bered cobaltacyclic ring, and we will comment later on its electronic structure.[17] The facts of its existence and its ability to take part in catalytic substitution reactions give strong support to the dissociative model for reductively induced electron-transfer catalytic reactions of mononuclear complexes.

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Registry No. 1, 51614-82-5; **1**$^-$, 113353-94-9; **2**$^-$, 113353-92-7; **2**$^{2-}$, 113353-95-0; **3**, 113353-93-8; **3**$^-$, 113378-72-6.

(17) Donovan, B. T.; Rieger, P. H.; Geiger, W. E., work in progress.

Diastereoselective Reactions of Chiral-at-Iron Carbene Complexes $C_5H_5(CO)(PR_3)Fe{=}CHR^+$. Synclinal Isomers Are More Reactive Than Anticlinal Isomers

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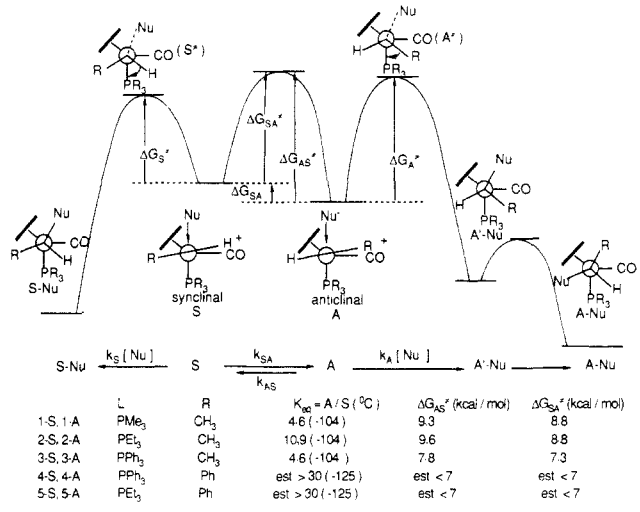
The $C_5H_5(NO)(PPh_3)Re-$ and $C_5H_5(CO)(PPh_3)Fe-$ groups have been used extensively as chiral auxiliaries to carry out diastereo- and enantioselective reactions.[1-4] Nucleophilic addition at C_α in carbene complexes of the type $C_5H_5(NO)(PPh_3)Re{=}CHR^+$ normally shows high diastereoselection since one face of the carbene ligand is shielded by PPh_3 and barriers to $Re{=}C_\alpha$ bond rotation are high; consequently, preparation and addition of nucleophiles to a single carbene isomer can be achieved.[1a-c,5]

We report here a study of addition of simple nucleophiles to chiral-at-iron carbene complexes of the type $Cp(CO)(PR_3)Fe{=}CHR^+$. These studies show that the factors controlling diastereoselectivity are surprisingly complex and involve not only anticlinal:synclinal isomer ratios but also the intrinsic differences in reactivity of these isomers, the nature and concentration of the nucleophile, and the ionic strength of the medium.

Iron–carbene complexes **1–5** were prepared by treatment of the α-ether complexes $Cp(CO)(L)FeCH(OCH_3)R$ with TMSOTf at −78 °C in CH_2Cl_2.[4] ^1H NMR analysis of CD_2Cl_2 solutions confirmed quantitative generation of **1–5**. For ethylidene systems **1–3**, the synclinal and anticlinal isomers (Scheme I) could be observed by low-temperature ^1H NMR (ca. −114 °C).[6,7] Equilibrium isomer ratios and $\Delta G^{\ddagger}$'s (from line shape analysis) for interconversions are listed in Scheme I. Benzylidene complexes exhibited a single set of resonances which showed no temperature dependence, and we assume a high anticlinal:synclinal ratio (>30) based on $Cp(NO)(PR_3)Re{=}CHC_6H_5^+$ as a model.[1b] The anticlinal:synclinal ratio has been independently established as >30:1 for **5**.[8]

Scheme I. Free Energy Diagram for the Reactions of $Cp(CO)PR_3Fe{=}CHR^+$ with Nucleophiles



	L	R	K_{eq} = A/S (°C)	$\Delta G_{AS}^{\ddagger}$ (kcal/mol)	$\Delta G_{SA}^{\ddagger}$ (kcal/mol)
1-S, 1-A	PMe_3	CH_3	4.6 (-104)	9.3	8.8
2-S, 2-A	PEt_3	CH_3	10.9 (-104)	9.6	8.8
3-S, 3-A	PPh_3	CH_3	4.6 (-104)	7.8	7.3
4-S, 4-A	PPh_3	Ph	est > 30 (-125)	est < 7	est < 7
5-S, 5-A	PEt_3	Ph	est > 30 (-125)	est < 7	est < 7

