

Advances in the Chemistry of Dipyrins and Their Complexes

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1. Introduction

1.1. Dipyrins: General Background

Research in the area of dipyrin chemistry has been traditionally pursued by research groups intent on the

synthesis of porphyrins. This is due to the historical application of dipyrins in the synthesis of porphyrins and the requisite familiarity with pyrrole chemistry in order to effect their synthesis; dipyrin chemistry was first popularized by Hans Fischer.¹ Formation of charge-neutral chelated complexes with a variety of metal cations has been the source of most new avenues of dipyrin research. The ability to synthetically manipulate dipyrins, which are usually crystalline molecules with intense molar absorptivities in the visible region, is increasing in scope. Unfortunately, memorable passages describing the “messy and often ruinous manipulation”² of dipyrins have done little for the recruitment of would-be dipyrin researchers. This review highlights the different uses that have been investigated for dipyrins and the advances that have been made toward rendering dipyrins and their metal complexes more available to researchers who do not specialize in dipyrin synthesis. Our apologies to researchers whose work is not mentioned in this review; we have, to the best of our knowledge, included a representation of all the modern dipyrin research.

1.2. Structure

The structures to be discussed in this review are shown in Figure 1. Dipyrins are formally composed of a pyrrole ring and an azafulvene attached to each other through the 2 positions: a dipyrromethane with one more degree of unsaturation. This added degree of unsaturation allows for delocalization of the electron density across the dipyrin such that structural data shows that the two pyrrolyl units are equivalent when they are identically substituted. There are very few reports^{3,4} regarding the analogous 2,3'- or 3,3'-dipyrromethenes.

Guidelines for the nomenclature to be used for dipyrins, and many other oligopyrrolic molecules, were established by IUPAC in 1987.⁵ Publications on the subject of dipyrin research date back nearly a century, and in this time these molecules have been known by many names: 4,6-dipyrin,⁶ dipyrromethene,⁷ 4,6-dipyrromethene,⁸ dipyrrolymethene,⁹ pyrrolymethene,¹⁰ pyrromethene,¹¹ 2,2'-dipyrrolylmethene,¹² dipyrrolemethene,¹³ diaza-*s*-indacene,¹⁴ 2-pyrrol-2-ylmethylene-2*H*-pyrrolenine,¹² and 2-(2*H*-pyrrol-2-ylidenemethyl)-pyrrole.⁶ The IUPAC-recommended numbering scheme for dipyrin nomenclature is shown in Figure 2. It is occasionally more illustrative to refer to the 1- and 9-positions as the α positions, following from historic pyrrole nomenclature, and the 5-position as the meso position, a term borrowed from the naming of porphyrins.

2. Dipyrins

2.1. Syntheses

The nature and number of substituents affects the stability of a dipyrin. Fully unsubstituted dipyrin was reported¹⁵ to

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Alison Thompson's research interests include the synthesis and applications of helical dipyrinato complexes, development of new methodology for the efficient synthesis of functionalized pyrroles, and design and synthesis of prodigiosins for evaluation as anticancer treatments. Born in Nottingham, England, Professor Thompson obtained her B.Sc. (Hons. Class I) degree from the University of Leicester, U.K., in 1993. In 1996 she received her Ph.D. degree from the University of Sheffield, U.K., for research on the development of catalytic asymmetric aziridination and epoxidation reactions with Professor Varinder Aggarwal. She then spent a year in Strasbourg, France, as a postdoctoral fellow with a Royal Society/NATO award. In 1997 Professor Thompson joined the University of British Columbia, Canada, to work with Professor David Dolphin. She moved to Halifax, Nova Scotia, in 2001 to take a faculty position at Dalhousie University with an NSERC University Faculty Award and was promoted with tenure in July 2006. In 2006 she was awarded the AstraZeneca Award in Chemistry and received the Faculty of Science Killam Award at Dalhousie University in 2007.

