terconversions. Whereas **5b** and **6b** were stable in refluxing acetonitrile, a 44:56 equilibrium was established from both sides in benzonitrile (E_T 42.0) at 139 °C with k_{cis} + k_{trans} = 2.0 10^{-5} s^{-1}. Isomerization was 5 times slower in the less polar *o*-dichlorobenzene (E_T 38.1). A 41:59 equilibrium was attained in 2 h at 135 °C in etheral 2.9 M LiClO$_4$, a medium resembling a salt melt.[14] Only in this medium was a slow cis,trans isomerization of **5a** observed. All this is in harmony with cis,trans isomerization via rotation of the ring-opened zwitterions **3** and **4**. The rate difference between series **a** and **b** parallels solvolysis rates of the corresponding alkyl chlorides.[15]

Cycloaddition of **2a** to dimethyl fumarate in THF was stereospecific and afforded 99% of **7** (^{1}H NMR analysis); the 500-MHz spectrum did not reveal the methyl signals of **8** (<0.03%). In contrast, reaction of **1a** with dimethyl maleate[16]
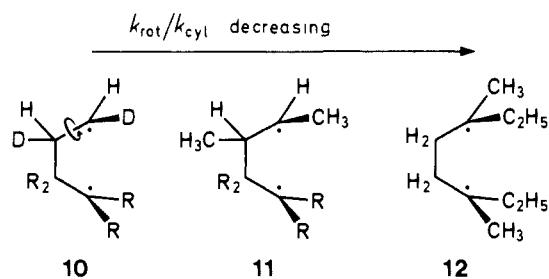

7   **8**   **9**
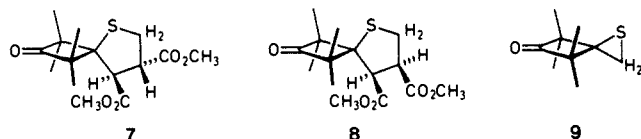
(3.5 equiv, neat, 8 h 40 °C) furnished 82% of **7** and **8**, 1.1:98.9, accompanied by the thiirane **9**.[8] The cis adduct **8**—alone or in presence of decomposing **1a**[17]—did not noticeably isomerize at 40 °C.

We interpret this result as minor participation of the zwitterionic pathway in the reaction of **2a** with maleic ester and no involvement in the fumaric ester case. Why is this two-step reaction less favored than for dimethyl dicyanofumarate? (1) The π-MO energies of the latter are lower than those of ethylenedicarboxylic esters. (2) *Steric shielding* of one terminus of the thiocarbonyl ylide **2** impairs *concerted* addition of fumaric and maleic esters less than that of the tetrasubstituted ethylene. The two-step mechanism, however, is less affected. The higher activity of dimethyl fumarate vs. maleate in concerted additions (early transition state) is well understood.[1] Rapid concerted addition of **2a** to dimethyl fumarate prevents occurrence of stereochemical leakage.

Is it conceivable that all 1,3-dipolar cycloadditions take the two-step course and that k_{rot}/k_{cycl} is too small as a rule to allow detection of the nonstereospecific portion? A retention of >99.997% was found for the addition of diazomethane to methyl tiglate;[18] $\Delta G_{rot}^{\ddagger} - \Delta G_{cycl}^{\ddagger} > 6.2$ kcal mol^{-1} is hard to rationalize for an intermediate.

The ratio k_{rot}/k_{cycl} for the related tetramethylene species decreases with terminal substitution: 12 for *cis*- and *trans*-**10**, R = H;[19] large for **10**, R = F;[20] 1.3 and 0.6 for *cis*- and *trars*-**11**, R = H;[21] 4.3 and 2.0 for *cis*- and *trans*-**11**, R = F;[22] and <0.02

(13) This heuristic criterion for dicarboxylic esters was introduced by A. von Baeyer, the discoverer of cis,trans isomerism in ring compounds: Baeyer, A. *Justus Liebigs Ann. Chem.* **1888**, *245*, 103; **1890**, *258*, 145; **1892**, *269*, 145.

(14) Pocker, Y.; Ellsworth, D. L. *J. Am. Chem. Soc.* **1977**, *99*, 2284 and references cited therein.

