Recent Advances in the Synthesis of Corroles and Core-Modified Corroles

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The aim of this review is to highlight recent progress in the synthetic methodologies leading to corroles and core-modified corroles. Emphasis is put on corroles with *meso* substituents.

1. Introduction

Corroles[1] are aromatic tetrapyrrole macrocycles bearing a direct pyrrole−pyrrole link, thereby constituting a bridge between porphyrins and corrins (Figure 1). The lack of a *meso*-carbon atom C-20 leads to a smaller cavity than in the case of porphyrins and also to a reduced symmetry, from D_{4h} in the case of the unsubstituted porphyrin to C_{2v} for the corrole (assuming N−H tautomerism is fast).

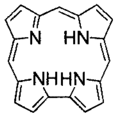

Figure 1. Corrole core

X-ray structural analysis shows the peripheral bonds of corrole[2] to be intermediate in length between those of typical C−C single and double bonds. Corroles differ from porphyrins in that they possess three central "pyrrole-type" nitrogen atoms and one "pyridine-type" nitrogen atom, whereas porphyrins contain two of each type. This difference has important effects on the chemistry of corroles. Corroles are stronger acids than porphyrins, but weaker bases.[3,4] UV/Vis spectroscopy of corroles confirms their aromaticity with an intense Soret band and weaker Q bands (500−600 nm). However, while the typical absorption spectrum of a porphyrin consists of bands at 419, 515, 548, and 591 nm, the typical absorption spectrum of a corrole has bands at 421, 578, 614, and 649 nm. Additionally, it was observed that the Soret band of corroles possessing at least two mesityl substituents in *meso* positions has a characteristic splitting (typically 410 and 430 nm).[5] The corroles show an intense luminescence band around 600 nm, with a lifetime in the nanosecond region and a very small Stokes shift.[6] They also form stable aromatic anions and mono- and dications.[3] The addition of a third proton causes the disappearance of the Soret band from the electronic spectrum, indicating *meso* protonation.[3]

The chemistry of corroles had its genesis with the work of Johnson and Kay in 1965.[4] Since that time corroles have been overshadowed by the easy accessibility of their porphyrin counterparts. This situation is now undergoing a highly significant change due to the breakthrough discover-

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

ies of their simple syntheses made by Gross et al.[7,8] and by Paolesse and co-workers in 1999.[9] While all previous approaches were quite lengthy and required elaborate preparation of precursors, both the Gross and Paolesse methods are one-pot procedures employing commercially available reagents. Furthermore, the unexpected observation by Vogel et al.[10] that these trianionic ligands stabilize the unusually high oxidation states of metal ions, has recently provided another important impetus to corrole chemistry. Both discoveries have generated increasing interest in this contracted macrocycle in the last few years, judging by the number of papers and the number of research groups dealing with corroles.

With regards to chelation, these properties of corroles have a dramatic effect on the formation of metallocorroles. The number of different metal ions that have been inserted into the corrole cavity is smaller than for porphyrins. Indeed, only a few binding arrangements have been achieved up to date. Simple and efficient synthetic methods have already opened a new avenue for in-depth studies of the coordination chemistry of corroles. A number of complexes of *meso*- as well as β-substituted corroles with Fe^{III},[11,12] Fe^{IV},[12−15] Co^{III},[13,16−18] Mn^{III},[19,20] Mn^{IV},[21,14] Mn^{V},[19,21] Cr^{V},[22−24] Ru^{III},[25] Rh^{III},[13,12] As^{III} and As^{V},[26] Sb^{III} and Sb^{IV},[26] Bi^{III} and Bi^{IV},[26] Ge^{IV},[12] Sn^{IV},[12] and P^{V} [12,27] were described within a short period of time.[24,28]

