J. Org. Chem. **1991,** *56,* 3497–3501

Synthesis of Isoascididemin, a Regioisomer of the Marine Alkaloid Ascididemin

Enrique Gómez-Bengoa and Antonio M. Echavarren*

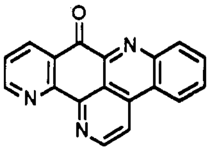
Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain

Received November 26, 1990

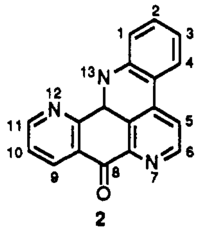
The synthesis of isoascididemin, a regioisomer of the naturally occurring ascididemin, has been completed in nine steps from 2,5-dimethoxyaniline. The key steps feature a selective palladium(0)-catalyzed cross-coupling reaction of 6-bromo-5,8-dimethoxy-4-[(trifluoromethanesulfonyl)oxy]quinoline with *N*-(*tert*-butoxycarbonyl)-2-(trimethylstannyl)aniline promoted by Cu(I) and a hetero-Diels–Alder reaction of a quinoline-5,8-dione with acrolein *N*,*N*-dimethylhydrazone.

Ascididemin (1) is a pentacyclic alkaloid with potent antineoplastic activity recently isolated from a tunicate.[1] Its structure was determined by extensive use of ^1H and ^{13}C NMR spectroscopy which led to the formulation of structure 1. The regioisomer 2 was excluded on the basis of comparison of its ^{13}C NMR spectrum with those of related alkaloids.[1] The original structural proposal was subsequently confirmed by synthesis.[2] Ascididemin belongs to a group of marine alkaloids that possess a common benzo[*de*][3,6]phenanthroline skeleton (3) including tetracyclic and pentacyclic compounds.[3,4] In this paper we report the synthesis of the nonnatural 2 (isoascididemin). The synthesis of 2 is of interest as this compound is the basic skeleton of one of the possible structures of neocalliactine, the degradation product of the marine alkaloid calliactine.[4q] Furthermore, this synthesis furnishes intermediates that could be of use in the synthesis of important tetracyclic alkaloids such as the cystodytins, diplamine, and the varamines.[4a–c,5]

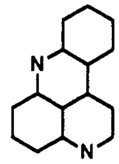
The retrosynthetic analysis shown in Scheme I is derived from that developed for the synthesis of amphimedine.[6]



1



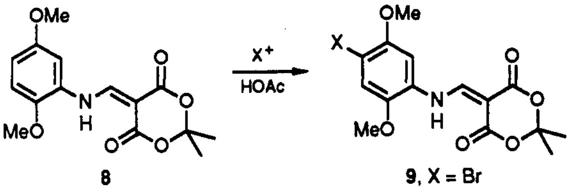
2



3

Isoascididemine (2) can be derived by regioselective hetero-Diels–Alder reaction[7,8] between acrolein *N*,*N*-dimethylhydrazone (4)[9] and 6-bromoquinoline-5,8-dione (5), available by the Stille palladium-catalyzed cross-coupling reaction of bromoquinolyl triflate 6 and arylstannane 7.[10] The coupling reaction of 6 was expected to proceed chemoselectively through the more reactive C-4 triflate.[10]

The synthesis of 6 takes advantage of the regioselective functionalization of [(arylamino)methylidene]-2,2-dimethyl-1,3-dioxane-4,6-diones[11] by electrophilic substitution reactions. Bromination of 8[11a] with Br_2 in glacial HOAc at 23 °C gave 9 in 95% yield. The (aminomethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione group is remarkably resistant to acid treatment, surviving under the conditions required for nitration of 8 with HNO_3 in HOAc at 23 °C to yield 10 (eq 1).



(1)

8

9, X = Br
10, X = NO_2

Thermolysis of 9 in diphenyl ether at 240–250 °C[11a] afforded quinolinone 11 in 81% yield, which was treated with trifluoromethanesulfonic anhydride, 2,6-lutidine, and

---

[1] Kobayashi, J.; Cheng, J.; Nakamura, H.; Ohizumi, Y.; Hirata, Y.; Sasaki, T.; Ohta, T.; Nozoe, S. *Tetrahedron Lett.* **1988**, *29*, 1177.

[2] (a) Bracher, F. *Heterocycles* **1989**, *29*, 2093. (b) Moody, C. J.; Rees, C. W.; Thomas, R. *Tetrahedron Lett.* **1990**, *31*, 4375. (c) See also: Bracher, F. *Justus Liebigs Ann. Chem.* **1990**, 205.

[3] Faulkner, D. J. *Nat. Prod. Rep.* **1990**, *7*, 269 and previous reports cited therein.

[4] (a) Cystodytins A, B, and C: Kobayashi, J.; Cheng, J.; Wälchli, M. R.; Nakamura, H.; Hirata, Y.; Sasaki, T.; Ohizumi, Y. *J. Org. Chem.* **1988**, *53*, 1800. (b) Varamines A and B: Molinski, T. F.; Ireland, C. M. *J. Org. Chem.* **1989**, *54*, 4256. (c) Diplamine: Charyulu, G. A.; McKee, T. C.; Ireland, C. M. *Tetrahedron Lett.* **1989**, *30*, 4201. (d) Dercitin: Gunawardana, G. P.; Kohmoto, S.; Gunasekera, S. P.; McConell, O. J.; Koehn, F. E. *J. Am. Chem. Soc.* **1988**, *110*, 4856. (e) Nordercitine, dercitamine, dercitamide, and cyclodercitin: Gunawardana, G. P.; Kohmoto, S.; Burres, N. S. *Tetrahedron Lett.* **1989**, *30*, 4359. (f) Shermilamine A: Cooray, N. M.; Scheuer, P. J.; Parkanyi, L.; Clardy, J. *J. Org. Chem.* **1988**, *53*, 4619. (g) Shermilamine B (debromoshermilamine A): Carrol, A. R.; Cooray, N. M.; Poiner, A.; Scheuer, P. J. *J. Org. Chem.* **1989**, *54*, 4231. See also refs 4h and 4j. (h) Kuonamines A, B, C, and D: Carroll, A. R.; Scheuer, P. J. *J. Org. Chem.* **1990**, *55*, 4426. (i) Segoline A, isosegoline A, and norsegoline: Rudi, A.; Benayahu, Y.; Goldberg, I.; Kashman, Y. *Tetrahedron Lett.* **1988**, *29*, 3861. See also ref 4k. (j) Eilatin: Rudi, A.; Benayahu, Y.; Goldberg, I.; Kashman, Y. *Tetrahedron Lett.* **1988**, *29*, 6655, see also 4k. (k) Segoline B: Rudi, A.; Kashman, Y. *J. Org. Chem.* **1989**, *54*, 5331. (l) Plakinidines A and B: Inman, W. D.; O'Neill-Johnson, M.; Crews, P. *J. Am. Chem. Soc.* **1990**, *112*, 1. See also ref 4m. (m) Plakinidine C: West, R. R.; Mayne, C. L.; Ireland, C. M.; Brinen, L. S.; Clardy, J. *Tetrahedron Lett.* **1990**, *31*, 3271. (n) Amphimedine: Schmitz, F. J.; Agarwal, S. K.; Gunasekera, S. P.; Schmidt, P. G.; Shoolery, J. N. *J. Am. Chem. Soc.* **1983**, *105*, 4835. (o) Petrosamine: Molinski, T. F.; Fahy, E.; Faulkner, D. J.; Van Duyne, G. D.; Clardy, J. *J. Org. Chem.* **1988**, *53*, 1340. (p) 2-bromoleptoclinidinone (2-bromoascididemin): de Guzman, F. S.; Schmitz, F. J. *Tetrahedron Lett.* **1989**, *30*, 1069. (q) Calliactine and neocalliactine acetate: Cimino, G.; Crispino, A.; De Rosa, S.; De Stefano, S.; Gavagnin, M.; Sodano, G. *Tetrahedron* **1987**, *43*, 4023. (r) 11-Hydroxyascididemin and meridine: Schmitz, F. J.; de Guzman, F.; Choi, Y.-H.; Hossain, M. B.; Rizvi, S. K.; Helm, D. *Pure Appl. Chem.* **1990**, *62*, 1393.

