Functionalization of Corroles: Formylcorroles

Roberto Paolesse,*[,1a] Laurent Jaquinod, Mathias O. Senge,[1b] and Kevin M. Smith*

Department of Chemistry, University of California, Davis, California 95616

Received April 15, 1997[⊗]

Porphyrins and metalloporphyrins can be readily functionalized at the meso-(5,10,15,20)-positions by using a variety of reagents, the Vilsmeier formylation reaction being universally regarded as the prototypical example. On the other hand, the literature shows that corroles and metallocorroles are unusually resistant to most functionalization procedures which are common to porphyrins. The first example of peripheral functionalization of the corrole ring is now reported. Octamethylcorrole **1** readily reacts with the Vilsmeier reagent ($POCl_3$/DMF), but the product is the 10-dimethylaminomethene derivative **2**, and not the expected meso-formyl derivatives **3** or **4**, as confirmed by a single crystal X-ray crystallographic study. Corrole **5**, where the 10-meso-position is substituted, affords the similar product **6**. When the reaction is extended to corrole **7** two different products, **8** and **9**, are obtained wherein the substitution is performed at both 5- and 10-meso-positions. Unlike the case of porphyrins, no reaction occurs at the β-unsubstituted pyrrolic positions. Coordination of cobalt to the dimethylaminomethenylcorroles **2** and **5** causes both metalation and tautomerization/hydrolysis to afford the originally targeted *meso*-formylcorrolato complexes in almost quantitative yields. Attempts to formylate cobalt complex **14** using TFA/trimethylorthoformate affords the corresponding β-formyl complexes **15** and **16**, the ratio of which depends on the reaction time. *meso*-Formylcorroles are also obtained by way of a new direct synthesis, described herein, using a prefunctionalized *a*,*c*-biladiene **22**.

Introduction

Corrole, the tetrapyrrolic macrocycle exemplified in octamethylcorrole **1**, has demonstrated some properties that make its chemistry intriguing by comparison with the more famous porphyrins. For example, the corrole macrocycle is able to stabilize higher oxidation states for coordinated metals:[2] iron is present in corroles in the +III/+IV states,[3] whereas the +II/+III states are the more common states found in porphyrins.[4] Nickel, copper, and cobalt show similar chemistry: high valent cobalt corrolates with the metal in formal +IV and +V oxidation states have recently been reported,[5] and it was shown that copper corrolates contain the metal in the +III oxidation state, compared with +II in porphyrins.[6] In the nickel corrolate case, the complex is neutral because the corrole exists as the corresponding Ni(II) π-cation radical.[6] Chromium is present in the +V oxidation state in corroles,[2] but strong oxidants are necessary to reach a similar state in porphyrins.[7]

A second interesting property of corroles is the unexpected flexibility of its molecular skeleton, which is able to maintain a planar conformation in the presence of full substitution at the peripheral positions:[8] similar porphyrins suffer severe deviations from planarity,[9,10] showing "saddled" or "ruffled" or even "waved" configurations.[11]

These interesting properties make corroles potentially useful as building blocks for the synthesis of heterodimeric systems consisting of different tetrapyrrole moieties. We have recently described syntheses of such systems (porphyrin−porphyrin, chlorin−chlorin, and chlorin−porphyrin) to enable studies of their application as model systems for the photosynthetic reaction center;[12] corrole moieties were also covalently linked through an aryl bridge to a second tetrapyrrole unit (a corrole or porphyrin). In this context, dimers of tetrapyrroles bearing an ethylene group as a covalent bridge are also interesting models because of the close approach between the macrocycles in the *cis* conformation. During the last few years we have developed a synthetic route to the preparation of these dimers using the McMurry coupling

* Phone: (916) 752-7170. FAX: (916) 752-8995. E-mail: smith@chem.ucdavis.edu.

⊗ Abstract published in *Advance ACS Abstracts*, August 1, 1997.

(1) Permanent address: (a) Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", 00173 Roma, Italy. (b) Institut für Organische Chemie (WE02), Freie Universität, Takustr. 3, D-14195 Berlin, Germany.

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S0022-3263(97)00673-7 CCC: $14.00

reaction.[13,14] This feature led us to explore the possibility of synthesizing similar face-to-face *cis* dimers containing one or more corrole units. An essential requisite for the McMurry coupling reaction is the presence of a formyl or ketone group as a peripheral substituent; such derivatives, however, have never been reported in the case of corroles, the synthetic chemistry of which is much less developed than for the corresponding porphyrins.[2] We therefore initiated a program aimed at the preparation of formylcorroles, both through the functionalization of a preformed corrole macrocycle and through the direct synthesis of a corrole from precursors bearing a formyl group at a peripheral position. In the present paper we report the unusual reactivity of corrole in the Vilsmeier reaction, and a direct synthesis of formylcorroles via prefunctionalized *a*,*c*-biladiene salts.