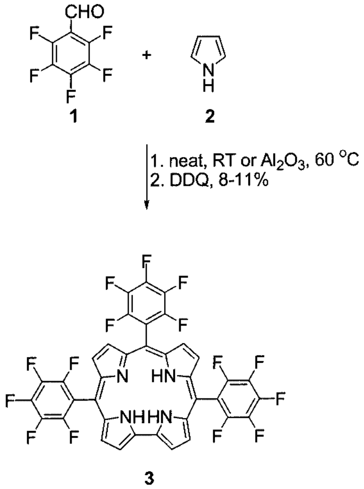
Stabilization of exceptionally high metal oxidation states is relevant to catalysis by heme enzymes and synthetic (porphyrin)iron in which Fe^{IV} complexes are key intermediates. The Gross group has examined iron, manganese, and rhodium complexes as catalysts for epoxidation,[19,21,29] cyclopropanation,[12,29] hydroxylation,[29] and aziridination[15] with very encouraging results. A gallium complex was investigated as a candidate for molecular magnets.[30] Studies on applications of metal complexes of corroles have been complemented by EPR measurements[12,20−23,31] and theoretical studies of their electronic structure.[32−34] The affinity of some corroles for cancer cells has also been investigated.[35]

The time therefore seems appropriate to review the recent contributions in synthetic corrole chemistry. The area prior to 1999 has been widely reviewed[1] and a commentary about metal complexes of triarylcorroles has also recently been published.[24] Historical and synthetic aspects to that date are well covered, so this review will focus on synthetic corrole chemistry over the last three years. The striking synthetic advances lead to the view that examination of many novel aspects of the coordination chemistry of (corrole)metal complexes will quickly become more accessible, especially with respect to high metal oxidation states. This will eventually lead to a much better understanding of the puzzling situation where an easily oxidized ligand stabilizes metal ions in high oxidation states. The structural characterization of metal complexes and their application as catalysts, interpretations of experimental data regarding oxidation state and development of synthetic methodology leading to more sophisticated corroles are the most probable directions of this field.

2. *meso*-Substituted A_3-Corroles

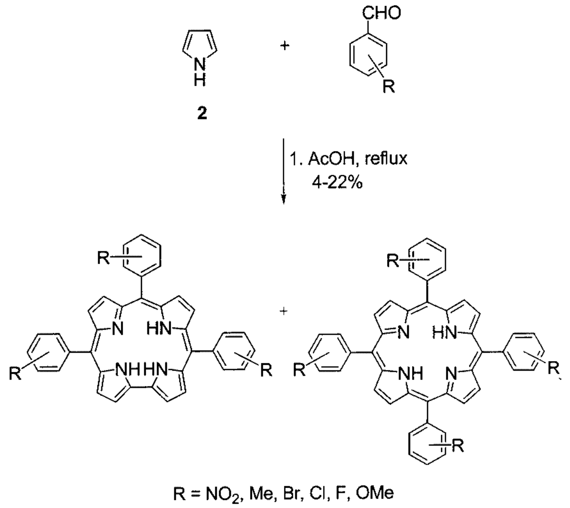
For many years *meso*-substituted porphyrins with four identical substituents were the most accessible and hence the most often used porphyrinoids in physicochemical studies as well as coordination studies. It is not surprising then, that *meso*-substituted corroles with three identical substituents were desired compounds for comparative studies. Additionally, since the observation that β-substituted corroles stabilize high oxidation states of transition metal centers, it was envisioned that their complexes can serve as catalysts for some interesting reactions. In agreement with the nomenclature employed for *meso*-substituted porphyrins, I propose to call such corroles A_3-corroles.

The pioneering studies by Gross et al. have demonstrated that pentafluorobenzaldehyde (**1**) reacts with pyrrole (**2**) under neat conditions without any catalyst. Oxidation of the resulting mixture with DDQ gives tris(pentafluorophenyl)corrole (**3**) in 8−11% yield (Scheme 1).[7,8] The same reaction occurs when the mixture of both reactants, supported on alumina is heated and then oxidized with DDQ. No porphyrins are formed under these conditions. The first corrole synthesis to start with commercially available reactants works also for 2,6-difluoro- and 2,6-dichlorobenzaldehydes and for heptafluorobutanal.[36] According to the authors, attempts to carry out this process with less reactive aldehydes led to the formation of porphyrins, albeit in low yield. However, Ghosh et al.[14] reported that they succeeded in the preparation of corrole from *p*-tolualdehyde under Gross conditions, but without providing reaction conditions, yields, and physical data.