[5] For a recent synthetic approach to the cystodytins, see: Ciufolini, M. A.; Byrne, N. E. *Tetrahedron Lett.* **1989**, *30*, 5559.

[6] Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 4051.

[7] (a) Serckx-Poncin, B.; Hesbain-Frisque, A.-M.; Ghosez, L. *Tetrahedron Lett.* **1982**, *23*, 3261. (b) Ghosez, L.; Serckx-Poncin, B.; Rivera, M.; Bayard, P.; Sainte, F.; Demoulin, A.; Hesbain-Frisque, A.-M.; Mockel, A.; Munoz, L.; Bernard-Henriet, C. *Lectures Heterocycl. Chem.* **1985**, *8*, 69.

[8] (a) Chigr, M.; Fillion, H.; Rougny, A. *Tetrahedron Lett.* **1988**, *29*, 5913. (b) Potts, K. T.; Walsh, E. B.; Bhattacharjee, D. *J. Org. Chem.* **1987**, *52*, 2285. (c) Lee, H.; Anderson, W. K. *Tetrahedron Lett.* **1990**, *31*, 4405. (d) Gesto, C.; Cuesta, E.; Avendaño, C. *Tetrahedron* **1989**, *45*, 4477. (e) For the reaction of some 1-aza dienes with quinones under Lewis acid catalysis, see: Echavarren, A. M. *J. Org. Chem.* **1990**, *55*, 4255.

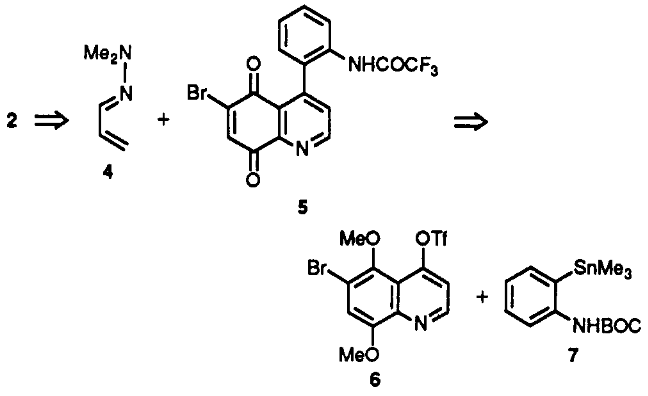
[9] Hydrazone 4 was prepared by a modification of the described procedure (see Experimental Section): Gol'din, G. S.; Balabina, T. A.; Ushakova, A. N.; Shor, G. S. *Zh. Org. Khim.* **1969**, *5*, 1321.

[10] Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

[11] (a) Cassis, R.; Tapia, R.; Valderrama, J. A. *Synth. Commun.* **1985**, *15*, 125. (b) Fernandez, M.; Lin, T.-S.; Sartoreli, A. C. *Synth. Commun.* **1989**, *19*, 2647.

0022-3263/91/1956-3497$02.50/0

Scheme I



Scheme II

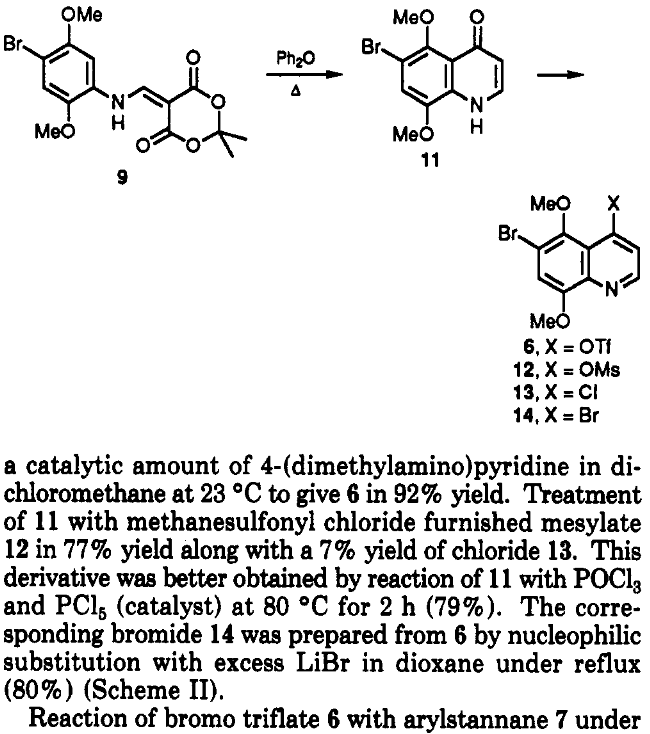


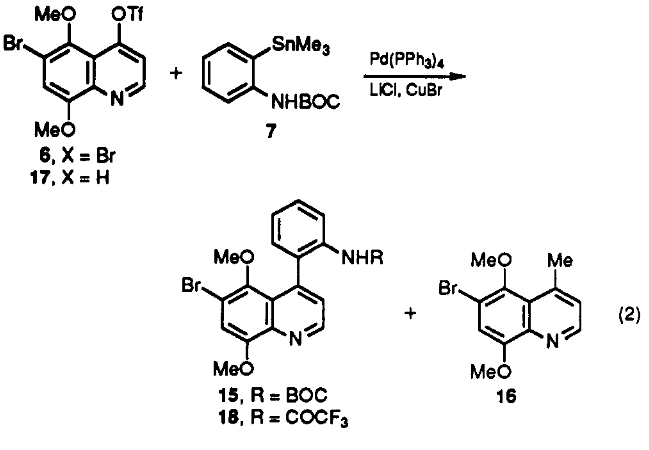
Table I. ^1H and ^{13}C NMR Data for Isoascididemin (2)[a]