Results and Discussion

Peripheral functionalization of a corrole ring represents relatively unexplored chemistry. The only reactions reported in the literature concern the alkylation and subsequent rearrangements of both free base and metallocorrolates;[15] attempts to use the Friedel−Crafts reaction on corroles is reported to cause the decomposition of the corrole ring.[16]

The Vilsmeier reaction is the method of choice for the introduction of a formyl group at the meso positions of a porphyrin[17] and it has been widely used for their functionalization.[17b] The reaction is carried out on metal complexes (generally Cu or Ni[18]) which are activated toward the substitution; the metal ion can be easily removed after the reaction in order to obtain the corresponding metal-free derivative. A similar approach is not possible in the case of corrole because metallocorrolates cannot be demetalated under acidic conditions without concomitant decomposition of the macrocycle. In addition, Ni corrolates have recently been reported to be the [Ni(II)(Corrole)$^{+\bullet}$] species, where the corrole ligand is present as the π-cation radical.[6]

We therefore decided to react the metal free corrole directly under Vilsmeier conditions, in the hope that its higher electron density might activate it to the substitution. Octamethylcorrole **1** was therefore reacted with

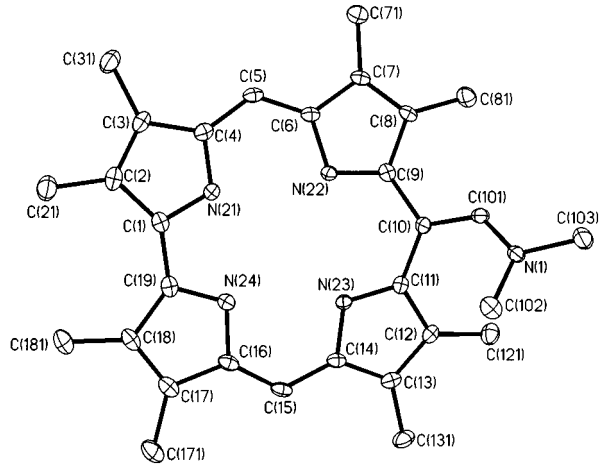
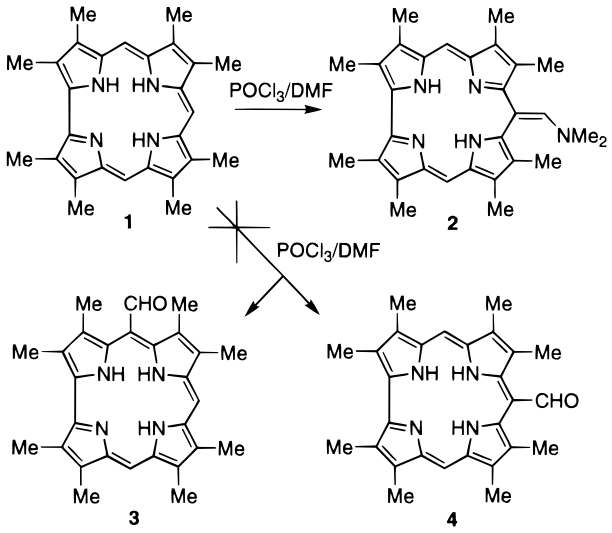


Figure 1. Molecular structure of dimethylaminomethylenecorrole **2**. Hydrogen atoms have been omitted for clarity.

$POCl_3$/DMF in dichloromethane solution at room temperature. The progress of the reaction was followed by



spectrophotometry, the absorbance of the corrole monocation[16b] present in these acidic conditions readily disappeared, with a corresponding increase of a band centered around 500 nm. After 5 min the starting material had completely disappeared, and the mixture was worked up with saturated Na_2CO_3 solution. A single product was obtained as a green powder. The subsequent characterization, however, ruled out the presence of a peripheral formyl group in the product; in the ^{1}H NMR spectrum, no resonances were observed in the δ 9−11 region. More surprisingly, the chemical shifts of the resonances of both the meso-protons and the β-methyl groups seemed to indicate the absence of any diamagnetic ring current effects. This feature was confirmed by the visible spectrum, wherein the typical corrole Soret-like band was substituted by an absorption around 450 nm. The evidence indicated that the substituent introduced on the corrole macroring had interrupted the conjugation pathway. A single crystal X-ray analysis allowed the identification of this product as the 10-dimethylaminomethene derivative **2**; its molecular structure is shown in Figure 1. It is interesting to note that structural characteristics further confirm the interruption of the π-aromatic system; the 23 atoms of the corrole core are not planar, but suffer severe deviations with respect to

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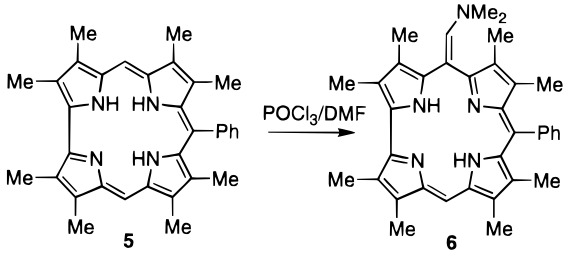
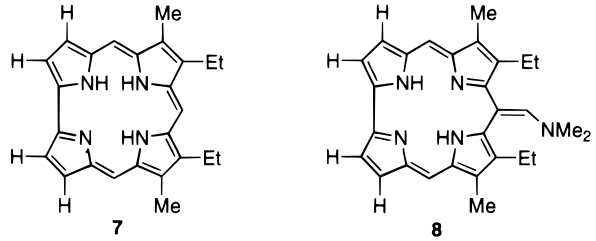
the plane identified by the four inner nitrogen atoms. The 10-meso-substituent is also tilted out of this plane, the deviation of the C(101) atom being 0.89 Å because of the steric interactions with the peripheral methyl groups.