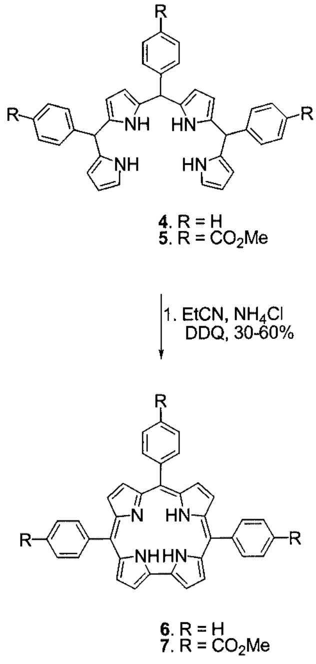


Scheme 1

Meanwhile, Paolesse and co-workers independently showed that the modification of Adler−Longo conditions by changing the ratio of pyrrole to aldehyde from 1:1 to 3:1 and replacing propionic acid by acetic acid results in the formation of an appreciable amount of corrole (besides porphyrins) (Scheme 2).[9,16] A fairly broad range of aldehydes with either electron-donating or electron-withdrawing substituents was successfully employed in this reaction, affording corroles in yields of 4−22%. The reaction failed in the case of sterically hindered aldehydes such as mesitaldehyde or 2,6-dichlorobenzaldehyde. It is quite reasonable to propose bilanes (tetrapyrranes − such as structures **4** and **5** in Scheme 3) as the precursors of the final corrole ring in both methods. The question remains whether the critical ring-closure step proceeds by an oxidative cyclization (mediated by DDQ or O_2) or an acid-catalyzed pyrrole−pyrrole coupling. Later work regarding cyclization of pentapyrranes to sapphyrins mediated by O_2[37] might indicate that oxidative cyclization is more probable.



Scheme 2



Scheme 3

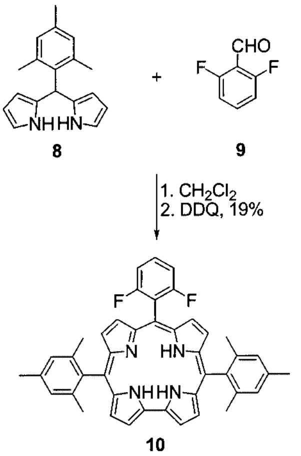
Another approach to A_3-corroles was developed by Lee and co-workers. Bilanes **4** and **5**, obtained by the condensation of aromatic aldehydes with excess pyrrole under neat conditions, were oxidized using DDQ to give corroles **6** and **7** (Scheme 3).[38] Bilanes − supposed precursors of corroles in the Paolesse and Gross approaches − were purified for the first time, thereby proving that bilanes indeed undergo radical oxidative cyclization. This process proceeds much more efficiently in MeCN and EtCN (especially in the presence of NH_4Cl) than in CH_2Cl_2. *meso*-Substituted A_3-corroles lacking β-substituents − compounds unavailable until 1999 −, thanks to the achievements described in this chapter, have now become a popular subject of studies.[12,13,18−23,30]

3. *meso*-Substituted *trans*-A_2B-Corroles

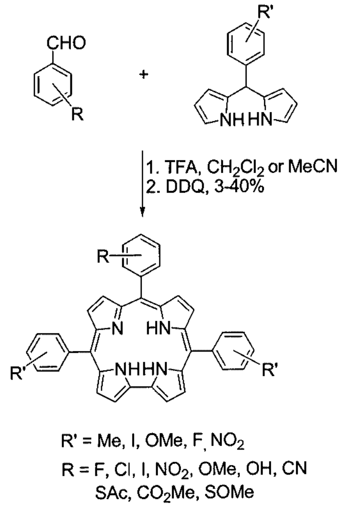
While the aforementioned A_3-corroles are easily accessible and provide suitable materials for physicochemical and coordination studies, a potential use of corroles as surrogates for vitamin B_{12} and related compounds would benefit significantly from the ability to incorporate different groups at distinct sites at the perimeter of the macrocycle. Such corroles can also serve as an ideal platform for obtaining more complex systems. In agreement with nomenclature typically used with porphyrins, corroles with two identical substituents at positions 5 and 15, and a different substituent at position 10 can be called *meso*-substituted *trans*-A_2B-corroles. From a conceptual viewpoint, contemporary methods for the synthesis of such corroles originate from the combination of the work of Gross et al.[7,8] described above and Lindsey's findings concerning the synthesis of *trans*-A_2B_2-porphyrins.