be unstable in solution at temperatures above $-40\text{ }^{\circ}\text{C}$ due to the susceptibility of the unsubstituted ring positions to electrophilic and nucleophilic attack. Dipyrins have been reported to react with a variety of nucleophiles,^{9,16–19} and consequently alkyl substituents at the 1,2,3,7,8,9-positions (incorporated from pyrrolic precursors) are often used to enhance the stability of the dipyrin skeleton against such reactions. Aryl substituents at the 5-position allow for the isolation of 1,2,3,7,8,9-unsubstituted dipyrins as stable compounds as well as increasing the stability of radical cations formed from the resulting dipyrin, making them

more suitable for optoelectrochemical applications than 5-unsubstituted dipyrins.²⁰

The array of methods generally employed for the synthesis of dipyrins has recently been expanded. "Traditional" methods are described in section 2.1.1 while more recent innovations are described in section 2.1.2. The classic methods are generally suitable for the preparation of asymmetrical dipyrins, or dipyrins with hydrogen substituents at the 5-position, and a publication from 1996 provides an extensive review of historical dipyrin syntheses in its introduction.²¹ Conversely, the more recent methods are better suited to preparing symmetrical dipyrins substituted with aromatic rings in the 5-position.

2.1.1. Synthesis of Dipyrins by Condensation of Pyrroles

The acid-catalyzed condensation of a 2-formyl pyrrole with a pyrrole that is unsubstituted in the 2-position yields a 5-unsubstituted dipyrin,²² as shown in Figure 3, when the substituent R^7 is a hydrogen atom. This procedure is frequently referred to as the MacDonald coupling, akin to the analogous reaction in porphyrin synthesis named for the pioneering Canadian porphyrin chemist Stewart Ferguson MacDonald.²³ Hydrobromic acid is commonly used⁷ in this procedure but also phosphorus(V) oxychloride,²⁴ and as a result of the acidic conditions of the reaction, the dipyrin products prepared in this way are isolated as salts. This is convenient because free-base 5-unsubstituted dipyrins are generally less stable than their salts.²² The MacDonald coupling is the most frequently employed method for the preparation of asymmetrical dipyrins because it relies upon the reaction of complementary functionalities in the pyrrolic precursors. Yields for these reactions are generally very high but can be limited by purification of the product from the reaction mixture, which is usually achieved by precipitation. In addition, reaction yields are reduced when 2-unsubstituted pyrroles with electron-withdrawing groups are used because in such cases self-condensation of the 5-formyl pyrrole can become competitive, giving an undesired symmetrical dipyrin salt.²² Figure 3 also shows an alternative synthetic route (when R^7 is an alkyl or aryl substituent) that allows for the synthesis of 5-substituted dipyrins by the condensation of two equivalents of a 2-unsubstituted pyrrole with a carboxylic acid or acid halide.

2.1.2. Synthesis of Dipyrins by Oxidation of Dipyrromethanes

Development of reliable methods for the preparation of dipyrins by oxidation of dipyrromethanes has been one of the most important advances in dipyrin chemistry in recent years. The general procedure, as outlined at the top of Figure 4, usually involves oxidation of 5-substituted dipyrromethanes to yield dipyrins which are often stable in their free-base form, unlike 5-unsubstituted dipyrins. Figure 4 also shows a synthetic route to 5-unsubstituted dipyrromethanes involving the self-condensation of an appropriate pyrrole carbonyl cation precursor under acidic conditions²⁵ (e.g., Montmorillonite clay²⁶ or *p*-toluenesulfonic acid,²⁷ *p*-TSA) or via the reaction of the same precursor species with a 2-unsubstituted pyrrole if asymmetrical dipyrromethanes are required.²²

Preparation of 5-aryl-substituted dipyrromethanes, precursors to 5-aryl dipyrins, has been made very accessible.^{28–34} Findings from these studies have revealed that the optimal conditions for reactions of this type are highly generaliz-