C	δC (m)[b]	$J(^{13}C–^1H)$, Hz	δH (m)[c]	$J(^1H–^1H)$, Hz
1	131.72 (dd)	164.6, 7.0	8.54 (br d)	8.2
2	131.98 (dd)	161.8, 7.4	7.93 (td)	8.1, 1.4
3	129.68 (dd)	162.7, 8.1	7.82 (td)	8.1, 1.2
4	122.72 (dd)	160.3, 8.2	8.62 (dd)	8.1, 1.2
4a	121.59 (t)	6.0		
4b	138.04 (dd)	5.5, 1.8		
5	120.28 (dd)	166.0, 8.5	8.71 (d)	5.6
6	149.55 (d)	183.4	9.23 (d)	5.6
7a	145.72 (d)	7.4		
8	181.48 (d)	3.3		
8a	128.77 (d)	6.1		
9	136.14 (dd)	168.4, 6.3	8.74 (dd)	8.0, 1.8
10	125.82 (dd)	167.5, 8.5	7.68 (dd)	8.0, 4.6
11	155.12 (ddd)	182.0, 5.5, 2.8	9.14 (dd)	4.6, 1.8
12a	151.00 (dd)	11.6, 5.0		
12b	147.49 (s)			
12c	118.56 (d)	11.0		
13a	145.24 (t)	7.4		

[a] 3.5:1.5 $CDCl_3$–CD_3OD, 30 °C. [b] ^{13}C NMR (75 or 50 MHz) assignments were made by $^1H–^{13}C$ heterocorrelation (J = 170 Hz) and by selective ^1H irradiation of H-4, H-6, and H-9. [c] ^1H NMR (300 MHz) assignments were made by COSY and NOESY experiments.

a catalytic amount of 4-(dimethylamino)pyridine in dichloromethane at 23 °C to give 6 in 92% yield. Treatment of 11 with methanesulfonyl chloride furnished mesylate 12 in 77% yield along with a 7% yield of chloride 13. This derivative was better obtained by reaction of 11 with $POCl_3$ and PCl_5 (catalyst) at 80 °C for 2 h (79%). The corresponding bromide 14 was prepared from 6 by nucleophilic substitution with excess LiBr in dioxane under reflux (80%) (Scheme II).

Reaction of bromo triflate 6 with arylstannane 7 under the standard coupling conditions [$Pd(PPh_3)_4$, LiCl or LiBr, dioxane][10] proceeded very sluggishly to give a mixture of coupling products 15 and 16 in variable yields after 70–90 h at 100 °C (eq 2). This is in sharp contrast with the smooth coupling observed with the parent triflate 17[6] and may be a consequence of the higher steric hindrance introduced by the arrangement of the C-5 methoxyl and the C-6 bromosubstituent of 6. The use of $PdCl_2(dppf)$[12] as the catalyst in DMF, in the absence of lithium salts, led to 16 in 80% yield by transfer of the methyl group of 7. Although the transfer of alkyl groups of trialkylarylstannanes has been previously observed as a minor pathway by using weakly ligated palladium catalysts,[10] this is the first report of a selective alkyl coupling with a trialkylarylstannane. After much experimentation, the desired coupling reaction was effected reproducibly by heating 6 and 7 with $Pd(PPh_3)_4$ catalyst (0.05 equiv) and LiCl (3.0 equiv) in dioxane at 90 °C in the presence of CuBr (0.05 equiv). Under these reaction conditions 15 was obtained in 60–64% yield (eq 2). The beneficial effect of added Cu(I) salts in several cross-coupling reactions has been recently observed,[13] although this is the first report of a rate acceleration in the coupling of an aryl triflate.



(2)

Similar results were obtained with dibromoquinoline 14, while 4-chloro derivative 13 gave only ca. 20% conversion into 15, and mesylate 12 was recovered unchanged under the same reaction conditions. Noteworthy is the fact that none of the coupled products resulting from reaction through the C-6 bromo were detected in the crude reaction mixtures.

Direct oxidation of 4-arylquinoline 15 with ammonium cerium(IV) nitrate (CAN) failed, yielding only unchanged starting material. On the other hand, exposure of 15 to a 1:1 mixture of CF_3CO_2H–$(CF_3CO)_2O$ at 23 °C for 2–3 h gave quantitatively trifluoroacetamide 18, which was oxidized to the quinolinequinone (5) (see Scheme I) in 48% yield with CAN in aqueous acetonitrile[14] in the presence of H_2SO_4 (2 M).[15]

The presence of the C-6 bromo substituent was expected to direct the attack of the nucleophilic C-4 terminus of the aza diene 4 to the electrophilic C-7 of the dienophile.[6–8] Thus, the hetero-Diels–Alder cycloaddition[7] of 5 with acrolein *N,N*-dimethylhydrazone (4)[9] in acetonitrile at 23 °C for 1 h gave a red-violet adduct, which was treated with

---

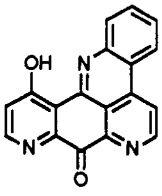
(12) Dppf = 1,1′-bis(diphenylphosphino)ferrocene. $PdCl_2(dppf)$ was the catalyst of choice in the coupling of anthraquinone triflates with organostannanes: Tamayo, N.; Echavarren, A. M.; Paredes, M. C.; Fariña, F.; Noheda, P. *Tetrahedron Lett.* **1990**, *31*, 5189.

(13) See: Liebeskind, L. S.; Fengl, R. W. *J. Org. Chem.* **1990**, *55*, 5359 and references cited therein.

(14) Jacob, P.; Callery, P. S.; Shulzin, A. T.; Castagnoli, N. *J. Org. Chem.* **1976**, *41*, 3627.

(15) See: Periasamy, M.; Bhatt, M. V. *Synthesis* **1977**, 330.