Bearing in mind that the acid-catalyzed reaction of dipyrromethanes (DPMs) (e.g., compound **8** in Scheme 4) with aldehydes gives the corresponding *trans*-A_2B_2-porphyrins,[39] it was reasonable to assume that the "noncatalyzed" reaction of DPMs with reactive aldehydes (or the acid-catalyzed reaction when a sizable excess of DPM is used) would lead to the formation of the corresponding A_2B-type *meso*-substituted corroles. Indeed, initial experiments showed that it is possible to carry out the "uncatalyzed" process although it is highly limited in scope. Only aromatic aldehydes possessing at least two fluorine atoms [for example 2,6-difluorobenzaldehyde (**9**)] are reactive enough to give rise to corroles as **10** (Scheme 4).[40] Observations regarding the presence of fluorobenzoic acids (ostensibly formed by an autooxidation of the respective aldehydes) in the reaction mixtures were crucial to the development of TFA-catalyzed conditions (Scheme 5).[41]

In reactions of aldehydes with sterically hindered DPMs, a low concentration of substrates and a high concentration of TFA favor formation of the *trans*-A_2B_2-porphyrins.[39] We found that if a low concentration of acid and a high concentration of substrates are used in the same reaction, corroles can be obtained in appreciable yields. Optimal conditions for the corrole-forming reaction were identified after examining various reaction parameters (solvent, acid, concentration, reaction time). The conditions identified {CH_2Cl_2, [DPM] = 33 mM, [aldehyde] = 17 mM, [TFA] = 1.3 mM (for sterically hindered DPMs) or [TFA] = 0.26 mM



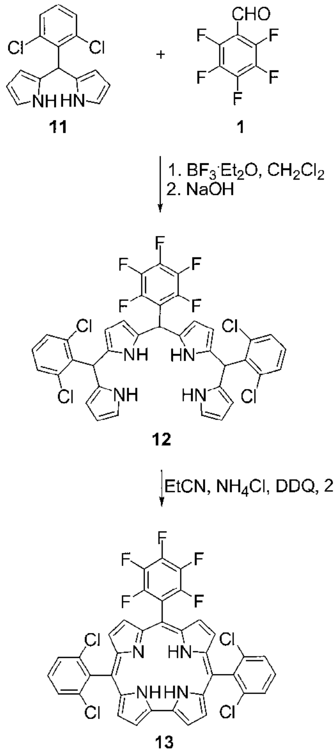
Scheme 4



Scheme 5

(for sterically unhindered DPMs), 5 h, room temperature} resulted in the formation of corroles in 3−25% yield. This process is compatible with diverse functionalities and proceeds without detectable "scrambling" even for sterically unhindered DPMs. Scrambling is the undesired rearrangement of substituted dipyrromethanes leading to a mixture of products bearing different types and/or patterns of substituents at the perimeter of the macrocycle.

Two other analogous, short reports appeared at about the same time. Brückner et al.[42] found that when aldehydes react with sterically unhindered DPMs (present in sixfold molar excess) under TFA catalysis, *trans*-A_2B-corroles are formed in 20−40% yield (Scheme 5). Dehaen and coworkers[43] used $BF_3{\cdot}OEt_2$ as a catalyst for the reaction of 5-(2,6-dichlorophenyl)dipyrromethane (**11**) with reactive aldehydes (Scheme 6). Often they separated the bilanes prior to conversion into corroles. Taking advantage of the earlier findings of the Lee group,[38] purified bilanes were oxidized to corroles in MeCN or EtCN. All attempts to apply these conditions to other substrates such as mesityldipyrromethane or less reactive aldehydes (benzaldehyde, 4-nitrobenzaldehyde) failed. Though these three papers differ slightly with regard to the procedures used, they showed the synthetic utility of the [2+1] approach.

