenson, J. C.; Heilweil, E. J. In *Time-Resolved Vibrational Spectroscopy V*; Takahashi, H., Ed.; Springer: New York, in press.

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(15) As was noted by a referee, the term "thermal back electron transfer" may not be appropriate to describe the fast reaction following MMCT excitation. Our results make it clear that the electronically excited MMCT state does not have time to thermalize. This suggests that attempts to model such fast electron-transfer reactions using theories that assume vibrational equilibration are inappropriate. However, the description of this process as a "back electron transfer", albeit from vibrationally hot states, is accurate as demonstrated by the typical $Ru^{III}C{\equiv}N$ frequency observed in the MMCT transient.

(16) The results of Barbara et al. (ref 3) showed a 1–2-ps transient, which was initially assigned to the back electron transfer. Our results show that the back electron transfer is much faster and that subsequent events on the 500-fs to 6-ps time scale are actually vibrational relaxation.

(17) For a general discussion of electron transfer in related systems, see: Meyer, T. J. In *Mixed-Valence Compounds*; Brown, D. B., Ed.; D. Reidel: Dordrecht, The Netherlands, 1980. Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850.

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Enantioselective Total Synthesis of (−)-Calicheamicinone

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Calicheamicin γ_1[11] is a prominent member of the enediyne class of anticancer antibiotics[2] possessing phenomenal anticancer

(1) Lee, M. D.; Dunne, T. S., Siegel, M. M.; Chang, C. C.; Morton, G. O.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3464. Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466. Lee, M. D.; Manning, J. K.; Williams, D. R.; Kuck, N. A.; Testa, R. T.; Borders, D. B. *J. Antibiot.* **1989**, *42*, 1070. Maiese, W. M.; Lechevalier, M. P.; Lechevalier, H. A.; Korshalla, J.; Kuck, N.; Fantini, A.; Wildey, M. J.; Thomas, J.; Greenstein, M. *J. Antibiot.* **1989**, *42*, 558.

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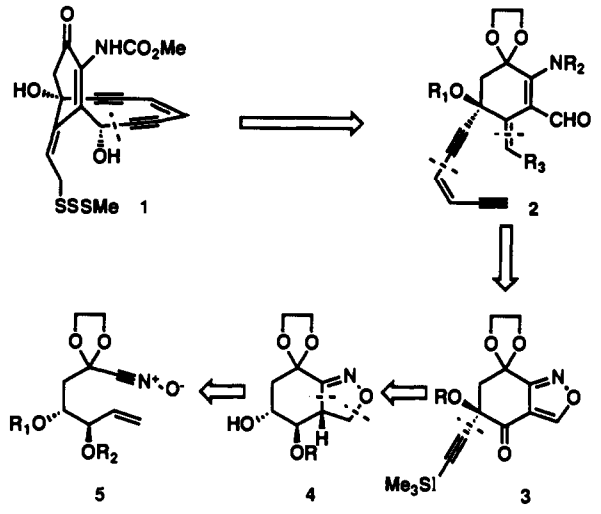
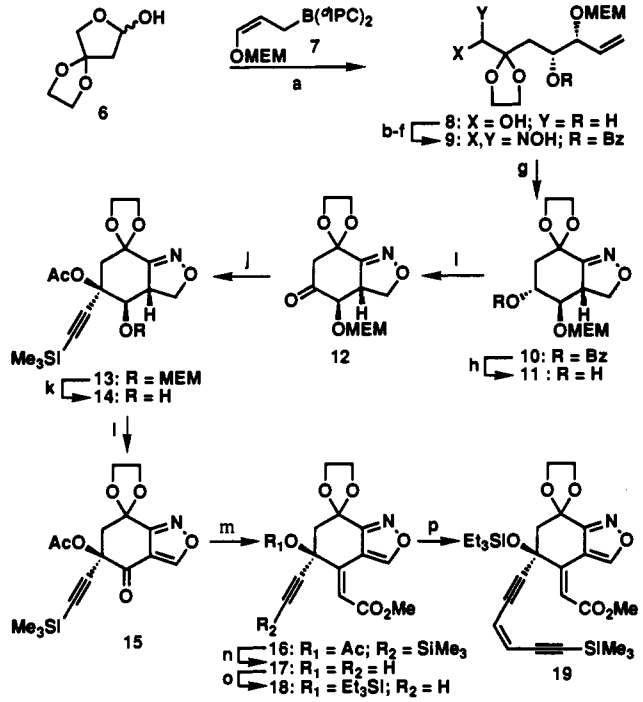
Scheme I[a]



[a] Retrosynthetic analysis of (−)-calicheamicinone (**1**).