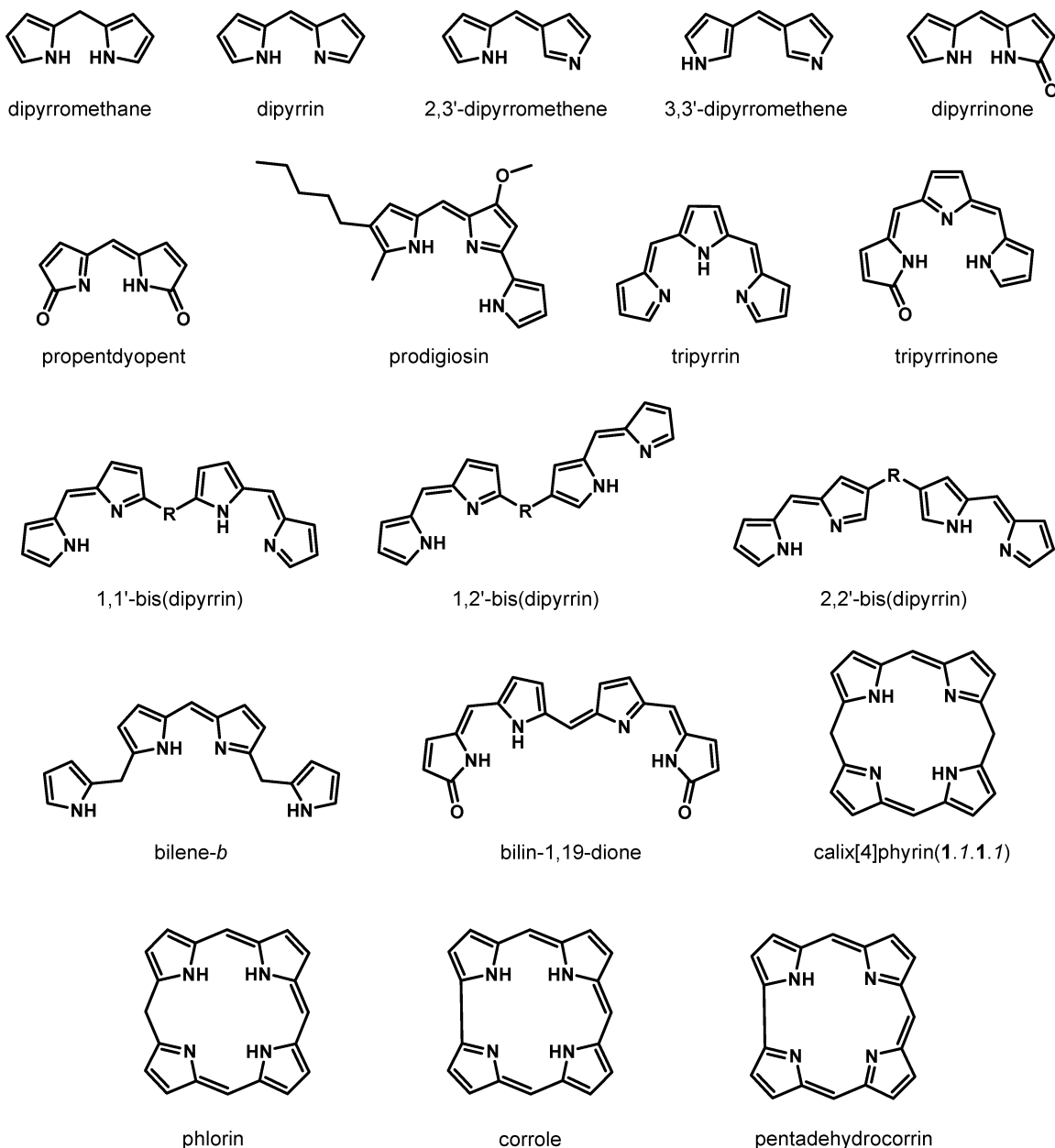


Figure 1. Representative structures for compounds discussed in this review.