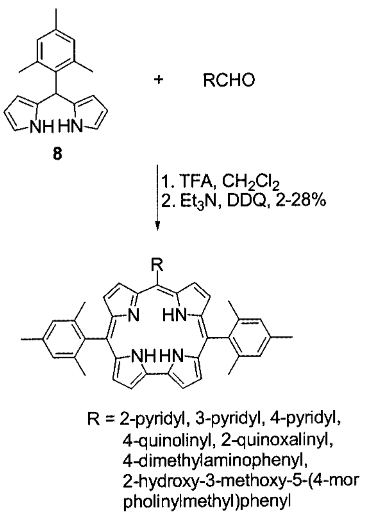


Scheme 6

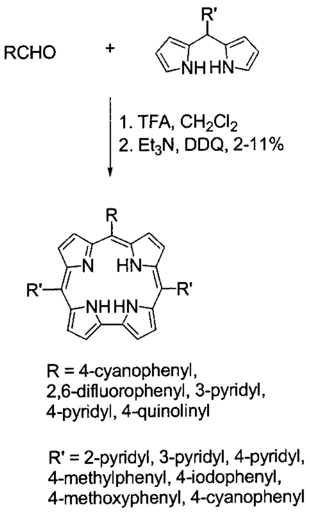
An extensive modification of the conditions used for the synthesis of *trans*-A_2B-corroles led to the development of a comprehensive method for the preparation of *trans*-A_2B-corroles bearing substituents with basic nitrogen atoms in the *meso* positions.[5] Pyridine-, quinoline-, and quinoxaline-derived aldehydes as well as other aromatic aldehydes containing tertiary amine groups [such as 4-(dimethylamino)benzaldehyde and 2-hydroxy-3-methoxy-5-(4-morpholinylmethyl)benzaldehyde] were successfully used in the condensation involving sterically hindered dipyrromethanes (Scheme 7). By contrast, in reactions with sterically unhindered dipyrromethanes, only aldehydes with the formyl group directly adjacent to the heterocyclic ring proved to be efficient substrates (Scheme 8).

For the remaining aldehydes, extensive scrambling was observed. The dilution of the reaction mixture before DDQ addition improves the yield by a factor of two,[44] which suggests that radical oxidative coupling occurs. Yet a different set of conditions was developed for the condensation involving pyridyldipyrromethanes. Reactions of aldehydes possessing electron-withdrawing groups with these DPMs led to the formation of corroles with two basic nitrogen atoms in *meso* substituents (Scheme 8).[5] Generally it was found that at least one equiv. of TFA per mol of "basic nitrogen" is needed for the reaction to proceed appreciably.

The disadvantage of the methodologies presented in this chapter lies in the parallel porphyrin formation, which com-



Scheme 7



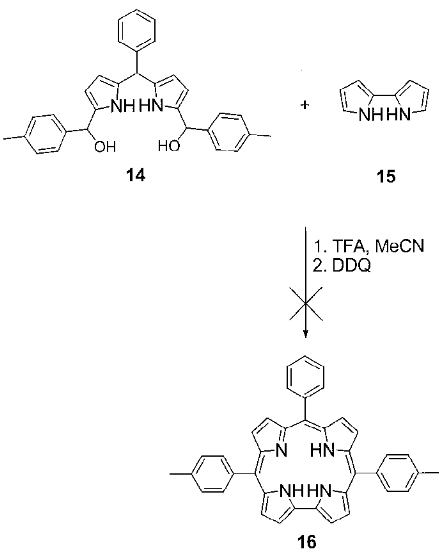
Scheme 8

plicates the corrole purification. The ultimate solution (rooted in Lindsey's recent methodology[45]) to this problem would lie in the reaction of diol **14** with bipyrrole (**15**). Unfortunately, this approach, similar to earlier attempts of Vogel et al.,[46] failed (Scheme 9).[47]