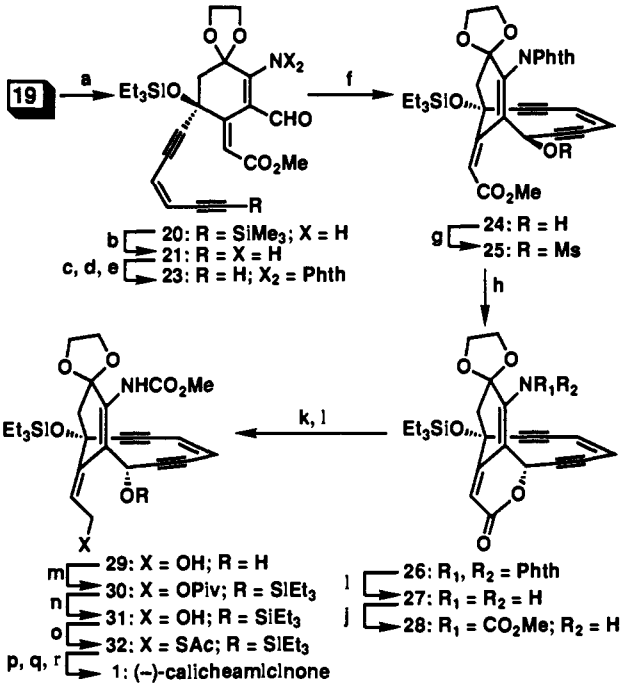
Scheme II[a]



[a] Reagents and conditions: (a) 1.1 equiv of **7**, THF, −78 °C, 3 h → 25 °C, 87%; (b) 1.0 equiv of $^tBuMe_2SiCl$, 2.0 equiv of imidazole, CH_2Cl_2, 25 °C, 2 h; (c) 2.0 equiv of PhCOCl, pyr, DMAP (catalytic), CH_2Cl_2, 25 °C, 12 h; (d) 3 equiv of $^nBu_4NF$, THF, 50 °C, 3 h; (e) Swern oxidation; (f) 3 equiv of $NH_2OH{\cdot}HCl$, 3 equiv of NaOAc, EtOH−H_2O (2:1), 25 °C, 30 min, 98% overall from **8**; (g) excess aqueous NaOCl, CH_2Cl_2, 0 °C, 2 h, 65% as a 4:1 mixture; (h) NaOMe (catalytic), MeOH, 0 °C, 12 h, 100%; (i) 1.5 equiv of Jones' reagent, acetone, 0 °C, 12 h, 95%; (j) 1.5 equiv of lithium (trimethylsilyl)acetylide, THF, −78 °C, 30 min; then 5 equiv of Ac_2O, −78 → 25 °C, 3 h, 67%; (k) 10 equiv of $ZnBr_2$, CH_2Cl_2, 25 °C, 2 h; (l) Swern oxidation, 54% overall from **13**; (m) 5 equiv of $Ph_3P{=}CHCO_2Me$, toluene, 90 °C, 16 h, 84%; (n) NaOMe (catalytic), MeOH−CH_2Cl_2 (1:1), 0 °C, 12 h, 80%; (o) 1.5 equiv of Et_3SiOTf, 2.0 equiv of 2,6-lutidine, CH_2Cl_2, 0 °C, 30 min, 96%; (p) 1.5 equiv of (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane, 0.07 equiv of $Pd(PPh_3)_4$, 0.20 equiv of CuI, 1.5 equiv of $^nBuNH_2$, PhH, 0 °C, 2 h, 91%.

properties and great potential for medical applications. Several approaches to model systems of the aglycon skeleton of this molecule have appeared in the literature.[3] An impressive landmark in the area is the total synthesis of racemic calicheamicinone (**1**), the aglycon portion of calicheamicin γ_1^I, recently recorded by the Danishefsky group.[4] In this communication we report a conceptually different approach to this molecule based upon an intramolecular alkenyl nitrile oxide dipolar cycloaddition reaction which leads directly to the incorporation of the full functionality