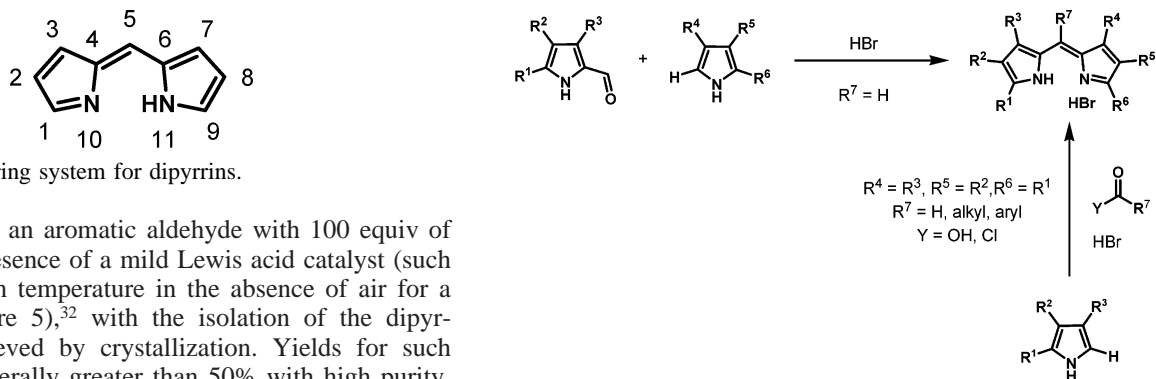


Figure 2. Numbering system for dipyrins.

able: reaction of an aromatic aldehyde with 100 equiv of pyrrole in the presence of a mild Lewis acid catalyst (such as InCl_3) at room temperature in the absence of air for a few hours (Figure 5),³² with the isolation of the dipyrromethanes achieved by crystallization. Yields for such reactions are generally greater than 50% with high purity, and the reactions are scalable. One of the most attractive features of this procedure is the use of pyrrole, a substance that is readily available commercially and can be purified by a non-rigorous distillation procedure, alleviating the need for knowledge of the synthesis and handling of substituted pyrroles. Techniques for the preparation of dipyrromethanes that bear substituents on the pyrrole rings have also been

Figure 3. Routes to the synthesis of dipyrins by acid-catalyzed condensation reactions.

developed. These procedures use two equivalents of the precursor 2-unsubstituted pyrrole in the reaction mixture as oligomerization side reactions are not as prominent.^{35–40}

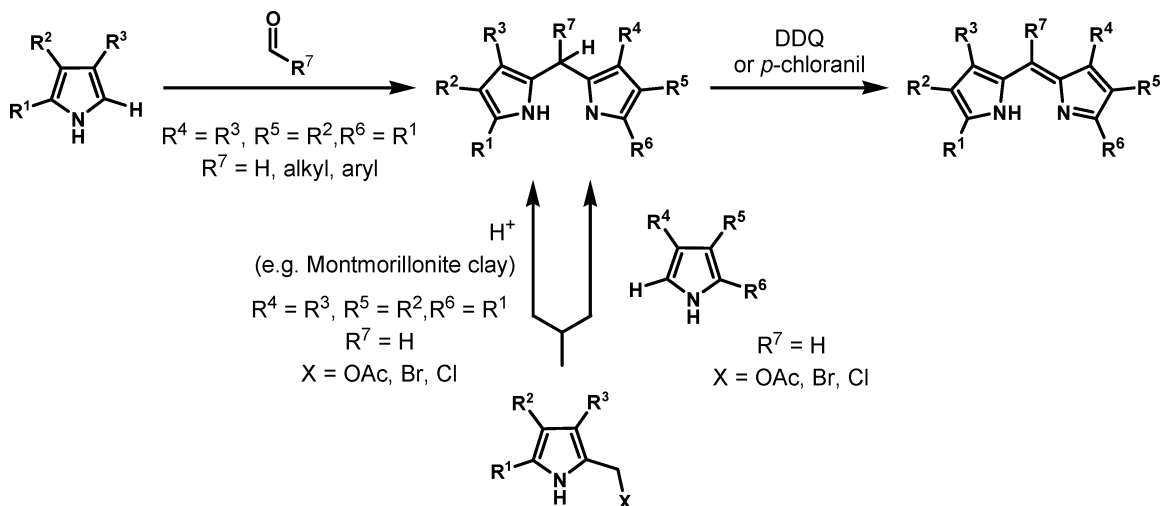


Figure 4. Routes to the synthesis of dipyrriins by oxidation of dipyrromethanes.

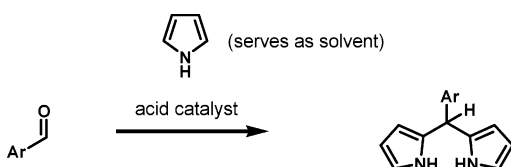


Figure 5. Synthesis of 5-substituted dipyrromethanes using excess pyrrole.