Reactions of carbene complexes **1–5** with nucleophiles were carried out by quenching into stirred methanol solutions. Large molar excesses (>6 equiv) of nucleophile were present so concentrations changed little during the quench. Two diastereomers were formed in each quench. Results of Gladysz,[1] Davies[2] and Liebeskind[3] clearly establish that the phosphine ligand shields one face of the carbene moiety.[9] Thus, one diastereomer (S–Nu) should arise from attack on the Si face of the synclinal isomer, while the other (A–Nu) presumably comes from attack on the Re face of the anticlinal isomer (Scheme I).

Diastereomer ratios from quenching **1–5** were determined by ^1H NMR analysis of crude products. Complexes **1**-A-Nu:**1**-S-Nu, **2**-A-Nu:**2**-S-Nu, and **3**-A-Nu:**3**-S-Nu were separated by chromatography and structures assigned by ^1H and ^{13}C NMR.[7] In each pair only one diastereomer exhibited a $^4J_{P-H}$ (1.3–1.7 Hz); it was assigned the A-Nu configuration based on the *P*-Fe-C_α-CH_3 "W" geometry and a previous analogous assignment.[10] X-ray structures of **1**-S-SC_6H_5 and **3**-S-$SCOCH_3$ confirm these assignments.[11] Equilibration of diastereomers of **4**-OMe occurs at 25 °C via PPh_3 dissociation; the equilibrium ratio is 70:1.[8] Isomer **4**-A-OMe is expected to be the more stable,[12,2d] and assignment is made on this basis. Assignments of **5**-A-OMe and **5**-S-OMe were based on NMR comparisons with **4**-A-OMe and

(1) For examples from the Gladysz lab, see: (a) Constable, A. G.; Gladysz, J. A. *J. Organomet. Chem.* **1980**, *202*, C21. (b) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4862. (c) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (d) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4103. (e) O'Connor, E. J.; Kobayashi, M.; Floss, H. G.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4837.

(2) For examples from the Davies lab, see: (a) Baird, G. J.; Davies, S. G. *J. Organomet. Chem.* **1983**, *248*, C1. (b) Ambler, P. W.; Davies, S. G. *Tetrahedron Lett.* **1985**, *26*, 2129. (c) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* **1984**, *3*, 1764. (d) Ayscough, A. P.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1648. (e) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *J. Organomet. Chem.* **1985**, *285*, 213. (f) Davies, S. G.; Dordor-Hedgecock, I. M.; Warner, P. *Tetrahedron Lett.* **1985**, *26*, 2125. (g) Brown, S. L.; Davies, S. G.; Warner, P.; Jones, R. H.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1985**, 1446. (h) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 609.

(3) For examples from the Liebeskind lab, see: (a) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328. (b) Liebeskind, L. S.; Fengl, R. W.; Welker, M. E. *Tetrahedron Lett.* **1985**, *26*, 3075, 3079. (c) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (d) Liebeskind, L. S.; Welker, M. E. *Organometallics* **1983**, *2*, 194.

(4) (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (c) Brookhart, M.; Timmers, D.; Tucker, J. R.; Williams, G. D.; Husk, G. R.; Brunner, H.; Hammer, B. *J. Am. Chem. Soc.* **1983**, *105*, 6721. (d) Buck, R. C.; Brookhart, M. Abstracts 191st National Meeting of the American Chemical Society; New York, New York, April 13–18, 1986; Inorg. Abstract no. 422.

(5) S. G. Davies has reported diastereoselective hydride additions to complexes of the type $Cp(CO)(PPh_3)Fe{=}C(OR)(R)^+$.

(6) Low-temperature ^1H NMR data of C_α-*H*: **1** (−114 °C, CD_2Cl_2), 15.92 ppm (synclinal), 17.46 ppm (anticlinal); **2** (−114 °C, CD_2Cl_2), 15.69 ppm (synclinal), 17.65 ppm (anticlinal); **3** (−126 °C, CD_2Cl_2/SO_2ClF), 17.05 ppm (synclinal), 18.24 ppm (anticlinal).

(7) See Supplementary Material for complete spectral and analytical data.