6 M HCl–THF at 80 °C for 45 min, yielding isoascididemine **2** in 92% yield (two steps). This pentacyclic heterocycle showed ^1H and ^{13}C NMR spectra (Table I) to be *similar to, but clearly distinguishable from*, those of ascididemin (**1**). The observation of the expected $^3J(^{13}C–^1H)$ coupling between the C-8 carbonyl and H-9 (J = 3.3 Hz)[16] confirmed the regiochemistry of the Diels–Alder cycloaddition. The alternative regiochemistry should result in a pentacyclic compound with a singlet carbonyl resonance without 3-bond coupling. The quinonimine-like C-12b resonance appeared at 147.49 ppm as a singlet in the fully coupled carbon spectrum. The related compounds ascididemin,[1] 2-bromoleptoclinidinone,[4p] and 11-hydroxyascididemin[4r] showed this signal at 149–150 ppm. Neocalliactine acetate has a singlet resonance at 145.3 ppm[4q] and meridine (**19**) showed the corresponding carbon at 152 ppm.[4r] The carbon data for rings D and E of **2** are closely similar to those of **19**.[4r]



19

It is also interesting that **2** failed to form a red complex with Fe(II), characteristic of unhindered 1,10-phenanthrolines. This result is consistent with the lack of chelation of Fe(II) by ascididemin,[1] 2-bromoleptoclinidinone,[4p] and neocalliactine acetate.[4q]

In summary, this synthesis emphasizes the utility of the palladium-catalyzed coupling of stannanes with electrophiles in a concise preparation of heterocycles. Furthermore, the intermediates produced are adequately functionalized to allow for the construction of the cystodytins and related tetracyclic alkaloids. These studies are in progress and will be reported in due course.

Experimental Section[17]

5-[[(4-Bromo-2,5-dimethoxyphenyl)amino]methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (9). A solution of bromine (2.40 g, 15.0 mmol) in acetic acid (25 mL) was added to a suspension of Meldrum acid derivative **8**[11a] (4.50 g, 14.6 mmol) in acetic acid (50 mL) at ca. 5 °C. The resulting mixture was stirred at 23 °C for 30 min and then poured into 200 mL of ice–water. The pale yellow solid was filtered to yield **9** (5.40 g, 95%). Recrystallization from EtOH (ca. 85% yield) gave yellow crystals: mp 152 °C (EtOH); IR (KBr) 1740, 1680, 1630, 1600, 1435, 1290, 1275, 1200 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 11.40 (d, J = 14.6 Hz, 1 H), 8.53 (d, J = 14.5 Hz, 1 H), 7.03 (s, 1 H), 6.82 (s, 1 H), 3.80 (s, 6 H), 1.62 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.05, 163.57, 150.76, 150.46, 143.49, 126.67, 117.00, 108.57, 104.99, 100.00, 87.75, 57.10, 56.69, 26.94 (2×); MS m/z 387 (M^+ + 2, 11), 385 (M^+, 11), 329 (9), 327 (8), 254 (98), 252 (100). Anal. Calcd for $C_{15}H_{16}BrNO_6$: C, 46.65; H, 4.18; N, 3.63. Found: C, 46.72; H, 4.08; N, 3.88.

5-[[(2,5-Dimethoxy-4-nitrophenyl)amino]methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (10). A solution of HNO_3 (d = 1.38, 1.20 mL, 15.8 mmol) in acetic acid (5 mL) was added to a suspension of **8** (3.88 g, 12.6 mmol) in acetic acid (60 mL) at 0–5 °C. The resulting mixture was stirred at ca. 5 °C for 1 h, warmed to 23 °C, and stirred at this temperature for 3 h. The mixture was diluted with water and filtered to yield **10** as a yellow solid (4.33 g, 97%): mp 192–194 °C; IR (KBr) 1730, 1720, 1680, 1640, 1605, 1525, 1465, 1440, 1350, 1300–1250 (br), 1225, 1030 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 11.62 (d, J = 14.1 Hz, 1 H), 8.66 (d, J = 14.2 Hz, 1 H), 7.60 (s, 1 H), 7.03 (s, 1 H), 4.00 (s, 3 H), 3.99 (s, 3 H), 1.75 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 164.81, 163.16, 150.31, 149.27, 142.10, 135.56, 132.47, 109.57, 105.44, 100.67, 89.97, 57.52, 56.90, 27.11 (2×); MS m/z 352 (M^+, 10), 294 (12), 220 (13), 219 (100), 172 (12). Anal. Calcd for $C_{15}H_{16}N_2O_8$: C, 51.14; H, 4.58; N, 7.95. Found: C, 51.02; H, 4.40; N, 8.20.

6-Bromo-5,8-dimethoxy-4(1*H*)-quinolinone (11). A mixture of **9** (6.00 g, 15.5 mmol) in diphenyl ether (250 mL) was heated at 250–260 °C for 20 min. After cooling to room temperature, the mixture was diluted with hexanes (ca. 350 mL) and the pale brown solid was filtered to yield **11** (3.58 g, 81%): mp 244–245 °C; IR (KBr) 3180, 1620, 1570, 1510, 1390, 1300, 1210, 1180, 1070, 840 cm^{-1}; ^1H NMR (Me_2SO-d_6, 300 MHz) δ 11.20 (br s, 1 H), 7.65 (br s, 1 H), 7.38 (s, 1 H), 5.92 (d, J = 7.4 Hz, 1 H), 3.96 (s, 3 H), 3.70 (s, 3 H); ^{13}C NMR (Me_2SO-d_6, 50 MHz) δ 175.31, 148.29, 144.96, 137.62, 132.29, 120.85, 114.54, 111.81, 109.66, 61.00, 56.66; MS m/z 285 (M^+ + 2, 22), 283 (M^+, 22), 270 (98), 268 (100), 240 (16), 238 (13), 161 (39). Anal. Calcd for $C_{11}H_{10}BrNO_3$: C, 46.50; H, 3.55; N, 4.96. Found: C, 46.83; H, 3.61; N, 5.15.

6-Bromo-5,8-dimethoxy-4-[(trifluoromethanesulfonyl)oxy]quinoline (6). To a solution of quinolinone **11** (2.30 g, 8.10 mmol), 2,6-dimethylpyridine (1.50 mL, 12.4 mmol), and 4-(dimethylamino)pyridine (98 mg, 0.82 mmol) in CH_2Cl_2 (60 mL) was added trifluoromethanesulfonic anhydride (1.50 mL, 8.92 mmol). After being stirred at 23 °C for 12 h, the solution was partitioned between CH_2Cl_2 and aqueous NH_4Cl (saturated, pH 8). After the usual workup, the residue was chromatographed (1:1 hexanes–EtOAc) to yield **6** as a tan solid (3.10 g, 92%): mp 124–126 °C; IR (KBr) 1935, 1595, 1495, 1430, 1245, 1230, 1200, 1155, 1050, 915, 860, 815, 755, 610 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.94 (d, J = 4.9 Hz, 1 H), 7.33 (d, J = 4.9 Hz, 1 H), 7.23 (s, 1 H), 4.06 (s, 3 H), 3.87 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.19, 151.30, 149.55, 143.79, 142.55, 118.63 [q, $^1J(^{13}C–^{19}F)$ = 321.0 Hz], 118.16, 116.97, 115.16, 113.56, 61.71, 56.53; MS m/z 417 (M^+, 50), 284 (85), 282 (88), 255 (49), 253 (51), 202 (60), 174 (100). Anal. Calcd for $C_{12}H_9BrF_3NO_5S$: C, 34.63; H, 2.18; N, 3.37; S, 7.70. Found: C, 34.93; H, 2.38; N, 3.61; S, 8.00.