Oxidation of dipyrromethanes to dipyrriins can be achieved with a number of reagents, but by far the most common is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), although *p*-chloranil is popular as a more mild oxidizing agent (Figure 4).^{21,35} Although this technique is highly successful for the synthesis of dipyrriins, some limitations have been encountered: for example, oxidation of 5-alkyl and 5-unsubstituted dipyrromethanes by DDQ has been shown to consume the starting material without yielding the appropriate product.⁴¹

An advantage of 5-substituted dipyrriins lies in the possibility to perform functional-group interconversions⁶ and thus use the 5-substituent as a point for elaboration and as a linking handle through which to build larger architectures.^{41–44} Research has been performed into the chemical manipulation of functional groups present on dipyrriin 5-aryl substituents, and this is described in more detail in section 3.1.7. The nuclear magnetic resonance (NMR) spectra of free-base 5-substituted dipyrriins show rapid tautomerization, and the signal arising from the hydrogen atom bonded to nitrogen is not always apparent in ¹H NMR spectra. A disadvantage of the 5-aryl dipyrriins is their reported sensitivity to low pH conditions.⁴⁵

2.2. Properties

Many of the physical properties of dipyrriins such as solubility, structure, nuclear magnetic resonance spectra, fluorescence spectra, and light absorbance spectra are described in the book *The Chemistry of Linear Oligopyrroles and Bile Pigments*,⁴⁶ and such discussion is not repeated here. Data pertaining to the solvation properties, light absorption spectra, and thermal decomposition values of some dipyrriin hydrobromide salts, bis(dipyrriin) hydrobromide salts, and dipyrriinato metal complexes were reported recently.^{3,4,47–50} In a study of the antioxidant properties of two bis(dipyrriin)s and several other oligopyrrolic compounds it was shown that the 1,1'-linked bis(dipyrriin), which mimics the linkage of

natural linear tetrapyrrolic compounds, exhibited effective antioxidant activity while the unnatural 2,2'-bis(dipyrriin) did not.⁵¹

Free-base dipyrriins are regarded as relatively strong bases.²² For a series of dipyrriins the *pK_a* of the hydrogen atom bonded to the nitrogen atoms has been measured using spectrophotometric titrations, and the results illustrated the effects of electron-withdrawing and electron-donating substituents upon the acidity of the proton.⁵² Deprotonation of dipyrriin hydrobromide salts by organic solvents such as DMF, DMSO, and pyridine has been investigated by spectrophotometric titrations, and these studies showed a correlation between the proton affinity of a dipyrriin and its thermodynamic constant of zinc(II)-ion complexation.^{4,49,50}

A study regarding the use of ¹⁵N NMR chemical shifts for a series of dipyrrolic molecules including dipyrromethanes, dipyrriins, and dipyrriinato complexes has been reported.⁵³ The ¹⁵N chemical shifts of the dipyrrolic compounds were found to be difficult to interpret in regard to fine structure but were diagnostic of gross structure concerning the oxidation and complexation states of the dipyrrolic compounds.

3. Dipyrriinato Complexes

3.1. Syntheses

3.1.1. Side-Products of Porphyrin Syntheses

Dipyrriinato metal complexes have been obtained as side-products during the synthesis of sterically crowded porphyrins using Rothemund⁵⁴ condensation conditions.^{55–59} Porphyrin syntheses using 2-chlorobenzaldehyde,⁵⁵ 2,6-dichlorobenzaldehyde,⁵⁶ 2-acetoxybenzaldehyde,⁵⁸ and mesitaldehyde⁵⁷ have been documented to yield zinc(II) dipyrriinato complexes. It is believed that the steric hindrance provided by ortho-substituents of the aromatic aldehyde reagents makes cyclization to form the porphyrin unlikely, and so dipyrriins, although they are not thought to be intermediates for successful porphyrin synthesis,⁵⁹ become isolable side-products. Indeed, sometimes the dipyrriinato metal complex is the major product of the reaction.⁵⁶ One report provides an interesting example of an attempted Rothemund-type porphyrin synthesis that yielded the two dipyrriinato metal complexes **1** and **2** as illustrated in Figure 6.⁵⁷ It has also been noted that the presence of metal ions