Scheme III[a]



[a] Reagents and conditions: (a) 1.0 equiv of $Mo(CO)_6$, MeCN−H_2O (20:1), 80 °C, 1.5 h, 76%; (b) NaOMe (catalytic), CH_2Cl_2−MeOH (1:1), 0 °C, 12 h, 92%; (c) 1.4 equiv of phthaloyl chloride, 4 equiv of pyr, $MeNO_2$, 0 °C, 30 min; (d) silica gel, CH_2Cl_2, 25 °C, 2 h; (e) excess Ac_2O, $MeNO_2$, 25 °C, 1 h, 78% from **21**; (f) 1.1 equiv of KHMDS, toluene, −90 °C, 5 min, 44%; (g) 10 equiv of MsCl, 20 equiv of pyr, DMAP (catalytic), CH_2Cl_2, 0 °C, 2 h; (h) silica gel, 2 equiv of pyridine, PhH, 25 °C, 5 h, 90% from **24**; (i) 10 equiv of $MeNHNH_2$, PhH, 25 °C, 30 min, 99%; (j) 3 equiv of triphosgene, 15 equiv of pyridine, CH_2Cl_2, 25 °C, 40 min; *then* 15 equiv of pyridine, excess MeOH, 0 °C, 30 min, 82%; (k) 3 equiv of DIBAL, CH_2Cl_2, −78 °C, 30 min, 95%; (l) excess $NaBH_4$, MeOH, 0 °C, 1 h, 88%; (m) 3 equiv of PivCl, 15 equiv of pyr, CH_2Cl_2, 25 °C, 4 h; *then* 3 equiv of TESOTf, 0 °C, 10 min, 67%; (n) 3 equiv of DIBAL, CH_2Cl_2, −78 °C, 1 h, 84%; (o) 8 equiv of DEAD, 10 equiv of PPh_3, 8 equiv of AcSH, THF, 0 °C, 30 min, 93%; (p) 5 equiv of DIBAL, CH_2Cl_2, −78 °C, 30 min; (q) 5 equiv of *N*-(methyldithio)phthalimide, CH_2Cl_2, 25 °C, 30 min, 71% from **32**; (r) TsOH (catalytic), aqueous THF, 25 °C, 16 h, 66%.

(2) For a review, see: Nicolaou, K. C.; Dai, W.-M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1387.

(3) (a) Nicolaou, K. C.; Zuccarello, G.; Ogawa, Y.; Schweiger, E. J.; Kumazawa, T. *J. Am. Chem. Soc.* **1988**, *110*, 4866. (b) Nicolaou, K. C.; Ogawa, Y.; Zuccarello, G.; Kataoka, H. *J. Am. Chem. Soc.* **1988**, *110*, 7247. (c) Danishefsky, S. J.; Mantlo, N. B.; Yamashita, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 6890. (d) Haseltine, J. N.; Danishefsky, S. J.; Schulte, G. *J. Am. Chem. Soc.* **1989**, *111*, 7638. (e) Mantlo, N. B.; Danishefsky, S. J. *J. Org. Chem.* **1989**, *54*, 2781. (f) Haseltine, J. N.; Danishefsky, S. J. *J. Org. Chem.* **1990**, *55*, 2576. (g) Kende, A. S.; Smith, C. A. *Tetrahedron Lett.* **1988**, *29*, 4217. (h) Magnus, P.; Lewis, R. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 6921. (i) Magnus, P.; Carter, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 1626. (j) Magnus, P.; Annoura, H.; Harling, J. *J. Org. Chem.* **1990**, *55*, 1709. (k) Magnus, P.; Lewis, R. T.; Bennett, F. *J. Chem. Soc., Chem. Commun.* **1989**, 916. (l) Magnus, P.; Lewis, R. T. *Tetrahedron Lett.* **1989**, *30*, 1905. (m) Tomioka, K.; Fujita, H.; Koga, K. *Tetrahedron Lett.* **1989**, *30*, 851. (n) Schreiber, S. L.; Kiessling, L. L. *J. Am. Chem. Soc.* **1988**, *110*, 631. (o) Schreiber, S. L.; Kiessling, L. L. *Tetrahedron Lett.* **1989**, *30*, 433. (p) Schoenen, F. J.; Porco, J. A., Jr.; Schreiber, S. L.; Van Duyne, G. D.; Clardy, J. *Tetrahedron Lett.* **1989**, *30*, 3765.