(15) k_{solv} in 80% ethanol at 25 °C: 1-Methyl-1-cyclobutyl chloride 6.2 × 10^{-7} s^{-1},[a] 2-methyl-2-adamantyl chloride 6.5 × 10^{-5} s^{-1}.[b] (a) Brown, H. C.; Borkowski, M. *J. Am. Chem. Soc.* **1952**, *74*, 1894. (b) Schleyer, P. v. R.; Harris, M., private communication.

(16) Commercial dimethyl maleate contained 0.34 ± 0.03% fumarate. Fumaric ester content dropped to 0.0037% (i.e., below the analytical limit) after reaction with 12 mol % diphenyldiazomethane at 0 °C and distillation; the percentage is based on a measured competition constant of 36 for fumaric vs. maleic ester. A 0.0037% content of dimethyl fumarate in dimethyl maleate should give rise to 0.011% **7** (negligible), based on a competition constant of 52, determined separately. After the experiment, the fumaric ester content remained below the analytical limit.

(17) Test was necessary because thiocarbonyl ylides are basic; see: Mloston, G.; Huisgen, R. *Tetrahedron Lett.* **1985**, *26*, 1053.

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(22) Bartlett, P. D.; Hummel, K.; Elliott, S. P.; Minns, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 2898.

k_{rot}/k_{cyl} decreasing

10   **11**   **12**

for **12**.[23] Thus, the deuterium-labeled methylene rotor offers the highest chance to bring to light an intermediate in cycloadditions. This was why Houk, Firestone, et al.[24] tested addition of 4-nitrobenzonitrile oxide to *cis*- and *trans*-dideuterioethylene; ≥98% retention was observed! In contrast, the nonstereospecific 1,3-cycloadditions described here concern terminally persubstituted intermediates **3** and **4**.[25] The conclusion: *normal* stereospecific 1,3-dipolar cycloadditions follow a *fundamentally different mechanism* involving no intermediates.

(23) Bartlett, P. D.; Porter, N. A. *J. Am. Chem. Soc.* **1968**, *90*, 5317.

(24) Houk, K. N.; Firestone, R. A.; Munchausen, L. L.; Mueller, P. H.; Arison, B. H.; Garcia, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 7227.

(25) Further convincing evidence comes from trapping reactions of the zwitterionic intermediate from **2a** and tetracyanoethylene: Huisgen, R.; Mloston, G.; Langhals, E. *J. Org. Chem.*, in press.
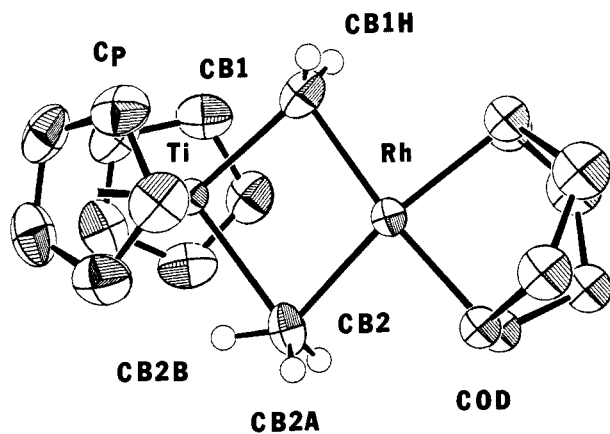
Carbon–Hydrogen Bond Activation through a Binuclear C–H Bond Complex

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Contribution No. 7412, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

There is increasing interest in agostic interactions between a metal and a carbon–hydrogen bond.[1] This interaction is thought to be especially important in the carbon–hydrogen bond activation process (eq 1).[2] Systems that show such interactions are useful

A   **B**   (1)
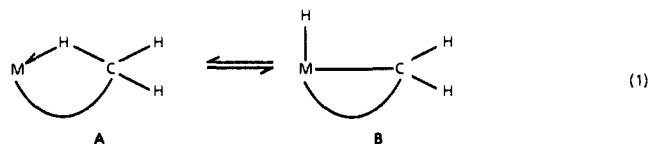
as models to provide characteristic reaction types and characteristic spectroscopic features. We were interested in the possibility of such interactions for heteronuclear systems which could be thought of as the simplest models for mixed-metal heterogeneous catalysts[2] and systems that show strong metal–support interactions.