A hypothetical reaction pathway leading to the formation of **2** is reported in Scheme 1. The first attack of the Vilsmeier reagent complex on the corrole monocation, the species present under the reaction conditions (spectrophotometry), leads to a species in which the conjugation pathway is interrupted. The band observed at 500 nm is an indicator for the formation of such an intermediate since it can be considered as two condensed dipyrromethene units.[18] The subsequent elimination of HCl under basic conditions leads to the final product. The corrole is able to act also as a dianionic ligand and in this way it can stabilize this structure.

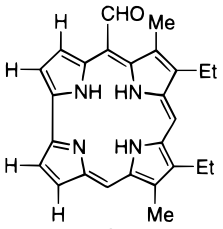
This unusual result led us to study this reaction in deeper detail. In the case of meso-unsubstituted corroles, the reactive point is the 10-position, and we did not obtain any isomers from reaction at the 5- or 15-positions. Corrole **5**, bearing a phenyl at the 10-position, was then subjected to the Vilsmeier reaction. This corrole likewise reacted readily and after purification compound **6** was obtained in good yield by a mechanism similar to that shown in Scheme 1.



5 **6**



7 **8**



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The preference for reaction at the 10-position (in 10-unsubstituted substrates) can be probably ascribed to both electronic and steric effects; the 10-position has been calculated to possess the greatest charge density;[19] steric crowding of the inner hydrogen atoms causes a deviation from planarity of ring D, with concomitant decrease in the π-character of the 5- and 15-positions.[20]

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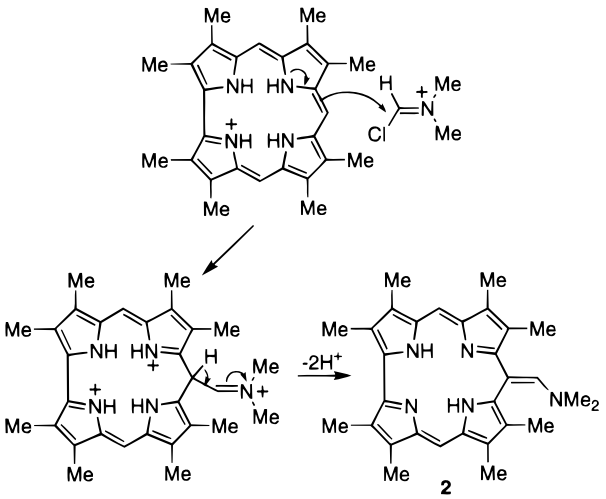
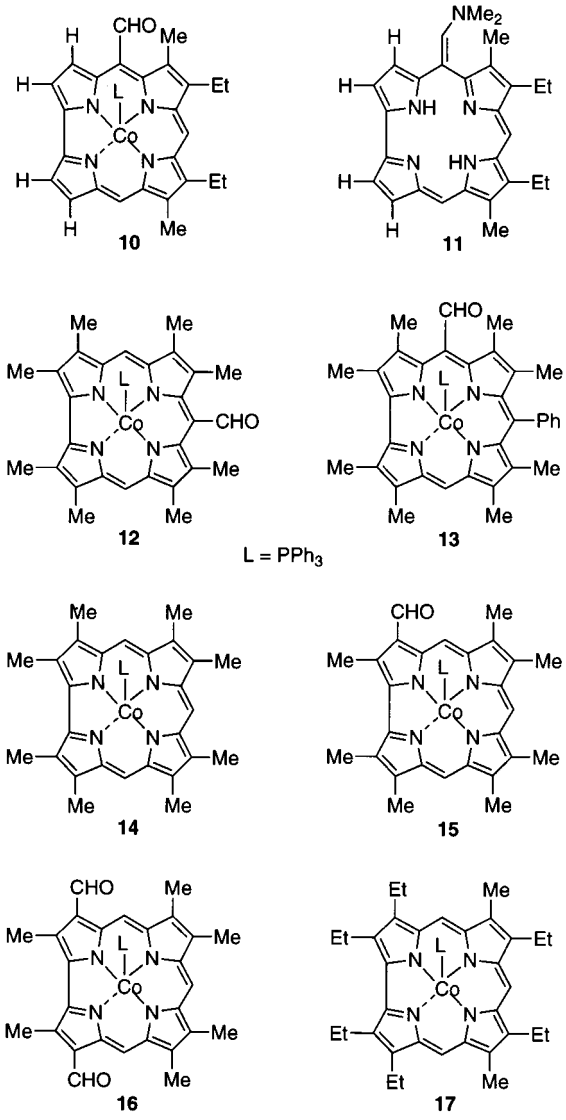
Scheme 1



2

A different result was obtained when **7** was reacted under similar conditions. This corrole was used in order to ascertain the regioselectivity of the reaction when both meso- and β-positions are unsubstituted. Two products were obtained; the first was the expected meso-substituted compound **8** (similar to **2**). The second product **9**, obtained in slightly higher yield, retained the Soret-like absorption band in the electronic spectrum, thereby indicating full conjugation of the macrocycle. Moreover, the FAB mass spectrum had a molecular ion peak at *m*/*z* 410, corresponding to a formyl derivative of **7**. In fact, in the ^{1}H NMR spectrum, a resonance at δ 11.71 was present, and this could be attributed to a peripheral formyl substituent. Because a superimposition of the resonances of both β and meso-hydrogens did not allow an easy interpretation regarding the position substituted, we synthesized the cobalt complex of **9**, as the triphenylphosphine derivative **10**. In this case two sets of resonances attributable to the β-pyrrolic protons were present in the ^{1}H NMR spectrum, thereby excluding the possibility that the reaction took place at the β-pyrrolic positions. In addition, the signals due to the meso-protons were present as two singlets of equal intensity, indicating that the macrocycle was no longer symmetrical. These characteristics seem to indicate that the substitution occurred, in this case, at the 5-position (or the equivalent 15-position), probably because the vicinally unsubstituted rings A and D make this position favorable for the reaction. The intermediate **11**, in this case, is not stable and hydrolyzes during the purification procedures, to give **9**.