6-Bromo-5,8-dimethoxy-4-[(methanesulfonyl)oxy]quinoline (12). To a solution of quinolinone **11** (300 mg, 1.06 mmol), 2,6-dimethylpyridine (0.20 mL, 1.7 mmol), and (dimethylamino)pyridine (13 mg, 0.11 mmol) in CH_2Cl_2 (20 mL) was added methanesulfonyl chloride (0.10 mL, 1.3 mmol) at 0 °C. After being stirred at 23 °C for 20 h, the solution was partitioned between CH_2Cl_2 and aqueous NH_4Cl (saturated solution, pH 8). After the usual workup, the residue was chromatographed (1.5:1 hexanes–EtOAc) to yield **13** (25 mg, 7%) (see below) and **12** (more polar fraction) as a white solid (294 mg, 77%): mp 201–203 °C; IR (KBr) 1625, 1580, 1375, 1215, 1190, 1050 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.94 (d, J = 4.8 Hz, 1 H), 7.56 (d, J = 4.9 Hz, 1 H), 7.25 (s, 1 H), 4.08 (s, 3 H), 3.92 (s, 3 H), 3.22 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.53, 150.94, 150.00, 143.99, 142.64, 118.32, 116.71, 116.48, 112.97, 61.98, 56.58, 37.97. Anal. Calcd for $C_{12}H_{12}BrNO_5S$: C, 39.79; H, 3.34; N, 3.84. Found: C, 40.07; H, 3.43; N, 3.66.

6-Bromo-4-chloro-5,8-dimethoxyquinoline (13). A mixture of quinolinone **11** (500 mg, 1.75 mmol) and PCl_5 (10 mg, 0.05 mmol) in $POCl_3$ (3 mL) was heated at 80 °C for 21 h. After being cooled to room temperature, the mixture was poured into cool (ca. 5 °C) 5% aqueous $NaHCO_3$. After the usual workup with EtOAc, the residue was chromatographed (1.5:1 hexanes–EtOAc) to yield **13** as a pale yellow solid (421 mg, 79%): mp 92–93 °C (hexanes); IR (KBr) 1595, 1580, 1500, 1465, 1395, 1340, 1330, 1310, 1235, 1220, 1045, 1020, 955, 830 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 8.74 (d, J = 4.7 Hz, 1 H), 7.54 (d, J = 4.6 Hz, 1 H), 7.23 (s, 1 H), 4.07 (s, 3 H), 3.90 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.35, 148.50, 145.60, 141.72, 139.82, 125.17, 122.61, 116.58, 112.83, 62.16, 56.50. Anal. Calcd for $C_{11}H_9BrClNO_2$: C, 43.67; H, 3.00; N, 4.63. Found: C, 43.79; H, 3.04; N, 4.77.

4,6-Dibromo-5,8-dimethoxyquinoline (14). A suspension of triflate **6** (100 mg, 0.07 mmol) and lithium bromide (63 mg, 0.73

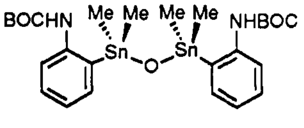
---

[16] (a) A 3.0–3.7-Hz ^3J coupling constant was observed in related compounds: amphimedine: 3.5 Hz,[4n] 2-bromoleptoclinidinone: 3.0 Hz,[4p] 8-aza-1,2,3,4-tetrahydrobenz[*a*]anthracene-7,12-dione: 3.6 Hz,[17b] and 11-aza-1,2,3,4-tetrahydrobenz[*a*]anthracene-7,12-dione: 3.7 Hz.[17b] Neocalliactine acetate showed the carbonyl resonance at 181.4 ppm as a doublet with J = 3.8 Hz.[4q] (b) Haber, A.; Hilton, B. D. *Org. Magn. Reson.* 1983, *21*, 168.

[17] See general procedure section in ref 8e. "Usual workup" means extraction, drying with Na_2SO_4, filtration, and evaporation.

mmol) in 1,4-dioxane (3.0 mL) was heated to reflux for 14 h. After being cooled to room temperature, the mixture was partitioned between EtOAc and water. After the usual workup, the residue was chromatographed (1:2 hexanes–EtOAc) to yield **14** as a pale yellow solid (67 mg, 80%): mp 118–120 °C; IR (KBr) 1595, 1580, 1495, 1440, 1385, 1305, 1240, 1005, 840, 815 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (d, J = 4.6 Hz, 1 H), 7.81 (d, J = 4.6 Hz, 1 H), 7.23 (s, 1 H), 4.07 (s, 3 H), 3.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.28, 148.27, 145.66, 141.44, 129.26, 127.70, 123.53, 116.41, 112.90, 62.17, 56.47; MS m/z 349 ($M^+ + 4$, 8), 347 ($M^+ + 2$, 17), 345 (M^+, 9), 334 (50), 332 (100), 330 (52), 197 (9), 195 (11). Anal. Calcd for $C_{11}H_9Br_2NO_2$: C, 37.89; H, 2.94; N, 3.72. Found: C, 38.07; H, 2.61; N, 4.04.