4. β- and *meso*-Substituted Corroles

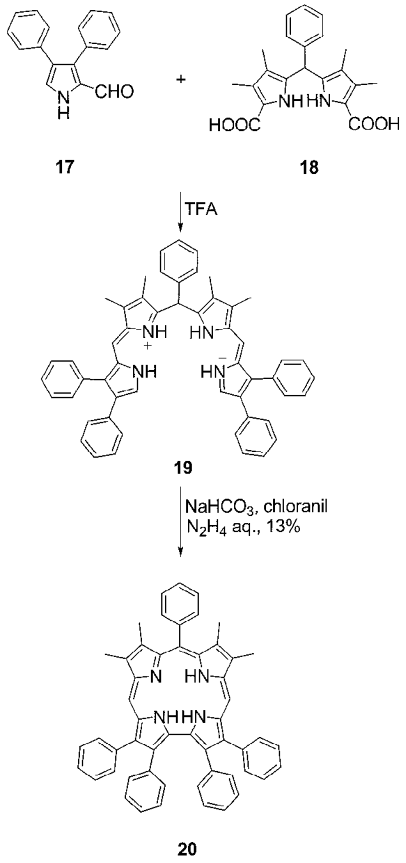
In the covered period of time, research on the synthesis of corroles with both *meso* and β substituents was pursued mainly by Guilard, Kadish, and co-workers.

Their earlier studies led to the conclusion that *meso*-substituted corroles with alkyl substituents in β-pyrrole positions often exhibit reduced stability due to oxidative ring opening.[48] From this vantage point, they developed a strategy to obtain more stable analogs (Scheme 10).[17] They found a simple way for the introduction of aryl groups in β-pyrrole positions 2, 3, 17, and 18, which prevents corrole



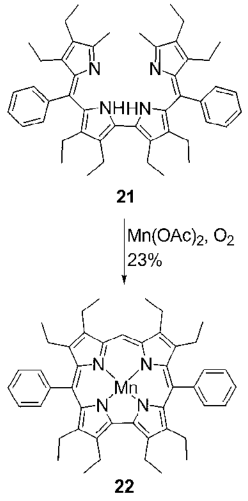
Scheme 9

oxidation from occurring. Final ring closure was achieved by the reaction of aldehyde **17** with DPM **18** to give *a,c*-biladiene **19**, which subsequently cyclized to corrole **20**. This strategy was further utilized for the synthesis of "face-to-face" bis(corroles) with an anthracenyl bridge.[49]



Scheme 10

Very recently, an entirely new approach has been reported by Bröring et al. Treatment of the bis(dipyrrin) **21** with manganese(II) acetate in the presence of molecular oxygen leads to the formation of (corrole)manganese(III) (**22**), which can be readily demetalated to the respective free-base corroles using HBr in HOAc (Scheme 11).[50]