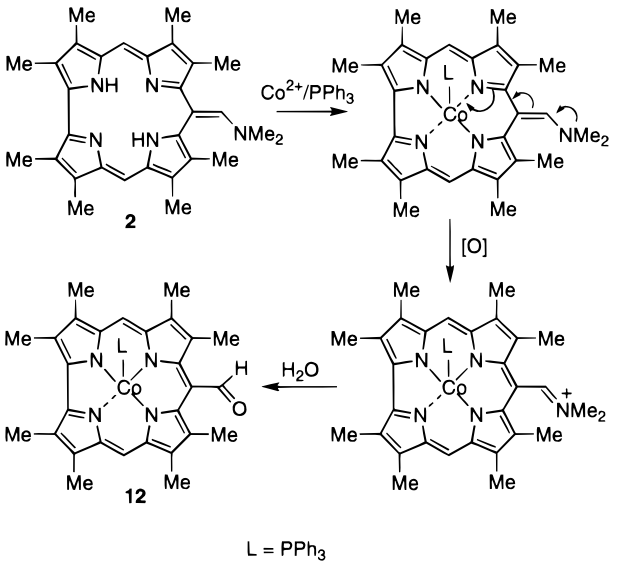
We considered it worthwhile to study the coordination properties of **2**. The first metal tested was zinc, the macrocycle being formally a dianionic ligand. The optical spectrum in solution indicated coordination of the metal, but attempts to isolate this zinc complex failed; purification procedures led to decomposition to the starting material. The metalation reaction carried out with cobalt(II) acetate and triphenylphosphine was completely different; in this case the color of the solution turned to red and visible absorption spectrum of the reaction mixture was similar to that of a normal cobalt corrolate.[2] Purification afforded **12**, and this compound was most likely obtained through the reaction pathway proposed in Scheme 2. The coordination of a trivalent metal ion drives the macrocycle to recover its aromatic conjugation by participation of the dimethylamino group. Subsequent



hydrolysis of the iminium salt leads to the final *meso*-formylcorrole complex. The same result was obtained when **6** was reacted under these conditions, and the corresponding complex **13** was obtained; to our knowledge, this is the first example of a corrole derivative functionalized with two different groups at the meso-positions.

The failure of the Vilsmeier reaction to give *directly* the corresponding formyl derivative led us to explore the possibility of using different reactions for formylation. The use of orthoformate esters in TFA is an alternative approach for the formylation of pyrroles, so we decided to use these reagents with corroles. The corrole free base was not reactive under these conditions; in TFA the corrole is present as a mixture of mono- and dications and this is probably the reason for inhibition of the reaction. The cobalt complex **14** of the corrole was next used because of its stability in TFA; in this case we noted a slow reaction (spectrophotometry) and after 24 h we obtained a mixture of two products, together with some starting material. These products, however, were not the expected meso-functionalized corroles, but instead the complexes **15** and **16** in which the formyl groups are present at the 3- and 3,17-positions. Complex **16** has been previously synthesized by oxidation of **14** with DDQ.[21] The presence of a methyl group in the 3- and 17-positions is essential for the reaction. If **17** is used

Scheme 2



under the same conditions, no reaction occurs and the complex slowly decomposes in TFA.

Because formylation of the preformed corrole was not successful, we decided to develop a rational route in which a formyl group would be inserted in a synthetic precursor of the macrocycle. The method of choice for synthesis of corroles is via the cyclization of a 1,19-diunsubstituted *a*,*c*-biladiene.[2] Such open-chain tetrapyrroles are prepared by acidic condensation of a dipyrromethane dicarboxylic acid with 2 equiv of a 2-formylpyrrole;[2] our previous success in the synthesis of meso-substituted *a*,*c*-biladienes through functionalized dipyrromethanes[12,22] led us to explore the synthetic route outlined in Scheme 3. The first step was the formation of the functionalized dipyrromethane **18**, which was obtained by condensation of the pyrrole **19** with dichloromethylacetaldehyde diethyl acetal, using Montmorillonite K10 clay as condensing agent.[23] The dichloromethyl group is a potential precursor of the aldehyde function; subsequent hydrogenation (to give **20**) and acidic condensation with 2-formylpyrrole **21** afforded the corresponding *a*,*c*-biladiene **22** in good overall yield. Cyclization of **22** in methanol with cobalt(II) acetate and triphenylphosphine afforded the corresponding complex **23** in good yield. The spectral characteristics of this complex are in good agreement with those observed for the similar complex **12**, obtained from the previously reported reaction of the Vilsmeier product. Following this route we were also able to synthesize the manganese complexes **24**, in order to use these compounds in the McMurry coupling reaction, but attempts to obtain dimers via low-valent titanium coupling failed; compound **23** decomposed under the reaction conditions, and **24** afforded the corresponding meso-unsubstituted corrole complex. However, our studies show that corrole chemistry can be manipulated to afford novel results, and though their chemistry is not as predictable as that of porphyrins systems, new reactivity will almost certainly be identified.