We recently developed an efficient route to heteronuclear μ-methylene complexes Cp$_2$TiML$_n$(μ-CH$_2$)(μ-Cl).[3] The μ-chloride

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Communications to the Editor

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Figure 1. ORTEP diagram of Cp$_2$TiRh(COD)(μ-CH$_2$)(μ-CH$_3$). The ellipsoids are drawn at the 50% probability level except for the hydrogen atoms. The hydrogen atoms of the cyclopentadienyl rings and COD are omitted for clarity. Selected bond distances (Å): Ti-CB1, 2.147 (5); Ti-CB2, 2.294 (6); Rh-CB1, 2.094 (5); Rh-CB2, 2.110 (6); CB1-CB1H, 0.91 (3); CB2-CB2B, 0.92 (5); CB2-CB2A, 0.98 (4); Rh-Ti, 2.835 (1). Selected bond angles (deg): Ti-CB1-Rh, 83.9 (2); Ti-CB2-Rh, 80.0 (2); CB1-Ti-CB2, 94.4 (2); CB1-Rh-CB2, 101.7 (2); Ti-CB1-CB1H, 123 (2); CB1H-CB1-CB1H, 108 (3); CB1H-CB1-Rh, 105 (2); Ti-CB2-CB2B, 61 (3); Ti-CB2-CB2A, 124 (3); CB2B-CB2-CB2A, 102 (4); CB2A-CB2-CB2A, 110 (4); Rh-CB2-CB2A, 100 (3); Rh-CB2-CB2B, 141 (3).

functionality of this family of compounds allows the introduction of wide variety of other bridging groups via substitution. Herein we report the synthesis and characterization of the novel compound **3**, obtained by treating the μ-chloride complex **2** with methyllithium (eq 2, 3). A unique feature of this compound is the
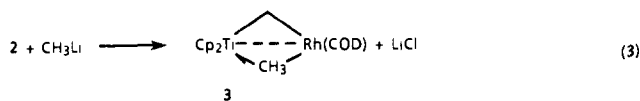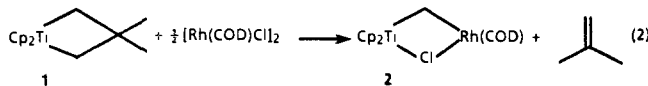
bridging methyl group which forms a three-center 2-electron agostic bond with the titanium center. Crystallographic and spectroscopic studies of this molecule have been carried out to fully characterize the static and dynamic behavior of this agostic interaction.

Titanacycle **1** reacts rapidly at room temperature with [Rh-(COD)Cl]$_2$ in toluene to give the bridging methylene complex **2** quantitatively.[3,4] Treatment of **2** with 2 equiv of methyllithium at room temperature yields the μ-CH$_3$ complex **3**. The bridging methyl complex is formed in 90% yield as determined by ^{1}H NMR[5] but could only be isolated in 10% yield due to difficulties encountered in purifying it. Multiple recrystallization yielded orange-yellow crystals of **3** suitable for an X-ray structure determination.[6,7]

As shown in Figure 1, carbon atom CB2 and hydrogen atom CB2B form an agostic interaction with the titanium atom. For the bridging methyl group, the Ti-H bond distance is 2.02 (5) Å and the Ti-C bond distance is 2.294 (6) Å. These distances can be compared to those in Green's compound Ti(dmpe)(Et)Cl$_3$,[8] for which they are 2.29 and 2.52 Å, respectively. In the bridging methylene group the hydrogen CB1H-carbon CB1 bond is tilted toward the rhodium atom and the Ti-CB1-CB1H bond angle is 123 (2)°. Although the metal-metal bond distance of 2.835 (1) Å is in the range of a metal-metal bond, we are not certain that one is present.

At room temperature the μ-CH$_3$ group shows a broad resonance at -3.13 ppm in the ^{1}H NMR spectrum. When cooled to -90 °C, this resonance is replaced by two resonances at 1.28 ppm (doublet) and -12.15 ppm (triplet, J = 12.8 Hz). The observed coalescence temperature is -40 °C at 90 MHz. The calculated $\Delta G^{\ddagger}$ for the rotation through rhodium carbon CB2 bond is +9.8 kcal/mol.[9]

In the ^{13}C NMR (^{1}H coupled with NOE) at room temperature, the μ-CH$_3$ resonance is at 49.7 ppm (doublet of quartet, J_{CH} = 114, J_{CRh} = 29 Hz). The carbon rhodium coupling constant for the μ-CH$_3$ group is markedly different from values for [Rh-(COD)(μ-CH$_3$)]$_2$ (9.5 Hz),[10] which implies that the bonding character of the methyl group is considerably different. We prepared 51% ^{13}C-enriched **3** to measure the individual CH coupling constants. At -92 °C, the μ-CH$_3$ resonance was observed at 51.1 ppm. The coupling constant for the bridging proton ($^bJ_{CH}$) is 87.7 Hz; for the terminal proton, this value ($^1J_{CH}$) is 126.7 Hz. As expected, we found an abnormally low coupling constant for the agostic hydrogen atom. To our knowledge, this is the first case where the exact CH coupling constant of an agostic bond in a fluxional system has been determined directly.