(8) A complete analysis of this diastereomer interconversion has been carried out (Buck, R. C. Ph.D. Dissertation, 1987, University of North Carolina) and will be published elsewhere.

(9) Most of systems studied in ref 1–4 are triphenylphosphine containing systems with the exception of reactions of $[(C_5H_5)Re(NO)(PMe_3)(=CHC_6H_5)]^+PF_6^-$ reported by Gladysz.[1b] The 20:1 product ratio of **1**-S-$SCOCH_3$:**1**-A-$SCOCH_3$ in entry 2 of Table I shows that PMe_3 can effectively sterically shield one face of carbene moiety.

(10) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Whittaker, M. *J. Organomet. Chem.* **1987**, *320*, C19.

(11) Liu, Y.; Singh, P.; Brookhart, M., unpublished results.

(12) Crocco, G. L.; Gladysz, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 1154.

0002-7863/88/1510-2337$01.50/0

Table I. Diastereoselective Reactions of $Cp(CO)PR_3Fe{=}CHR^+$ with Nucleophiles

entry	carbene	nucleophile	$[Nu^-]$ (M)	T (°C)	S-Nu:A-Nu	S:A
1	$Cp(CO)PMe_3Fe{=}CHCH_3^+$, **1**	NaSPh	0.19	−30	4.7:1.0	1.0:2.8[h]
2	$Cp(CO)PMe_3Fe{=}CHCH_3^+$, **1**	$KSCOCH_3$	0.20	−30	20:1.0	1.0:2.8[h]
3[a]	$Cp(CO)PPh_3Fe{=}CHCH_3^+$, **3**	NaSPh	0.28	−30	4.1:1.0	1.0:2.8[h]
4	$Cp(CO)PPh_3Fe{=}CHCH_3^+$, **3**	$KSCOCH_3$	0.28	−30	24:1.0	1.0:2.8[h]
5[b]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	NaSPh	0.02	−30	6.0:1.0	1.0:5.2[h]
6	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	NaSPh	0.08	−30	2.5:1.0	1.0:5.2[h]
7	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	NaSPh	0.16	−30	1.6:1.0	1.0:5.2[h]
8	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	NaSPh	0.33	−30	1.1:1.0	1.0:5.2[h]
9[c]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	NaSPh	0.17	−30	1.4:1.0	1.0:5.2[h]
10[c]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	$NaSPh/NaBF_4$	0.17/0.55	−30	2.2:1.0	1.0:5.2[h]
11[d,e]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	NaSPh	0.07	−30	3.1:1.0	1.0:5.2[h]
12[d,e]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	$NaSPh/NaBF_4$	0.07/0.19	−30	4.9:1.0	1.0:5.2[h]
13[f]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	$KSCOCH_3$	0.04	−30	13:1.0	1.0:5.2[h]
14[g]	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	$KSCOCH_3$	0.08	−30	8.9:1.0	1.0:5.2[h]
15	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	$KSCOCH_3$	0.18	−30	3.9:1.0	1.0:5.2[h]
16	$Cp(CO)PEt_3Fe{=}CHCH_3^+$, **2**	$KSCOCH_3$	0.32	−30	3.0:1.0	1.0:5.2[h]
17	$Cp(CO)PPh_3Fe{=}CHC_6H_5^+$, **4**	$NaOCD_3$	0.2	0	1.6:1.0	<1.0:30(est)
18	$Cp(CO)PPh_3Fe{=}CHC_6H_5^+$, **4**	$NaOCD_3$	1.0	0	1.0:1.1	<1.0:30(est)
19	$Cp(CO)PPh_3Fe{=}CHC_6H_5^+$, **4**	$NaOCD_3$	2.0	0	1.0:1.9	<1.0:30(est)
20	$Cp(CO)PPh_3Fe{=}CHC_6H_5^+$, **4**	$NaOCD_3$	4.0	0	1.0:4.2	<1.0:30(est)
21	$Cp(CO)PEt_3Fe{=}CHC_6H_5^+$, **5**	$NaOCH_3$	0.5	0	1.0:3.0	<1.0:30(est)
22	$Cp(CO)PEt_3Fe{=}CHC_6H_5^+$, **5**	$NaOCH_3$	1.0	0	1.0:4.0	<1.0:30(est)
23	$Cp(CO)PEt_3Fe{=}CHC_6H_5^+$, **5**	$NaOCH_3$	2.0	0	1.0:5.0	<1.0:30(est)

[a] $[Nu^-]$/TMSOTf = 3.1. [b] $[Nu^-]$/TMSOTf = 3.4. [c] Parallel experiments. [d] $[Nu^-]$/TMSOTf = 4.2. [e] Parallel experiments. [f] $[Nu^-]$/TMSOTf = 2.9. [g] $[Nu^-]$/TMSOTf = 4.0. [h] Isomer equilibrium ratios at −30 °C extrapolated from −104 °C.