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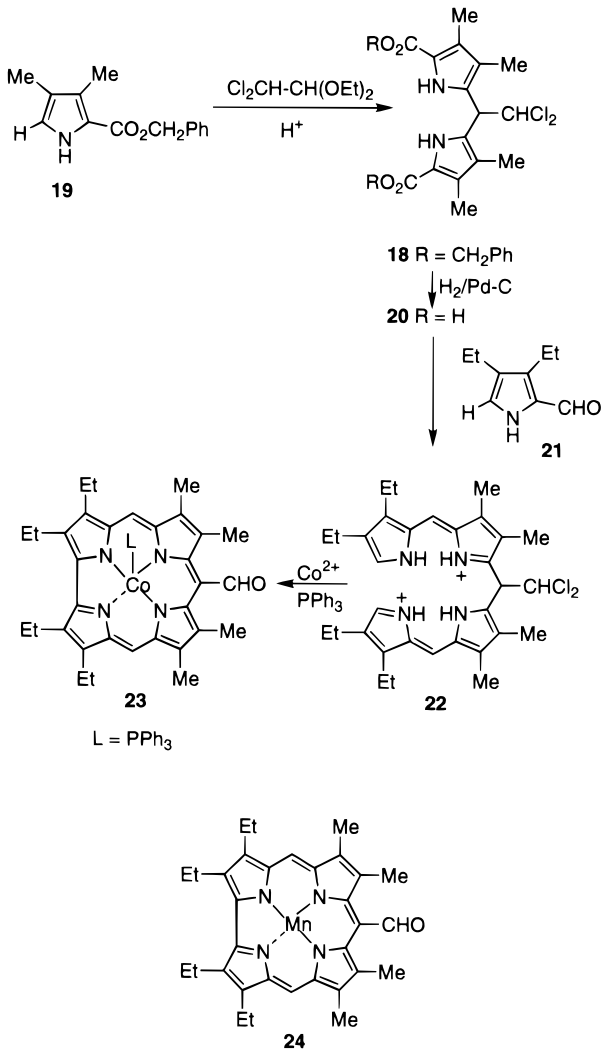
Scheme 3



Experimental Section

General experimental conditions were as reported in an earlier paper,[24] except that ^{1}H NMR spectra were measured in $CDCl_3$ solution either at 300 MHz or at 400 MHz, mass spectra were obtained in Rome (FAB) or at the University of California, San Francisco, Mass Spectrometry Resource, and electronic absorption spectra were measured in dichloromethane.

2,3,7,8,12,13,17,18-Octamethyl-10-dimethylaminomethenylcorrole (2). Vilsmeier reagent [prepared from freshly distilled $POCl_3$ (0.6 mL) and DMF (1 mL) at 0 °C] was added dropwise to a CH_2Cl_2 solution of 2,3,7,8,12,13,17,18-octamethylcorrole (**1**) (200 mg, 0.49 mmol). The solution turned green and after 5 min spectrophotometry showed no more starting material to be present. A saturated solution of sodium carbonate (100 mL) was then added and the mixture was stirred overnight. The organic phase was separated, washed with brine, and then dried over anhydrous sodium sulfate. The crude mixture was chromatographed on alumina (Brockmann Grade III, elution with CH_2Cl_2); the green fraction was collected. Crystallization from $CHCl_3$/hexane afforded **2** as green crystals (190 mg, 83%), mp >250 °C. UV−vis: λ_{max} 456 nm (ϵ 53 300), 552 (8200), 592 (10 100). ^{1}H NMR: δ 8.78 (br s, 2 H), 8.25 (s, 1 H), 7.73 (s, 2 H), 2.77 (s, 6 H), 2.62 (s, 6 H), 2.60 (s, 12 H), 2.51 (s, 6 H). LRMS (FAB): *m*/*z* 466 (M^+). Anal. Calcd for $C_{30}H_{35}N_5$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.05; H, 7.21; N, 15.31.

2,3,7,8,12,13,17,18-Octamethyl-10-phenylcorrole (5). 2,3,7,8,12,13,17,18-Octamethyl-10-phenyl-*a*,*c*-biladiene dihydrobromide[22] (0.5 g, 0.77 mmol) and an excess of $NaHCO_3$ were suspended in ethanol. Chloranil (190 mg, 0.77 mol) was added and the mixture was stirred at room temperature for 5 min. Next, 1 mL of 15% N_2H_4 solution in water was added, the solvent was evaporated under vacuum, and the residue was chromatographed on neutral alumina (Brockmann Grade III, elution with CH_2Cl_2). A red-violet fraction was collected and crystallized from CH_2Cl_2/CH_3OH to afford **5** as violet crystals (116 mg, 31%), mp >250 °C. UV−vis: λ_{max} 401 nm (ϵ 115 000), 545 (13 200), 598 (15 100). ^{1}H NMR: δ 9.35 (s, 2 H), 7.94−7.61 (m, 5 H), 3.55 (s, 6 H), 3.40 (s, 12 H), 2.35 (s, 6 H), −2.50 (br s, 3 H). LRMS (FAB): *m*/*z* 487 (M^+). Anal. Calcd for $C_{33}H_{34}N_4$: C, 81.45; H, 7.04; N, 11.51. Found: C, 81.23; H, 6.92; N, 11.32.