Agostic hydrogens also exhibit characteristic IR absorbance bands between ca. 2700 and 2350 cm^{-1}. Compound **3** displays a weak absorbance at 2460 cm^{-1}. Upon deuteration of the methyl group, **3**-d_3 shows new absorbances at 2196, 2110, and 1854 cm^{-1}. The first two absorbances are assigned to the stretching mode of the nonagostic CD bonds and the latter absorbance to stretching mode of the agostic CD bond.

The existence of both a μ-methylene and a μ-methyl ligand in this molecule raised the intriguing possibility of a hydrogen-transfer reaction between the bridging alkyl ligands. Indeed, when the ^{13}C-labeled complex **3a** was allowed to stand at room temperature for several months, the ^{13}C label was incorporated into the μ-methylene position ($t_{1/2} \approx$ 5 months at room temperature and $\approx$ 15 days at 65 °C). The role of the agostic interaction in this
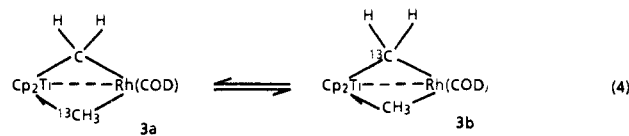
hydrogen-transfer reaction is not yet clear. However, this reaction represents a well-characterized example of an alkyl group with an agostic hydrogen interaction which is subsequently activated by the metal center.

We have evidence of similar chemistry in the Ir, Pt analogues of **3**.[3] We anticipate that these related systems will define the general characteristics of heteronuclear agostic CH bonds.

(3) (a) Mackenzie, P. B.; Ott, K. C.; Grubbs, R. H. *Pure Appl. Chem.* **1984**, *56*, 59. (b) Mackenzie, P. B.; Grubbs, R. H., manuscript in preparation.

(4) COD represents 1,5-cyclooctadiene.

(5) The yield was based on relative Cp peak integration.

(6) ^{1}H NMR (toluene-d_8/THF-d_8 = 3/1; room temperature) δ 7.24 (s, 2 H, μ-CH$_2$), 5.30 (s, 10 H, Cp), 4.13-4.09 (m, 4 H, COD), 2.18-2.08 (m, 4 H, COD), 2.02-1.98 (m, 4 H, COD), -3.13 (br, 3 H, μ-CH$_3$); ^{1}H NMR (-92 °C) δ 1.28 (d, 2 H, J = 12.8 Hz, μ-CH$_3$), -12.15 (t, 1 H, J = 12.8 Hz, μ-CH$_3$); ^{13}C NMR (toluene-d_8/THF-d_8 = 3/1; room temperature) δ 185.4 (dt, 1 C, J_{CH} = 129, J_{CRh} = 24 Hz, μ-CH$_2$), 104.7 (dm, 10 C, J_{CH} = 172 Hz, Cp), 84.1 (d, 2 C, J_{CH} = 151 Hz, COD), 82.9 (d, 2 C, J_{CH} = 158 Hz, COD), 49.7 (dq, 1 C, J_{CH} = 114, J_{CRh} = 29 Hz, μ-CH$_3$), 32.4 (t, 2 C, J_{CH} = 126 Hz, COD), 31.6 (t, 2 C, J_{CH} = 128 Hz, COD); ^{13}C NMR (-92 °C) δ 51.1 (ddt, 1 C, $^bJ_{CH}$ = 87.7, $^1J_{CH}$ = 126.7, J_{CRh} = 29.9 Hz, μ-CH$_3$). Anal. Calcd for C$_{20}$H$_{27}$RhTi: C, 57.44; H, 6.51. Found: C, 57.36; H, 6.51. IR (cm^{-1}, KBr) 3030, 3018, 2999, 2959, 2924, 2874, 2868, 2820, 2460.