4-S-OMe. Control experiments indicate the diastereomers to be stable under reaction conditions and workup procedures.[13]

Table I summarizes our results. Interpretation of diastereomer ratios is most easily discussed in terms of the complete solution of the Curtin–Hammett–Winstein–Holness equation applied to Scheme I.[14]

$$\frac{[\text{A-Nu}]}{[\text{S-Nu}]} = K_{eq}\frac{k_A}{k_S}\frac{k_S[Nu^-] + k_{SA} + k_{AS}}{k_A[Nu^-] + k_{SA} + k_{AS}} \quad (1)$$

boundary condition I: $k_A[Nu^-]$, $k_S[Nu^-] \gg k_{AS} + k_{SA}$

$$\frac{[\text{A-Nu}]}{[\text{S-Nu}]} = K_{eq} \quad (2)$$

boundary condition II: k_{AS}, $k_{SA} \gg k_A[Nu^-]$, $k_S[Nu^-]$

$$\frac{[\text{A-Nu}]}{[\text{S-Nu}]} = K_{eq}\frac{k_A}{k_S} \quad (3)$$

It is clear that none of the product ratios represent kinetic quenching (boundary condition I) of the anticlinal:synclinal equilibrium ratios. For the ethylidene systems, the major product always arises from quenching of the minor synclinal isomer. For the benzylidene systems **4** and **5**, the A-Nu/S-Nu ratio varies between 5 and 0.6 and is never as large as the anticlinal:synclinal isomer ratio. These results imply that the synclinal isomers are intrinsically more reactive than the anticlinal isomers (i.e., $k_S > k_A$). If boundary condition II applied to these systems (i.e., isomer interconversion much faster than nucleophile quenching), then the diastereomer ratios should be *independent* of nucleophile concentration and given simply by $(k_A/k_S)K_{eq}$. This is clearly not the case for **2**, **4**, or **5**. The observed behavior is best rationalized as an intermediate case where the rates of quenching ($k_A[Nu^-]$, $k_S[Nu^-]$) are approximately equal to the rates of isomer interconversion (k_{AS}, k_{SA}) as shown in the free energy diagram in Scheme I.[15] Quenching rates are dependent on $[Nu^-]$, while isomer interconversions are not. Thus, as $[Nu^-]$ increases boundary condition I is approached, and the fraction of product arising from the more stable anticlinal isomer will increase.[16] This behavior is observed in each of the three cases and further validates the structural assignments of diastereomers.

A comparison of $C_6H_5S^-$ versus CH_3COS^- at similar concentrations shows that the weaker nucleophile CH_3COS^- is less reactive and thus gives higher S-Nu/A-Nu ratios than the more reactive $C_6H_5S^-$. Extremely reactive nucleophiles should give kinetic or near-kinetic quenches, and this has been verified in the case of **5** quenched with BD_4^-.[8] An ionic strength effect is noted in entries 9, 10, 11, and 12. Increasing ionic strength will stabilize the fully charged ions **2**-A and **2**-S relative to partially neutralized transition states **2**-A‡ and **2**-S‡ and thus increase $\Delta G^{\ddagger}_A$ and $\Delta G^{\ddagger}_S$. As observed, this will lead to higher fractions of synclinal quenching.

The higher intrinsic reactivity of the synclinal isomers relative to the anticlinal isomers can be explained by using the conformational model for $Cp(CO)(PPh_3)Fe$-CHRR′ and $Cp(NO)(PPh_3)Re$-CHRR′ systems.[12,2d,17] Attack by Nu^- on the anticlinal isomer results in rehybridization of C_α toward sp^3 and, as shown in transition state A‡, forces R into the least favorable site between CO and PR_3 with initial formation of the high-energy conformation A′-Nu. On the other hand, addition of Nu^- to the synclinal isomer places the smallest substituent H between CO and PR_3 and leads directly to the most favorable conformation of S-Nu.