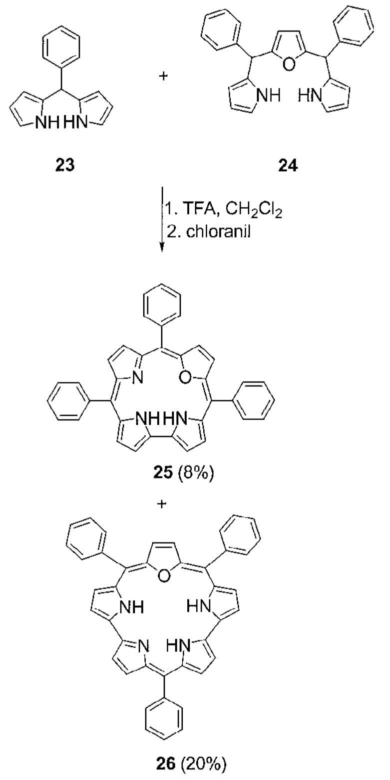
Scheme 11

5. Core-Modified Corroles

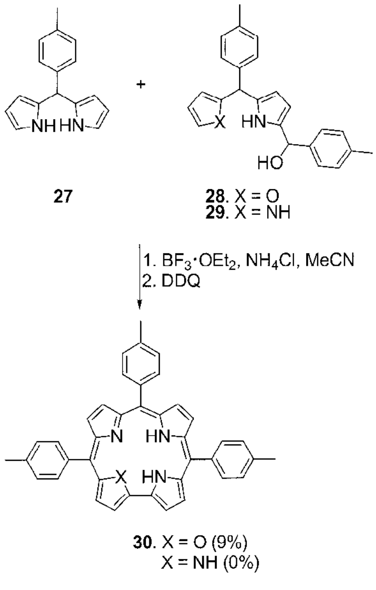
Coincidentally, the advent of synthetic methodologies for core-modified corroles started at the same time as those for all-nitrogen corroles. Chandrashekar and co-workers found that the acid-catalyzed coupling of dipyrromethane **23** and 16-oxatripyrrane **24** catalyzed by BF_3·OEt_2 leads, in addition to the expected core-modified smaragdyrin (**26**), also to core-modified corrole **25** as a side product (Scheme 12).[51]

The formation of core-modified corroles in this [3+2] reaction is due to the fact that both substrates are susceptible to acid-catalyzed rearrangements and are known to undergo fragmentation.

A different approach was developed by Lee et al., who condensed alcohols such as **28** with dipyrromethanes such as **27** to give oxacorrole **30** in 9% yield (Scheme 13).[52] Interestingly, the analogous reaction of 2-[hydroxy(*p*-tolyl)methyl]-5-(*p*-tolyl)dipyrromethane (**29**) with dipyrromethane **11** leads only to the respective porphyrin (Scheme 13).[52] Complexes of oxacorroles with Cu^{II}, $Ni,^{II}$ or Co^{II} have already been prepared by reaction with $CuCl_2$, $NiCl_2$, or $Co(OAc)_2$ in DMF.[51]

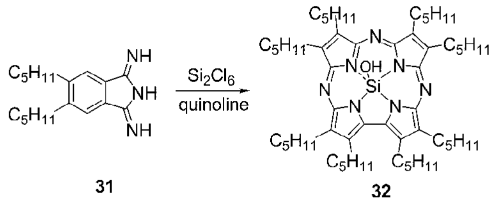


Scheme 12

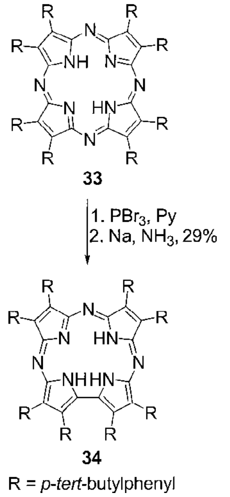


Scheme 13

The chemistry of triazatetrabenzocorroles, first obtained by Fujiki et al.,[53] was recently further developed by Hanack and co-workers. They found that reaction of diiminoisoindoline **31** with Si_2Cl_6 leads to the ring-contracted (hydroxy)(α,β,γ-triazatetrabenzocorrole)silicon **32** (Scheme 14).[54] Rhodium complexes of triazatetrabenzocorroles have also been obtained by Rathke et al.[55] The same parent skeleton can also be reached by the reaction of phthalocyanines with PBr_3 in pyridine.[56] An analogous strategy was used by Goldberg et al. to transform porphyrazine **33** into corrolazine **34** (Scheme 15).[57] This facile synthesis should be compatible with a variety of peripheral substituents, which would enable preparation of a new family of corrole-type compounds with adjustable steric and electronic properties.