(4) Cabal, M. P.; Coleman, R. S.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 3253. Haseltine, J. N.; Cabal, M. P.; Mantlo, N. B.; Iwasawa, N.; Yamashita, D. S.; Coleman, R. S.; Danishefsky, S. J.; Schulte, G. K. *J. Am. Chem. Soc.* **1991**, *113*, 3850.

of the aglycon and which is amenable to enantioselective synthesis (Scheme I). This approach has culminated in a highly enantio- and stereoselective total synthesis of (-)-calicheamicinone (**1**).

The execution of the synthesis proceeded as summarized in Schemes II and III.[5] Thus lactol **6**, readily prepared from tetronic acid via ketalization and DIBAL reduction, was treated with the allylborane **7** according to the general procedure reported by Brown[6] to give **8** in a highly stereo- and enantioselective manner (95% ee, >98% de).[7] Compound **8** was converted to aldoxime **9** by standard chemistry. Generation of the nitrile oxide with aqueous sodium hypochlorite was accompanied by spontaneous cyclization,[8] resulting in a 4:1 mixture of isoxazoline diastereoisomers, from which the major isomer **10** was isolated by flash chromatography. Addition of lithium (trimethylsilyl)acetylide to **12** at -78 °C proceeded with complete stereoselectivity, delivering the incoming nucleophile from the opposite side to the OMEM group to give, after quenching with acetic anhydride, acetate **13**.[9] Removal of the MEM group[10] followed by Swern oxidation[11] and concomitant aromatization gave the keto isoxazole **15**. Stereocontrolled olefination of **15** proceeded smoothly upon heating with methyl (triphenylphosphoranylidene)acetate, resulting in exclusive formation of the desired geometrical isomer **16**. Coupling of **18** with (*Z*)-(4-chloro-3-buten-1-ynyl)trimethylsilane by palladium (0)–copper(I) catalysis completed the construction of the enediyne moiety,[12] leading to compound **19**. Unmasking of the amino aldehyde functionality was realized by reductive opening of the isoxazole ring with molybdenum hexacarbonyl,[13] furnishing **20**.

The propensity of the aldehyde group of **21** to enolize via the vinylogous amine led us to protect the latter functionality as the phthalimide[14] before proceeding further. Scheme III summarizes the final stages of the synthesis. Ring closure of **23** took place upon exposure to base,[3g,4] leading to a mixture of **24** (wrong stereochemistry at the newly generated center) and lactone **26** (44% total yield, ca. 9:1 in favor of **24**). Taking advantage of proximity effects, we corrected the stereochemistry of the newly generated hydroxy-bearing center by conversion to a mesylate followed by exposure to silica gel leading directly to lactone **26**. The completion of the synthesis was based on chemistry previously developed by Danishefsky[4] and Magnus[3k] on similar compounds.[15] (-)-Calicheamicinone (**1**) ($[\alpha]^{25}_D = -472°$, *c* 0.21, CH_2Cl_2) exhibited spectral data identical to those reported by Danishefsky et al.[4,16,17]

The described chemistry provides a facile entry into the calicheamicin- and esperamicin-type aglycon skeletons in their optically active forms and opens the way for an eventual total synthesis of these naturally occurring substances. In addition, the efficacy and flexibility of the strategy allow for the construction of rationally designed mimics of these compounds that may prove useful in biotechnology as DNA-cleaving molecules and in chemotherapy as anticancer agents.

Acknowledgment. We thank Drs. Raj Chadha, Dee H. Huang, and Gary Siuzdak, of The Scripps Research Institute, for their X-ray crystallographic, NMR, and mass spectroscopic assistance, respectively. This work was supported financially by a NATO (SERC, U.K.) fellowship (to A.L.S.), by the National Institutes of Health, and by The Scripps Research Institute.