2,3,7,8,12,13,17,18-Octamethyl-10-phenyl-5-dimethylaminomethenylcorrole (6). The reaction was carried out as reported for **2**, starting from corrole **5** (100 mg, 0.20 mmol). Chromatographic separation (neutral alumina) and crystallization from CH_2Cl_2/hexane afforded **6** as green crystals (87 mg, 80%), mp >250 °C. UV−vis: λ_{max} 349 nm (ϵ 32 000), 420 (43 500), 625 (22 000). ^{1}H NMR: δ 8.35 (br s, 2 H), 8.05 (s, 1 H), 7.64−7.20 (m, 7 H), 3.18 (s, 6 H), 2.79, 2.72, 2.60, 2.55, 2.49, 2.33, 1.58, 1.42 (each s, 24 H). LRMS (FAB): *m*/*z* 542 (M^+). Anal. Calcd for $C_{36}H_{39}N_5$: C, 79.82; H, 7.26; N, 12.93. Found: C, 80.05; H, 7.15; N, 12.72.

7,13-Dimethyl-8,12-diethylcorrole (7). This corrole was prepared starting from 7,13-dimethyl-8,12-diethyl-*a*,*c*-biladiene dihydrobromide (1.5 g, 2.75 mmol) as reported for **5**. Corrole **7** was crystallized from CH_2Cl_2/hexane to afford dark red crystals (642 mg, 61%), mp 204−206 °C. UV−vis: λ_{max} 403 nm (ϵ 126 000), 543 (15 600), 566 (19 500), 587 (23 000). ^{1}H NMR: δ 9.28 (s, 2 H), 9.01 (s, 1 H), 8.78 (d, 2 H), 8.62 (d, 2 H), 3.79 (q, 4 H), 3.37 (s, 6 H), 1.70 (t, 6 H), −2.52 (br s, 3 H). LRMS (FAB): *m*/*z* 383 (M^+). Anal. Calcd for $C_{25}H_{26}N_4$: C, 78.50; H, 6.85; N, 14.65. Found: C, 78.16; H, 6.69; N, 14.51.

Vilsmeier Reaction of 7. This reaction was carried out as reported above, starting from **7** (100 mg, 0.26 mmol). The crude mixture was chromatographed (alumina, elution with CH_2Cl_2) to afford a green fraction; recrystallization from CH_2Cl_2/hexane afforded **8** as green crystals (36 mg, 32%), mp >250 °C. UV−vis: λ_{max} 461 nm (ϵ 52 000), 581 (8000). ^{1}H NMR: δ 9.52 (br s, 2 H), 8.22 (s, 1 H), 7.80 (s, 2 H), 7.53 (d, 2 H), 7.41 (d, 2 H), 3.02 (m, 2 H), 2.88 (m, 2 H), 2.59 (s, 6 H), 1.19 (t, 6 H). LRMS (FAB): *m*/*z* 438 (M^+). Anal. Calcd for $C_{28}H_{31}N_5$: C, 76.86; H, 7.14; N, 16.00. Found: C, 76.61; H, 6.99; N, 15.71. Elution with CH_2Cl_2/CH_3OH (95:5) afforded a second green band: crystallization from CH_2Cl_2/hexane afforded **9** as green microcrystals (47 mg, 44%), mp >250 °C. UV−vis: λ_{max} 414 nm (ϵ 92 000), 581 (23 000), 644 (18 000). ^{1}H NMR: δ 11.78 (s, 1 H), 8.99, 8.92, 8.88 (each s, 3 H), 8.59 (s, 3 H), 3.72−3.64 (m, 4 H), 3.30 (s, 3 H), 3.16 (s, 3 H), 1.63 (t, 6 H), −2.59 (s, 3 H). LRMS (FAB): *m*/*z* 410 (M^+). Anal. Calcd for $C_{26}H_{26}N_4O$: C, 76.07; H, 6.38; N, 13.65. Found: C, 76.33; H, 6.17; N, 13.39.

(Triphenylphosphine)(7,13-dimethyl-8,12-diethyl-5-formylcorrolato)cobalt(III) (10). Corrole **9** (25 mg, 0.06 mmol), Co(II) acetate (50 mg), and triphenylphosphine (50 mg) were dissolved in methanol and the solution was refluxed for 1 h. At the end of this time the solvent was evaporated under vacuum and the residue was chromatographed on basic alumina (type T) to give the corresponding complex **10** (32 mg, 73%), mp >250 °C. UV−vis: λ_{max} 382 nm (ϵ 68 000), 569 (13 300). ^{1}H NMR: δ 11.72 (s, 1 H), 9.60, 9.43 (each s, 2 H), 9.03, 8.89, 8.59, 8.42 (each d, 4 H), 6.98 (m, 3 H), 6.62 (m, 6 H), 4.69 (m, 6 H), 3.70 (q, 4 H), 3.28 (s, 6 H), 1.63 (t, 6 H). LRMS (FAB): *m*/*z* 729 (M^+), 466 ($M^+ - PPh_3$). Anal. Calcd for $C_{44}H_{38}CoN_4OP$: C, 72.52; H, 5.26; N, 7.69. Found: C, 72.34; H, 5.37; N, 7.56.