***N*-(*tert*-Butoxycarbonyl)-2-(trimethylstannyl)aniline (7).** This stannane was prepared according to the described procedure[6,18] as follows: to a solution of *N*-(*tert*-butoxycarbonyl)aniline (4.00 g, 20.70 mmol) in THF (40 mL) cooled at –78 °C was added *t*-BuLi (36.0 mL, 1.3 M in pentane, 46.80 mmol). The mixture was warmed up to –20 °C over 1 h and stirred at this temperature for 2 h. A solution of trimethyltin chloride (8.50 g, 42.7 mmol) in THF (5 mL) was added. After being stirred for 30 min at –20 °C, the cooled mixture was immediately poured into an aqueous NH_4Cl solution (saturated, pH 8) and extracted with EtOAc. After the usual workup, the residue was chromatographed (100:1 hexanes–EtOAc) to yield the title stannane as a white crystalline solid (6.06 g, 82%). Usual yields ranged between 80 and 85%, although occasionally yields of 95–98% were also realized. After the addition of trimethyltin chloride, it is essential to stir the reaction mixture at –20 °C for only 30–45 min before the aqueous treatment. When the reaction mixture was stirred at 23 °C a polar byproduct was observed by TLC. In one instance, after stirring at 23 °C for 14 h, this byproduct was isolated in 33% yield by chromatography (eluting with 10:1 hexanes–EtOAc) as a tan solid: bis[2-[(*tert*-butoxycarbonyl)amino]phenyl]dimethyltin oxide (i): mp 132–136 °C; IR (KBr) 3300, 2990, 1650, 1595, 1540, 1470, 1325, 1260, 1160, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.21 (dd, J = 7.4, 1.7 Hz, 2 H), 7.28 (td, J = 7.5, 1.7 Hz, 2 H), 7.19 (td, J = 7.4 Hz, 1.6 Hz, 2 H), 7.00 (br s, 2 H), 6.77 (dd, J = 7.9, 1.2 Hz, 2 H), 1.51 (s, 18 H), 0.81 [s, $^{2}J(^{1}H-^{119}Sn)$ = 73.4 Hz, $^{2}J(^{1}H-^{117}Sn)$ = 70.1 Hz, 12 H]; ^{13}C NMR ($CDCl_3$, 50 MHz; DEPT) δ 156.69 (s), 142.35 (s), 138.07 (d), 129.87 (d), 129.80 (s), 124.47 (d), 119.18 (d), 83.93 (s), 28.24 (q), 2.90 (q) [$^{1}J(^{119}Sn-^{13}C)$ = 557 Hz, $^{1}J(^{117}Sn-^{13}C)$ = 532 Hz]; MS m/z 446 (M^+, 12), 362 (6), 310 (18), 308 (37), 307 (22), 306 (100), 286 (59). Anal. Calcd for $C_{26}H_{40}N_2O_5Sn_2$: C, 44.74; H, 5.78; N, 4.02. Found: C, 44.81; H, 5.74; N, 4.09.



i

6-Bromo-4-[2-[(*tert*-butoxycarbonyl)amino]phenyl]-5,8-dimethoxyquinoline (15). A mixture of triflate **6** (1.35 g, 3.25 mmol), stannane **7** (1.68 g, 4.70 mmol), lithium chloride (330 mg, 7.80 mmol), copper(I) bromide (25 mg, 0.16 mmol), and tetrakis(triphenylphosphine)palladium(0) (180 mg, 0.16 mmol) in 1,4-dioxane (60 mL) was heated at 90 °C for 60 h. After being cooled to room temperature, the mixture was partitioned between EtOAc and a 5% aqueous ethylenediamine solution.[19] After the usual workup, the residue was chromatographed (1.5:1 hexanes–EtOAc) to yield **15** as a white solid (952 mg, 64%, several other fraction contained **15** contaminated with **16**): mp 166–168 °C; IR (KBr) 3420, 3100, 2960, 1720, 1590, 1540, 1465, 1340, 1240, 1165, 1080, 1050, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.99 (d, J = 4.3 Hz, 1 H), 7.96 (d, J = 8.1 Hz, 1 H), 7.48–7.39 (m, 1 H), 7.34 (d, J = 4.3 Hz, 1 H), 7.31 (s, 1 H), 7.28–7.16 (m, 2 H), 5.92 (br s, 1 H), 4.13 (s, 3 H), 3.13 (s, 3 H), 1.36 (s, 9 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.90, 152.72, 149.20, 146.31, 142.86, 140.90, 135.92, 132.12, 129.02, 128.72, 125.85, 123.42, 122.87, 120.96, 115.20, 112.46, 80.47, 60.95, 56.51, 28.18 (3×); MS m/z 460 ($M^+ + 2$, 10), 458 (M^+, 11), 387 (11), 329 (52), 327 (78), 278 (100). Anal. Calcd for $C_{22}H_{23}BrN_2O_4$: C, 57.53; H, 5.05; N, 6.10. Found: C, 57.86; H, 5.36; N, 6.11.

6-Bromo-5,8-dimethoxy-4-methylquinoline (16). This quinoline was obtained in low yield as a byproduct in the above preparation and was purified by recrystallization from hexanes as a white solid: mp 63–65 °C; IR (KBr) 2930, 1590, 1510, 1460, 1395, 1340, 1205, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.74 (d, J = 4.4 Hz, 1 H), 7.24 (d, J = 4.3 Hz, 1 H), 7.15 (s, 1 H), 4.05 (s, 3 H), 3.85 (s, 3 H), 2.89 (s, 3 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 152.63, 149.01, 147.35, 143.92, 140.79, 125.25, 124.80, 114.23, 111.60, 61.58, 56.28, 22.67. Anal. Calcd for $C_{12}H_{12}BrNO_2$: C, 51.08; H, 4.29; N, 4.96. Found: C, 50.70; H, 4.64; N, 5.30.

6-Bromo-5,8-dimethoxy-4-[2-[(trifluoroacetyl)amino]phenyl]quinoline (18). A solution of **15** (340 mg, 0.74 mmol) in trifluoroacetic acid (7 mL) and trifluoroacetic anhydride (6.5 mL) was stirred at 23 °C for 2 h. The solvent was evaporated, and the residue was partitioned between CH_2Cl_2 and 2% aqueous $NaHCO_3$. After the usual workup, pure **18** was obtained as a white solid (335 mg, 100%): mp 200–202 °C (1:1 benzene–hexanes); IR (KBr) 3300–3100 (br), 3020, 2940, 1730, 1590, 1350, 1230, 1220, 1210, 1160, 1145, 1075, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.00 (d, J = 4.3 Hz, 1 H), 7.92 (d, J = 7.9 Hz, 1 H), 7.56–7.50 (m, 2 H), 7.41–7.39 (m, 1 H), 7.36 (s, 1 H), 7.34 (d, J = 4.4 Hz, 1 H), 4.12 (s, 3 H), 3.09 (s, 3 H); MS m/z 456 ($M^+ + 2$, 33), 454 (M^+, 34), 441 (100), 439 (99). Anal. Calcd for $C_{19}H_{14}BrF_3N_2O_3$: C, 50.13; H, 3.10; N, 6.15. Found: C, 50.03; H, 3.39; N, 5.92.