These studies demonstrate that the generalized Curtin–Hammett principle must be invoked in addition of nucleophiles to $Cp(CO)(PR_3)Fe{=}CHR^+$ complexes. Since nucleophilic attack and isomer interconversion are competitive and since the minor synclinal isomers are intrinsically more reactive than major anticlinal ones, not only may the major products arise from the minor synclinal isomers but also stereoselectivity can be a function of both the strength and concentration of the nucleophile. Clearly this point must be carefully considered in interpreting *any* diastereoselective reactions of $Cp(CO)(PR_3)Fe$ complexes where isomer interconversion may compete with reactions. For example, enantioselective carbene transfers to alkenes may also proceed mainly via synclinal isomers of $Cp(CO)(PR_3)Fe{=}CHR^+$ which would suggest cyclopropane ring closure via a backside mechanism.[4c,18]

(13) For **4**-A-OMe, **4**-S-OMe quenches were carried out at 0 °C, and samples were immediately cooled to −78 °C prior to analysis to prevent isomer interconversion.

(14) (a) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83. (b) Zifirov, N. S. *Tetrahedron* **1977**, *33*, 2719.

(15) Fitting known rates of interconversion of **2**-A ⇌ **2**-S and values for [**2**-S-SPh]/[**2**-A-SPh] at low PhS^- concentrations to eq 1 gives approximate values of k_S and k_A of 2.1×10^6 and 4.9×10^4 s^{-1} $L\text{-}M^{-1}$ at −30 °C.

(16) Higher ratios of **2**-A-SPh:**2**-S-SPh and **2**-A-$SCOCH_3$:**2**-S-$SCOCH_3$ were observed when quenching reactions were conducted at lower temperatures.

(17) (a) Seeman, J. I.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1984**, 1019. (b) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522.

(18) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

Acknowledgment is made to the National Institutes of Health and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We thank E. L. Eliel for helpful discussions.

Registry No. 1-S^+·OTf^-, 113109-87-8; 1-A^+·OTf^-, 113214-87-2; 1-S^+·BF_4^-, 113215-02-4; 1-A^+·BF_4^-, 113299-11-9; 1-S-SPh, 113109-92-5; 1-A-SPh, 113215-04-6; 1-S-$SCOCH_3$, 113109-93-6; 1-A-$SCOCH_3$, 113215-07-9; 2-S^+·OTf^-, 113109-89-0; 2-A^+·OTf^-, 113214-89-4; 2-S^+·BF_4^-, 113215-03-5; 2-A^+·BF_4^-, 113299-12-0; 2-S-SPh, 113109-96-9; 2-A-SPh, 113215-06-8; 2-S-$SCOCH_3$, 113109-97-0; 2-A-$SCOCH_3$, 113215-08-0; 3-S^+·OTf^-, 113214-91-8; 3-A^+·OTf^-, 113214-93-0; 3-S-SPh, 113109-94-7; 3-A-SPh, 113299-13-1; 3-S-$SCOCH_3$, 113109-95-8; 3-A-$SCOCH_3$, 113215-05-7; 4-S^+·OTf^-, 113214-95-2; 4-A^+·OTf^-, 113214-97-4; 4-S-OCD_3, 113109-98-1; 4-A-OCD_3, 113215-00-2; 4-S-OCH_3, 113350-82-6; 4-A-OCH_3, 104832-41-9; 5-S^+·OTf^-, 113109-91-4; 5-A^+·OTf^-, 113214-99-6; 5-S-OCH_3, 113109-99-2; 5-A-OCH_3, 113215-01-3; NaSPh, 930-69-8; $KSCOCH_3$, 10387-40-3; $NaOCD_3$, 6552-73-4; $NaOCH_3$, 124-41-4.

Supplementary Material Available: IR, ^1H, ^{13}C NMR, and elemental analysis data for 1-S-SPh, 1-A-SPh, 1-S-$SCOCH_3$, 2-S-SPh, 2-A-SPh, 2-S-$SCOCH_3$, 2-A-$SCOCH_3$, 3-S-$SCOCH_3$, 3-A-$SCOCH_3$, 5-S-OCH_3, and 5-A-OCH_3; IR, ^1H NMR, and elemental analysis data for 1-A-$SCOCH_3$; ^1H NMR data for 4-A-OCH_3, 1, and 2; IR, ^1H, and ^{13}C NMR data for 3-S-SPh and 3-A-SPh; ^1H and ^{13}C NMR data for 4-S-OCH_3 and 5 (12 pages). Ordering information is given on any current masthead page.