(Triphenylphosphine)(2,3,7,8,12,13,17,18-octamethyl-10-formylcorrolato)cobalt(III) (12). The title compound was prepared starting from **2** (50 mg, 0.11 mmol) as reported for **10**. Complex **12** was obtained as red crystals from CH_2Cl_2/hexane (63 mg, 76%), mp >250 °C. UV−vis: λ_{max} 382 nm (ϵ 68 200), 576 (13 800). ^{1}H NMR: δ 11.75 (s, 1 H), 9.00 (s, 2 H), 6.97 (m, 3 H), 6.61 (m, 6 H), 4.58 (m, 6 H), 3.22 (s, 6 H), 3.01 (s, 18 H). LRMS (FAB): *m*/*z* 757 (M^+), 494 ($M^+ - PPh_3$).

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Anal. Calcd for $C_{46}H_{42}CoN_4OP$: C, 73.01; H, 5.59; N, 7.40. Found: C, 72.94; H, 5.41; N, 7.52.

(Triphenylphosphine)(2,3,7,8,12,13,17,18-octamethyl-5-formyl-10-phenylcorrolato)cobalt(III) (13). This complex was obtained as reported above in 68% yield, mp >250 °C. UV−vis: λ_{max} 377 nm (ϵ 72 000), 596 (11 300). ^{1}H NMR: δ 11.60 (s, 1 H), 9.01 (s, 1 H), 7.78−7.46 (m, 5 H), 6.99 (m, 3 H), 6.70 (m, 6 H), 4.98 (m, 6 H), 3.21, 3.19, 3.05 (each s, 18 H), 2.21 (s, 6 H). LRMS (FAB): *m*/*z* 836 (M^+), 574 ($M^+ - PPh_3$). Anal. Calcd for $C_{52}H_{49}CoN_4OP$: C, 74.72; H, 5.91; N, 6.70. Found: C, 74.61; H, 5.92; N, 6.62.

(Triphenylphosphine)(2,7,8,12,13,17,18-heptamethyl-3-formylcorrolato)cobalt(III) (15) and Triphenylphosphine(2,7,8,12,13,18-hexamethyl-3,17-diformylcorrolato)cobalt(III) (16). (Triphenylphosphine)(2,3,7,8,12,13,17,18-octamethylcorrolato)cobalt(III) **14** (100 mg, 0.14 mmol) was dissolved in TFA (2 mL) and trimethyl orthoformate (2 mL). The mixture was stirred for 5 h, then CH_2Cl_2 (100 mL) was added, and the solution was treated with saturated $NaHCO_3$ (2×) and brine. The organic phase was separated, dried over anhydrous sodium sulfate, and then chromatographed on neutral alumina (Brockmann Grade V, elution with CH_2Cl_2). A green band was first collected and crystallized from CH_2Cl_2/hexane to afford **15** (31 mg, 30%), mp >250 °C. UV−vis: λ_{max} 372 nm (ϵ 29 000), 546 (12 000), 614 (15 000). ^{1}H NMR: δ 10.70 (s, 1 H), 9.81 (s, 1 H), 9.18 (s, 1 H), 8.93 (s, 1 H), 6.93 (m, 3 H), 6.56 (m, 6 H), 4.63 (m, 6 H), 3.44 (s, 3 H), 3.11 (s, 6 H), 3.07 (s, 6 H), 3.05 (s, 3 H), 3.02 (s, 3 H). LRMS (FAB): *m*/*z* 743 (M^+), 480 ($M^+ - PPh_3$). Anal. Calcd for $C_{45}H_{40}CoN_4OP$: C, 72.77; H, 5.43; N, 7.54. Found: C, 72.53; H, 5.52; N, 7.41. A second blue-green fraction was then eluted and crystallized from CH_2Cl_2/hexane to afford **16** (46 mg, 43%), mp >250 °C. UV−vis: λ_{max} 370 nm (ϵ 32 000), 550 (13 100), 596 (13 900), 625 (27 000). ^{1}H NMR: δ 10.49 (s, 2 H), 9.27 (s, 2 H), 8.71 (s, 1 H), 6.82 (m, 3 H), 6.40 (m, 6 H), 4.40 (m, 6 H), 3.00 (s, 6 H), 2.87 (s, 12 H). LRMS (FAB): *m*/*z* 757 (M^+), 494 ($M^+ - PPh_3$). Anal. Calcd for $C_{45}H_{38}CoN_4O_2P$: C, 71.43; H, 5.06; N, 7.40. Found: C, 71.45; H, 5.10; N, 7.44.

Dibenzyl 2,3,7,8-Tetramethyl-5-(dichloromethyl)dipyrromethane-1,9-dicarboxylate (18). Benzyl 3,4-dimethylpyrrole-2-carboxylate (**19**)[25] (3.00 g, 13.1 mmol) and dichloroacetaldehyde diethyl acetal (0.9 mL, 7.3 mmol) were dissolved in dry CH_2Cl_2 (100 mL) and Montmorillonite K10 clay (35 g) was slowly added. TFA (10 mL) was then carefully added and the mixture was stirred for 3 days under nitrogen in the dark. The reaction mixture was filtered and the red solution was washed (2×) with a saturated solution of $NaHCO_3$. The organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum, and n-hexane was added to precipitate **18** (2.76 g, 76% yield), mp 190−192 °C. ^{1}H NMR: δ 9.71 (s, 2 H), 7.17 (m, 10 H), 6.44 (d, 1 H), 5.14 (s, 4 H), 4.81 (d, 1 H), 2.14 (s, 6 H), 1.93 (s, 6 H). LRMS (FAB): *m*/*z* 553.5 (M^+). Anal. Calcd for $C_{30}H_{30}Cl_2N_2O_4$: C, 65.10; H, 5.46; N, 5.06. Found: C, 65.03; H, 5.19; N, 5.16.