6-Bromo-4-[2-[(trifluoroacetyl)amino]phenyl]quinoline-5,8-dione (5). A solution of **18** (258 mg, 0.57 mmol) in MeCN (4 mL) was treated with a solution of ammonium cerium(IV) nitrate (1.34 g, 2.44 mmol) in 2 M H_2SO_4 (6 mL) at 23 °C. After being stirred at this temperature for 16 h, the mixture was partitioned between EtOAc and water. After the usual workup, the residue was chromatographed (1.5:1 hexanes–EtOAc) to yield **5** as a yellow solid (115 mg, 48%): mp 194–195 °C (1:1 benzene–hexanes); IR (KBr) 3220, 3060, 1720, 1680, 1200, 1170, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 9.07 (d, J = 4.8 Hz, 1 H), 7.73 (br s, 1 H), 7.69 (s, 1 H), 7.65 (dd, J = 8.4, 1.4 Hz, 1 H), 7.57 (td, J = 7.5, 1.6 Hz, 1 H), 7.55 (d, J = 4.9 Hz, 1 H), 7.46 (td, J = 7.4, 1.7 Hz, 1 H), 7.19 (dd, J = 7.4, 1.6 Hz, 1 H); UV–vis ($CHCl_3$) λ_{max} (ϵ) 250 (16 400), 274 (14 400), 350 (1300). Anal. Calcd for $C_{17}H_8BrF_3N_2O_3$: C, 48.02; H, 1.90; N, 6.59. Found: C, 48.15; H, 2.10; N, 6.90.

Acrolein *N*,*N*-Dimethylhydrazone (4). The reaction of *N*,*N*-dimethylhydrazine with acrolein in acetic acid at 0–23 °C[9] gave a mixture of 3-(dimethylamino)propionitrile and **4** in ca. 12–10:1 ratio as determined by ^{1}H NMR. The desired hydrazone **4** could be prepared according to the following modified procedure: To a solution of *N*,*N*-dimethylhydrazine (3.0 mL, 39.5 mmol) in Et_2O (5 mL) at 0 °C was added HOAc (0.20 mL, 3.5 mmol). After being stirred at this temperature for 10 min, a solution of acrolein (2.80 mL, 42.5 mmol) in Et_2O (5 mL) was slowly added (ca. 10 min). After additional 10 min at this temperature, the solution was washed with water, 1% aqueous HCl, and a saturated NaCl solution (1 mL each). After drying ($MgSO_4$), the solution containing pure **4** (as determined by ^{1}H NMR) was usually employed in the next reaction without further purification. Evaporation (ca. 40–50 mmHg) gave **4** in 25–40% yield as a colorless oil: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.99 (d, J = 9.0 Hz, 1 H), 6.48 (ddd, J = 17.2, 10.3, 8.9 Hz, 1 H), 5.28 (d, J = 17.7 Hz, 1 H), 5.24 (d, J = 10.6 Hz, 1 H), 2.87 (s, 6 H).

Isoascididemin (2). A solution of quinone **5** (57 mg, 0.13 mmol) in MeCN (3 mL) was treated with hydrazone **4** (ca. 20 molar equiv) in Et_2O (2 mL). The purple solution was stirred at 23 °C for 1 h. The solvent and excess **4** was evaporated, and the red solid was dissolved in THF (1.5 mL) and 6 M HCl (1.5 mL). This mixture was heated at 80 °C for 45 min. After being cooled to room temperature, the mixture was saturated with Na_2CO_3 and thoroughly extracted with EtOAc. After evaporation of the organic extract, the residue was chromatographed (10:1 EtOAc–MeOH) to yield **2** as a yellow solid (35 mg, 92%): mp >340 °C; IR (KBr) 1680, 1590, 1360, 1310, 720 cm^{-1}; ^{1}H NMR and ^{13}C NMR spectra, see Table I and supplementary material;

---

(18) See also: Salituro, F. G.; McDonald, I. A. *J. Org. Chem.* 1988, *53*, 6138.

(19) This treatment efficiently removes the Cu(I) from the crude product. If this treatment is omitted, the ^{1}H NMR spectrum of chromatographed **15** showed the H-2 and C-8 methoxyl (δ 4.13) as very broad signals because of the complexation of the quinoline with Cu(I).

MS m/z 283 (M^+, 100), 255 (64); UV-vis (MeOH) λ_{max} (ϵ) 234 (34800), 255 sh (24200), 281 (21000), 300 sh (13200), 313 sh (9400), 375 (7500); high-resolution mass spectrum calcd for $C_{18}H_9N_3O$ m/z 283.0746, found m/z 283.0735.

Acknowledgment. Financial support of this work by the DGICYT (PB87-0201-C-03-02) is gratefully acknowledged. We are also grateful to Dr. J. Kobayashi (Mitsubishi-Kasei Institute of Life Sciences, Tokio) for a sample of ascididemin and copies of the ^1H and ^{13}C NMR spectra and to Dr. M. Paneque (Universidad de Sevilla) for the high-resolution mass spectrum.

Registry No. 2, 133400-90-5; 4, 25368-52-9; 5, 133400-91-6; 6, 133400-92-7; 7, 114552-32-8; 8, 97545-51-2; 9, 133400-93-8; 10, 133400-94-9; 11, 133400-95-0; 12, 133419-80-4; 13, 133400-96-1; 14, 133400-97-2; 15, 133400-98-3; 16, 133400-99-4; 18, 133401-00-0; PhNHBOC, 3422-01-3; $ClSnMe_3$, 1066-45-1; $CH_2{=}CHCHO$, 107-02-8.

Supplementary Material Available: ^1H and ^{13}C NMR, COSY, and NOESY spectra for isoascididemin (2) (4 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Substituted (1,2-Naphthalocyaninato)iron Compounds and Bisaxially Coordinated Isocyanide Complexes

Michael Hanack,*[†] Günter Renz,[†] Joachim Strähle,[‡] and Siegbert Schmid[‡]

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II, Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany, and Institut für Anorganische Chemie, Lehrstuhl für Anorganische Chemie I, Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany

Received June 14, 1990

Tetrasubstituted (1,2-naphthalocyaninato)iron(II) compounds t-Bu_4-1,2-NcFe (**13**), Me_4-1,2-NcFe (**14**), and Ph_4-1,2-NcFe (**15**) are obtained from 7-substituted 1,2-dicyanonaphthalenes **12a–c** either by reaction with pentacarbonyliron in 1-chloronaphthalene (method a) or with iron(II) acetate in 1-hexanol (method b), respectively. Compounds **13–15** were characterized by UV/vis, IR, and Mössbauer spectroscopy, and the oxidation potentials, measured by cyclic voltammetry in pyridine, are compared with the oxidation potentials of 1,2-NcFe and PcFe. The substituted (1,2-naphthalocyaninato)iron compounds **13**, **14**, and **15** react with alkyl and aryl isocyanides R′NC (R′ = t-Bu, c-Hx, Bz, Me_2Ph), yielding the bisaxially coordinated isocyanide complexes of **13**, **14**, and **15**, R_4-1,2-NcFe $(R'NC)_2$. Due to their comparatively high solubility in organic solvents, it is possible to characterize the isocyanide complexes with ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectra of, for example, t-Bu_4-1,2-NcFe$(t\text{-BuNC})_2$ reveal that only one of the structural isomers of the unsymmetrical 1,2-naphthalocyanine macrocycle, namely, the 1,2-naphthalocyanine with C_{4h} symmetry (see Figure 1) is formed, if the synthesis starting with 7-*tert*-butyl-1,2-dicyanonaphthalene (**12a**) is carried out according to method a. The crystal structure of the isomer obtained, t-Bu_4-1,2-Nc$(t\text{-BuNC})_2$, is determined (Figure 4) and confirms these findings. All isocyanide complexes R_4-1,2-NcFe$(R'NC)_2$ are characterized by spectral data and thermoanalyses. The reaction of R_4-1,2-NcFe **13**, **14**, and **15** with diisocyanobenzene (dib) leads to the bridged compounds $[R_4\text{-1,2-NcFe(dib)}]_n$, R = t-Bu, Me, Ph. After being doped with iodine, the bridged complexes exhibit good semiconducting properties.

Introduction

Square-planar transition-metal macrocycles, linked by bidentate organic ligands to form bridged stacked arrangements of the macrocycles, have been investigated by us as semiconducting materials.[1] Thus phthalocyaninato (PcM), tetrabenzoporphyrinato (TBPM), or 2,3-naphthalocyaninato (2,3-NcM) transition-metal complexes can be linked bisaxially by bidentate bridging ligands L [L = pyrazine (pyz), tetrazine (tz), 1,4-diisocyanobenzene (dib), cyanide (CN^-), thiocyanate (SCN^-)] to form linear -PcM-L-PcM-L-, -TBPM-L-TBPM-L-, and -(2,3-Nc)-L-(2,3-Nc)-L- chains (M = Fe, Ru, Co, Rh).[1,2] This type of bridged metal complexes can be chemically and electrochemically doped, resulting in systems with good semiconducting properties.[3] The successful synthesis of, for example, $[PcM(tz)]_n$ (M = Fe, Ru),[2o] $[2,3\text{-NcFe(tz)}]_n$[2d] and $[MacML]_n$ (Mac = Pc, TBP; M = Fe, Co; L = CN^-, SCN^-)[1b,2g,o,4] indicates that even without additional oxidative doping, stable bridged stacked systems with relatively high powder conductivities ($\sigma_{RT} = \sim 10^{-1}$ S/cm) can be obtained.

Bridged 2,3-NcM systems $[2,3\text{-NcML}]_n$ too exhibit, without doping, comparatively high semiconductive properties. For example, $[2,3\text{-NcFe(dib)}]_n$ shows a powder conductivity of $\sigma_{RT} = 3.3 \times 10^{-3}$ S/cm (E_a = 0.13 eV).[2d,4c] On the contrary the comparable $[PcFe(dib)]_n$ with σ_{RT} =

[†] Institut für Organische Chemie.

[‡] Institut für Anorganische Chemie.

(1) (a) Hanack, M.; Datz, A.; Fay, R.; Fischer, K.; Keppeler, U.; Koch, J.; Metz, J.; Mezger, M.; Schneider, O.; Schulze, H.-J. In *Handbook of Conducting Polymers*; Skotheim, T., Ed.; Marcel Dekker: New York, 1986; p 133. (b) Hanack, M.; Deger, S.; Lange, A. *Coord. Chem. Rev.* **1988**, *83*, 115.

(2) (a) Hanack, M. *Chimia* **1983**, *37*, 238. (b) Diel, B. N.; Inabe, T.; Jaggi, N. K.; Lyding, J. W.; Schneider, O.; Hanack, M.; Kannewurf, C. R.; Marks, T. J.; Schwarz, L. H. *J. Am. Chem. Soc.* **1984**, *106*, 3207. (c) Keppeler, U.; Kobel, W.; Siehl, H.-U.; Hanack, M. *Chem. Ber.* **1985**, *118*, 2095. (d) Deger, S.; Hanack, M. *Isr. J. Chem.* **1986**, *27*, 347. (e) Keppeler, U.; Hanack, M. *Chem. Ber.* **1986**, *119*, 3363. (f) Kobel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103. (g) Hedtmann-Rein, C.; Hanack, M.; Peter, K.; Peters, E.-M.; Schnering, H. G. v. *Inorg. Chem.* **1987**, *26*, 2647. (h) Hanack, M.; Renz, G.; Strähle, J.; Schmid, S. *Chem. Ber.* **1988**, *121*, 1479. (i) Hanack, M.; Thies, R. *Chem. Ber.* **1988**, *121*, 1225. (k) Metz, J.; Hanack, M. *Chem. Ber.* **1988**, *121*, 231. (l) Rein, M.; Hanack, M. *Chem. Ber.* **1988**, *121*, 1601. (m) Hanack, M.; Grosshans, R. *Chem. Ber.* **1989**, *122*, 1665. (n) Hanack, M.; Hirsch, A. *Synth. Met.* **1989**, *29*, F9. (o) Hanack, M.; Lange, A.; Rein, M.; Behnisch, R.; Renz, G.; Leverenz, A. *Synth. Met.* **1989**, *29*, F1. (p) Hanack, M.; Vermehren, P. *Synth. Met.* **1989**, *32*, 257. (q) Hanack, M.; Vermehren, P. *Inorg. Chem.* **1990**, *29*, 134.

(3) (a) Keppeler, U.; Schneider, O.; Stöffler, W.; Hanack, M. *Tetrahedron Lett.* **1984**, *25*, 3679. (b) Hedtmann-Rein, C.; Keppeler, U.; Münz, X.; Hanack, M. *Mol. Cryst. Liq. Cryst.* **1985**, *118*, 361. (c) Hanack, M.; Keppeler, U.; Schulze, H.-J. *Synth. Met.* **1987**, *20*, 347. (d) Hanack, M.; Leverenz, A. *Synth. Met.* **1987**, *22*, 9.

(4) (a) Metz, J.; Hanack, M. *J. Am. Chem. Soc.* **1983**, *105*, 828. (b) Hanack, M.; Hedtmann-Rein, C. *Z. Naturforsch., B* **1985**, *40*, 1087. (c) Deger, S.; Hanack, M. *Synth. Met.* **1986**, *13*, 319.

0022-3263/91/1956-3501$02.50/0