Supplementary Material Available: A listing of selected physical data (R_f, $[\alpha]_D$, IR, ^1H and ^{13}C NMR, and HRMS) for compounds **8**, **10**, **13**, **15**, **19**, **21**, **23**, **24**, **26**, and **1** and X-ray crystallographic data for compound **13** (20 pages). Ordering information is given on any current masthead page.

(5) All new compounds exhibited satisfactory spectral and analytical and/or exact mass data. Yields refer to chromatographically and spectroscopically homogeneous materials.

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(7) The enantiomeric excess was determined by analysis of the ^1H NMR spectrum of the (+)-MTPA ester of compound **11** and comparison with the enantiomeric series, which has also been prepared.

(8) For an excellent review of nitrile oxide cycloaddition reactions, see: Caramella, P.; Grünanger, P. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 1, Chapter 3, pp 291-392.

(9) Confirmation of the stereochemistry at the acetylenic center came from X-ray analysis of compound **13**.

(10) Corey, E. J.; Gras, J.-L.; Ulrich, P. *Tetrahedron Lett.* **1976**, 809.

(11) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

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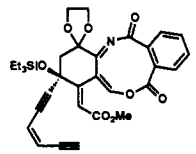
(13) Nitta, M.; Kobayashi, T. *J. Chem. Soc., Chem. Commun.* **1982**, 877.

(14) Reaction of **21** with phthaloyl chloride appears to occur first preferentially at the oxygen atom of the vinylogous amide system, resulting in **22**. The use of polar solvents seems to increase the proportion of reaction at the nitrogen atom. Hydrolysis of the enol ester and activation of the intermediate phthalamic acid gave the required phthalimide **23**.



22

(15) Direct treatment of diol **29** under the Mitsunobu conditions described by Danishefsky (see ref 4) for introduction of the thioacetate gave predominantly a dihydropyran byproduct; this was avoided by first protecting the secondary hydroxyl group.

(16) We thank Professor S. Danishefsky for providing us with IR and ^1H NMR spectra of calicheamicinone (**1**).

(17) For some recently reported attempts at enantioselective synthesis of calicheamicinone, see: (a) Yamashita, D. S.; Rocco, V. P.; Danishefsky, S. J. *Tetrahedron Lett.* **1991**, *32*, 6667. (b) Rocco, V. P.; Danishefsky, S. J.; Schulte, G. K. *Tetrahedron Lett.* **1991**, *32*, 6671.

Self-Assembling Metal Rotaxane Complexes of α-Cyclodextrin

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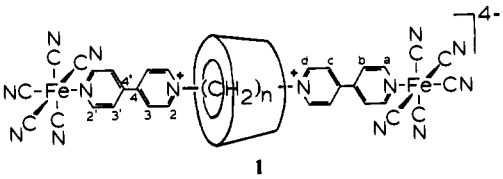
Received December 2, 1991

Rotaxanes are chemical species in which a cyclic molecular bead is threaded by a linear chain bearing bulky end units, which prevent the complex from dissociating into its cyclic and linear molecular components.[1] We report herein the rapid self-assembly of a series of stable α-cyclodextrin (α-CD) rotaxanes by the reaction of the labile $[Fe(CN)_5OH_2]^{3-}$ ions with prethreaded 1,1′′-(α,ω-alkanediyl)bis(4,4′-bipyridinium) dicationic ligands $(bpy(CH_2)_nbpy^{2+}$, where n = 8-12). The stability of the α-CD/ligand inclusion complex allows for the quantitative preparation of the rotaxane **1** in aqueous solution, the formation of which may be conveniently monitored by ^1H NMR spectroscopy.



1

Several examples of symmetrical rotaxanes based on the cyclic oligosaccharide α-cyclodextrin, threaded by alkyl chains bearing cationic aromatic N-heterocycle[2,3] or cobalt amine[4,5] end groups, have been reported. The preparation of an asymmetrical zwit-

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(2) Yonemura, H.; Saito, H.; Matsushima, S.; Nakamura, H.; Matsuo, T. *Tetrahedron Lett.* **1989**, *30*, 3143-3146.

(3) Saito, H.; Yonemura, H.; Nakamura, H.; Matsuo, T. *Chem. Lett.* **1990**, 535-538.

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