2,3,17,18-Tetraethyl-7,8,12,13-tetramethyl-10-dichloromethyl-*a*,*c*-biladiene Dihydrobromide (22). Dipyrromethane **18** was hydrogenated at room temperature and at atmospheric pressure in THF, using 10% Pd−C as catalyst, to quantitatively afford the corresponding dicarboxylic acid **20** as a pale pink powder. The diacid (1.00 g, 2.28 mmol) was dissolved in TFA (6 mL) and stirred for 5 min. Then a solution of 2-formylpyrrole **21** (840 mg, 5.56 mmol) in MeOH (10 mL) was added and the red solution was stirred for 15 min before addition of 30% HBr in acetic acid (5 mL). After dropwise addition of diethyl ether (50 mL) the title *a*,*c*-biladiene salt precipitated as a dark red powder (1.2 g, 74%), mp >300 °C. UV−vis: λ_{max} 452 nm (ϵ 137 000), 532 (71 500). ^{1}H NMR: δ 13.34 (s, 2 H), 12.57 (s, 2 H), 8.08 (s, 1 H), 7.87 (d, 1 H), 7.73 (s, 1 H), 7.36 (d, 1 H), 2.72 (q, 8 H), 2.30 (s, 6 H), 2.14 (s, 6 H), 1.91 (t, 12 H). Anal. Calcd for $C_{32}H_{42}Br_2Cl_2N_4$: C, 53.87; H, 5.93; N, 7.85. Found: C, 53.82; H, 6.01; N, 7.71.

(Triphenylphosphine)[2,3,17,18-tetraethyl-7,8,12,13-tetramethyl-10-formylcorrolato]cobalt(III) (23). *a*,*c*-Biladiene dihydrobromide **22** (200 mg, 0.28 mmol) was added to a solution of cobalt(II) acetate (200 mg), sodium acetate (500 mg), and triphenylphosphine (200 mg) in boiling MeOH. The mixture was refluxed for 2 h, then the solution was cooled to room temperature, and the solvent was evaporated under vacuum. The solid was dissolved in CH_2Cl_2 and chromatographed on neutral alumina (Brockmann Grade III, elution with CH_2Cl_2); the first red band afforded the title compound which was crystallized from CH_2Cl_2/MeOH to give dark red crystals (157 mg, 69%), mp >250 °C. UV−vis: λ_{max} 383 nm (ϵ 67 400), 578 (15 700). ^{1}H NMR: δ 11.63 (s, 1 H), 9.01 (s, 2 H), 6.95 (m, 3 H), 6.65 (m, 6 H), 4.93 (m, 6 H), 3.62 (m, 8 H), 3.01, 2.96 (each s, 12 H), 1.57 (t, 12 H). LRMS (FAB): *m*/*z* 814 (M^+), 552 ($M^+ - PPh_3$). Anal. Calcd for $C_{50}H_{51}CoN_4OP$: C, 73.79; H, 6.32; N, 6.88. Found: C, 73.67; H, 6.18; N, 6.93.

[2,3,17,18-Tetraethyl-7,8,12,13-tetramethyl-10-formylcorrolato]manganese(III) (24). *a*,*c*-Biladiene dihydrobromide **22** (200 mg, 0.28 mmol) was added to a solution of manganese(II) acetate (200 mg) and sodium acetate (500 mg) in boiling MeOH. The mixture was refluxed for 2 h, then the solution was cooled to room temperature, and the solvent was evaporated under vacuum. The solid was dissolved in THF and chromatographed on basic alumina (type T), using THF/diethyl ether (1:1) as eluant; the green band afforded the title compound which was crystallized from THF/hexane to give red-green crystals (90 mg, 59%), mp >250 °C. UV−vis: λ_{max} 410 nm (ϵ 63 400), 490 (36 000), 577 (16 500). LRMS (FAB): *m*/*z* 548 (M^+). Anal. Calcd for $C_{32}H_{36}MnN_4O$: C, 70.19; H, 6.63; N, 10.23. Found: C, 70.36; H, 6.49; N, 10.11.

Crystal Structure Determination[26] of 2. Crystals were grown from $CHCl_3$/hexane. Crystal data for $C_{30}H_{35}N_5 \cdot CHCl_3$ at 128 K (Cu Kα radiation, λ = 1.541 78 Å, θ_{max} = 56.21°), triclinic, space group *P* 1, *a* = 8.803(3), *b* = 10.207(3), *c* = 17.173(6) Å, α = 84.80(2)°, β = 80.16(2)°, γ = 71.44(2)°, *V* = 1440.2(8) Å^3. *Z* = 2, refinement against $|F^2|$, 3778 independent reflections collected, 352 parameters, 3523 reflections with $I > 2\sigma(I)$, *R*1 (all data) = 0.0690, *wR*2 (all data) = 0.1749, *R*1 [$I > 2\sigma(I)$] = 0.0658, *wR*2 [$I > 2\sigma(I)$] = 0.1718, *S* = 1.067.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-96 23117), the National Institutes of Health (HL-22252), CNR (Italy/USA Bilateral Project No. 95.01178), the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft.

JO9706739

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(26) The authors have deposited atomic coordinates and a full structure description for **2** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.