Scheme 14



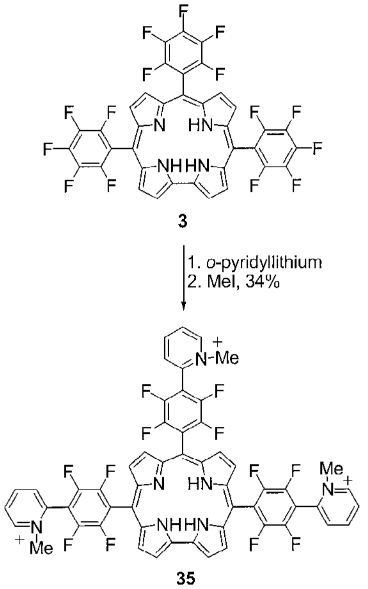
Scheme 15

6. Derivatization of Triarylcorroles

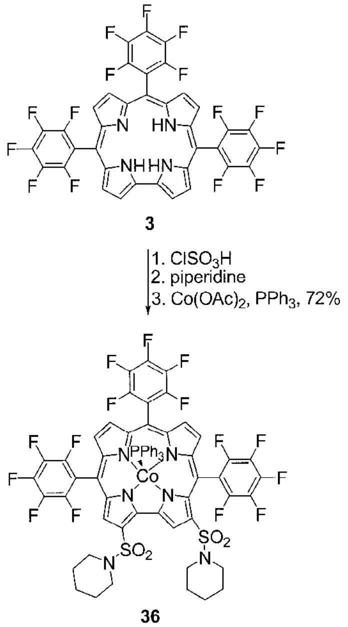
As can be seen, the prevalent synthetic route to new corroles involves the introduction of different units into an aldehyde precursor. A complementary but less often used route involves the derivatization of substituted corroles. Tris(pentafluorophenyl)corrole **3** may potentially serve as the precursor for many other corroles, given that its *p*-fluoro substituents can easily be replaced by nucleophilic substitution. This was demonstrated by the Gross group by the reaction of corrole **3** with *o*-pyridyllithium. Further reaction with iodomethane led to the first ionic corrole **35** (Scheme 16).[7]

The presence of β-pyrrole CH groups in *meso*-arylcorroles opens the opportunity for relatively straightforward skeleton modifications. This was first demonstrated by bromination of all β-pyrrole positions of 5,10,15-triarylcorroles; Paolesse et al. used NBS, free-base corrole, and subsequent cobalt insertion (low total yield)[16] while the Gross group employed Br_2 on the premetallated (corrole)Mn (high yield).[21]

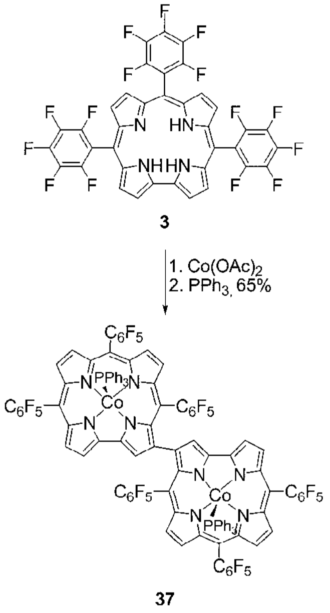
Obviously, introducing one or two substituents at designated places would be of great utility. The feasibility of such an approach was recently demonstrated by the Gross group; chlorosulfonation of tris(pentafluorphenyl)corrole **3** proceeded with an extremely high selectivity to afford one out of 139 possible isomers in very high yield.[58] Subsequent treatment with piperidine and insertion of a cobalt ion afforded the bis(sulfonamide) derivative **36** (Scheme 17), a metal complex with "planar chirality". In addition, hydrolysis of the same precursor yielded the bis(sulfonic acid) derivative, the first amphiphilic corrole. Even less expected was the formation of β-β dimer **37**, which was obtained by addition of cobalt(II) acetate to corrole **3** followed by triphenylphosphane (the reverse order of addition leads to the simple complex) (Scheme 18).[18] In 1999 Gross discerned that simple *N*-monoalkylation of free-base corroles leads to chiral molecules.[59] These ligands as well as chiral metal complexes described in Scheme 17 may be useful in enantioselective catalysis.



Scheme 16



Scheme 17



Scheme 18

7. Conclusion

The material covered by this review indicates that synthetic corrole chemistry is undergoing vibrant and rapid change. We are currently facing the revival of corrole chemistry induced by the first synthesis of *meso*-substituted A$_3$-corroles. Now that fairly efficient synthetic methodologies are available that afford access to these compounds, research is likely to focus on the physical and chemical properties of corroles. There is clearly a great deal of promise in catalysis. Other potential applications are on the horizon. Perhaps the expected further improvement in the synthetic methodology will also pave the road for the development of the synthesis of vitamin B$_{12}$ mimics.

Acknowledgments

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