(7) Crystals of **3** are orthorhombic, space group *Pbcm* (No. 57), with a = 8.219 (1) Å, b = 16.330 (2) Å, c = 12.613 (2) Å, Z = 4. The structure was refined to R = 0.025 for 1274 reflections; the goodness of fit is 1.98 for 1560 data and 134 parameters.

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(9) Martin, M. L.; Martin, G. J.; Delpuech, J. J. *Practical NMR Spectroscopy*; Heyden & Sons: London, 1980; p 339. $\Delta G^{\ddagger}$ = [45.45 - 1.98 log $(\Delta \nu / T_C)]T_C$, $\Delta \nu$ in Hz, T_C in absolute temperature. This activation energy can be thought of as the minimum agostic bond energy.

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Manzamine A, a Novel Antitumor Alkaloid from a Sponge

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In our quest for antitumor activity in marine organisms occurring in Okinawan waters, we discovered a sponge[1,2] which gave an extract inhibiting the growth of P388 mouse leukemia cells. Subsequent purification afforded a compound having an IC_{50} of 0.07 μg/mL, which proved to be a novel alkaloid. We now describe the isolation of manzamine A hydrochloride (1) and the determination of its absolute configuration by X-ray.

A sample (735 g, wet weight) of the sponge, collected off Manzamo, Okinawa, in April 1985, was steeped in acetone. Evaporation gave an aqueous suspension which on extraction with ethyl acetate furnished an oil (13.0 g). A portion (10.7 g) was chromatographed over silica gel[3] by eluting with n-heptane–ethyl acetate–isopropyl alcohol (5:10:1). The biologically active fraction was purified over silica gel by successive elution with chloroform and acetone. The acetone eluate gave manzamine A hydrochloride (1, 100 mg) as colorless crystals after recrystallization from methanol: mp > 240 °C dec, $[\alpha]^{20}$ +50° (c 0.28, CHCl₃).

The molecular formula of the free base of 1 was deduced as $C_{36}H_{44}N_4O$ from HREIMS (m/z 548.3510, Δ 0.5 mmu) and by LRFABMS (M⁺ + 1 at m/z 549).[4] The ¹³C NMR spectrum[4] showed that all 36 carbons were different (17 sp²- and 19 sp³-hybridized atoms). The UV spectral data [MeOH λ_{max} 219 (ϵ
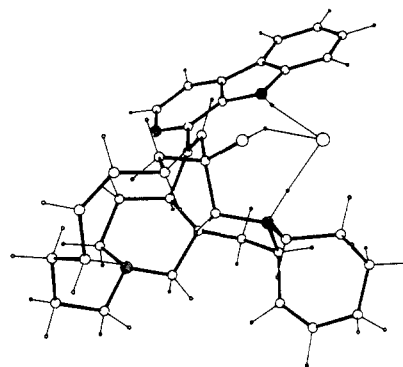

Figure 1. Perspective drawing of the absolute configuration of manzamine A hydrochloride (1). Nitrogen atoms are indicated by hatched spheres.
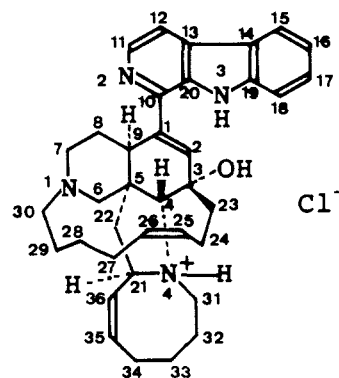

Figure 2. Numbering of the atoms of 1.

22 900), 236 (ϵ 18 600), 280 (ϵ 10 800), 290 sh (ϵ 9800), 346 (ϵ 5300), 357 nm (ϵ 5600)] were characteristic of the β-carboline chromophore.[5,6]

The presence of two di- and one trisubstituted double bonds was revealed by the six olefinic carbon NMR signals and the splitting of the contiguous olefinic proton signals. However, these data only account for 12 of the required 17 sites of unsaturation. Consequently, besides the β-carboline ring, manzamine A must possess *five* rings containing two nitrogen atoms, as well as a single tertiary hydroxy group (IR, 1065 cm⁻¹).