Isonitrile Biosynthesis in the Cyanophyte *Hapalosiphon fontinalis*

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In 1957 Hagedorn and Tonjes reported the isolation of the first naturally occurring isonitrile, xanthocillin from the fungus *Penicillium notatum*.[1] Since that time isonitriles have been found in other fungi,[2] bacteria,[3] and marine organisms[4] and more recently in blue-green algae.[5] The biosynthetic origin of the isonitrile group has intrigued chemists for three decades, but the data obtained to date with fungi, bacteria, and sponges do not present a simple picture. Studies on the biosynthesis of xanthocillin have suggested that L-tyrosine is the primary source of the isonitrile nitrogen,[6] but C_1 donors linked to tetrahydrofolate metabolism (methionine, formate, C-2 of glycine, and C-3 of serine)[7] as well as other C_1 donors (e.g., cyanide and carbamoyl phosphate)[8] are not sources of the isonitrile carbon. Puar et al.[9] have found, however, that L-[methyl-^{13}C]methionine labels the isocyano group of the hazimicins in the bacterium *Micromonospora echinospora* var. *challisensis*, and Garson[10] has discovered that [^{14}C]cyanide is incorporated into the isonitrile carbons of the marine sponge metabolite diisocyanoadociane. Garson's result is most interesting, since sponges frequently possess symbiotic microorganisms and certain bacteria and blue-green algae generate inorganic cyanide from amino acids.[11] Our interest in the possible role of symbiotic

Table I. Incorporation Experiments for Hapalindole A

precursor	amount fed (μCi)	total incorpn (%)	specific incorpn (%)	loss of ^{14}C upon acid hydrolysis of 1 to 2 (%)
[^{14}C]cyanide	24.5	0.16	1.21	94.8
[2-^{14}C]glycine	45.1	0.33	1.00	99.0
L-[3-^{14}C]serine	27.6	0.34	0.87	97.0
[^{14}C]formate	50.0	0.11	0.26	96.3
L-[*methyl*-^{14}C]methionine	27.3	0.05	0.08	97.6
[1,2-^{14}C]acetate	30.5	0.15	0.57	5.7
DL-[*methylene*-^{14}C]tryptophan	49.9	0.13	0.36	0.06

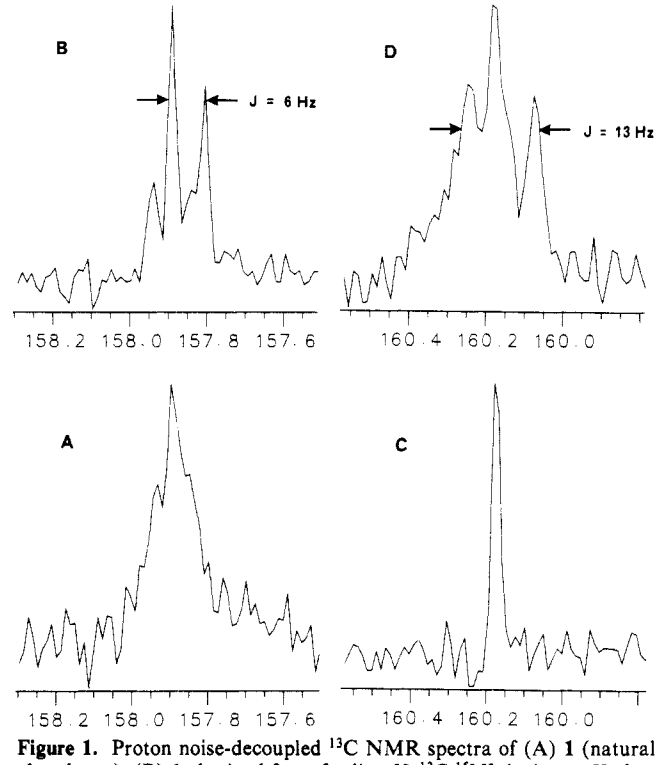

Figure 1. Proton noise-decoupled ^{13}C NMR spectra of (A) 1 (natural abundance); (B) 1 obtained from feeding [2-^{13}C,^{15}N]glycine to *H. fontinalis*; (C) 3 (natural abundance); and (D) 3 obtained from hydrolysis of 1 showing spectrum B.

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