As such complexity rendered conventional methods for structure determination impractical, a crystal of 1 was submitted to X-ray.[7] The resulting structure, shown in its absolute configuration, is unusual (Figure 1). Apart from the β-carboline substituent,[6,9] the molecule comprises a complicated array of 5-, 6-, 8-, and 13-membered rings (Figure 2). The piperidine and cyclohexene rings adopt chair and boat conformations, respectively, while the pyrrolidinium ring is an envelope. The conformation of the eight-membered cis-olefinic ring is as an envelope–boat P(0-++)[10] with a mirror plane passing through C(35) and C(31). The two six-membered rings bridged by a chain of nine carbon atoms constitute a 13-membered macrocycle which, unlike odd-membered macrocycles in general,[11] is perfectly ordered and rigid. Its

(1) Sponges are a rich source of chemically and biologically interesting molecules; see: Scheuer, P. J., Ed. *Marine Natural Products, Chemical and Biological Perspectives*; Academic Press: New York, 1978–1983; Vol. I-V. Faulkner, D. J. *Nat. Prod. Rep.* **1984**, 551–598. Uemura, D.; Takahashi, K.; Yamamoto, T.; Katayama, C.; Tanaka, J.; Okumura, Y.; Hirata, Y. *J. Am. Chem. Soc.* **1985**, *107*, 4796–4798.

(2) The sponge has been identified as *Haliclona sp.*

(3) Silica gel (230–400 mesh; 200 g) was stirred in a solution of heptane–ethyl acetate–isopropyl alcohol (5:10:1, 400 mL) containing aqueous ammonia (4 mL) and then packed into a column.

(4) Anal. Calcd for C₃₆H₄₄N₄O·HCl: C, 73.88; H, 7.75; N, 9.57; Cl, 6.06. Found: C, 73.80, H, 7.75; N, 9.44; Cl, 6.11. LREIMS, m/z 548 (4), 530 (100), 438 (19), 408 (66), 379 (26), 311 (55), 296 (27), 253 (23), 162 (46), 138 (27), 98 (32 rel %). IR (KBr) 3280, 3150, 3050, 3000, 2920, 2800, 2760, 2630, 2560, 1617, 1555, 1488, 1448, 1418, 1385, 1370, 1315, 1270, 1230, 1180, 1142, 1110, 1095, 1065, 1025, 820, 740, 725, 700 cm⁻¹. ¹H NMR (CDCl₃) δ 11.76 (1 H, br s), 10.62 (1 H, br s), 8.34 (1 H, d, J = 5.2 Hz), 8.08 (1 H, d, J = 7.9 Hz), 7.85 (1 H, d, J = 5.1 Hz), 7.83 (1 H, d, J = 7.9 Hz), 7.52 (1 H, t, J = 7.9 Hz), 7.23 (1 H, t, J = 7.9 Hz), 6.52 (1 H, s), 6.29 (1 H, m), 5.57 (2 H, m), 5.39 (1 H, t, J = 9.9 Hz), 4.94 (1 H, m), 4.03 (1 H, m), 3.72 (1 H, d, J = 6 Hz), 3.27 (1 H, m). ¹³C NMR (CDCl₃) δ 143.60 (s), 142.27 (d), 141.37 (s), 141.18 (s), 137.54 (d), 135.12 (d), 133.25 (s), 132.82 (d), 129.27 (s), 127.89 (d), 126.76 (d), 123.50 (d), 121.13 (s), 120.90 (d), 119.22 (d), 113.76 (d), 112.78 (d), 77.98 (d), 71.25 (s), 70.26 (t), 57.02 (d), 53.32 (t), 53.31 (t), 49.12 (t), 46.91 (s), 44.65 (t), 41.00 (d), 39.05 (t), 33.51 (t), 28.31 (t), 26.36 (t), 26.23 (t), 24.86 (t), 24.45 (t), 24.16 (t), 20.62 (t).

(5) Scott, A. I. *Interpretation of the Ultraviolet Spectra of Natural Products*; Pergamon Press: New York, 1964; p 176.

(6) Kobayashi, J.; Harbour, G. C.; Gilmore, J.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1526–1528.

(7) Crystal data for 1 (C₃₆H₄₄N₄O·HCl; M = 585.2): orthorhombic; space group P2₁2₁2₁; unit cell a = 12.989 (3) Å, b = 15.267 (5) Å, c = 15.890 (3) Å; V = 3151.0 Å³; Z = 4, D_c = 1.234 g·cm⁻³. The absolute configuration was determined by least-squares refinement of the absolute structure parameter x[8] (x = 0.01 (14)). The final R factor, based on 2447 reflections, was 0.046.

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