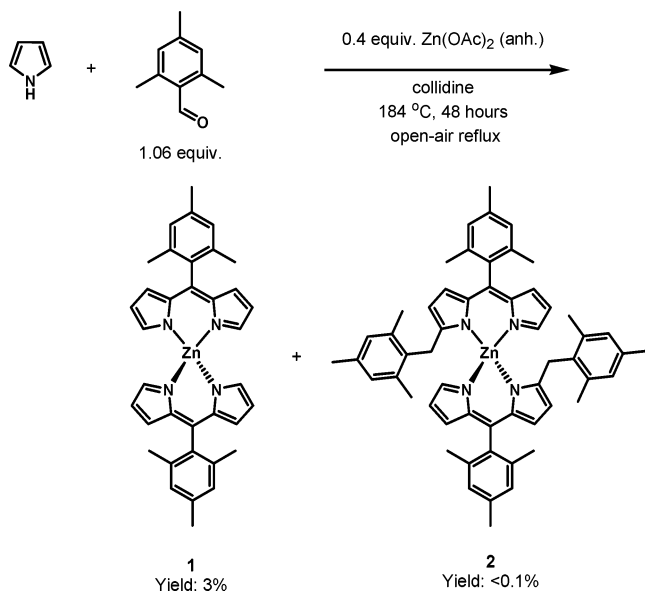


Figure 6. Zinc(II) dipyrinato complexes obtained from a Rothemund-type porphyrin synthesis.

during the reaction is not always necessary for obtaining dipyrin side products.⁵⁸

3.1.2. Scope of Metal Ions in Homoleptic Complexes

Dipyrins are known to form isolable complexes with a variety of metal ions. Upon deprotonation, the monoanionic dipyrinato ligands generally form neutral homoleptic (bearing two or more identical ligands on a metal center) complexes. Complexes of this type are known to form with magnesium(II),⁶⁰ calcium(II),^{61,62} chromium(III),⁶³ manganese(II),^{61,64,65} manganese(III),⁶⁴ iron(II),⁶⁶ iron(III),^{6,8,42,66–68} cobalt(II),^{11,69–77} cobalt(III),^{6,67,68} nickel(II),^{11,21,61,62,69,70,72–79} copper(II),^{21,41,42,45,47,48,60–62,69,70,72–77,80–82} zinc(II),^{11,21,41,47,48,55,56,61,69,70,72,73,76,77,83,84} gallium(III),⁸⁵ rhodium(II),⁸⁶ palladium(II),^{11,41,76,78,87} cadmium(II),^{11,76} indium(III),⁸⁵ mercury(II),^{11,76} thallium(I),⁸⁸ and thallium(III).⁸⁸ Although the free-base of 5-aryl dipyrins can be isolated in many cases, usually by chromatography or crystallization, preparation of homoleptic 5-aryldipyrinato metal complexes is made more convenient by preparing the dipyrin and subsequently treating the dipyrin in situ with a metal salt.^{6,89}

3.1.3. Complexation Geometries

In the vast majority of dipyrinato metal complexes the metal ion is bound by the ligand in a chelating κ^2 manner; however, some exceptions have been noted recently. Although the pyrrole anion is known to act as an η^5 ligand in coordination complexes such as azaferrocene (**3**),⁹⁰ the first example of a pyrrolic unit of a dipyrin that binds metal ions in such a manner was not reported until 2000 (Figure 7).⁹¹ It was demonstrated that reaction of a bis(dipyrin) with $\text{Ru}_3(\text{CO})_{12}$ produced a ruthenium–dipyrin cluster (**4**) in which one of the pyrrole rings was bound to a ruthenium ion in an η^5 manner.

The pyrrolic units of dipyrins can adopt a conformation such that the nitrogen atoms are oriented in the same direction as the 5-substituent, although reported complexes of dipyrins in this orientation are very rare. In 2004 one report presented solid-state structures such as that of compound **5** of dipyrin complexes in which protonated

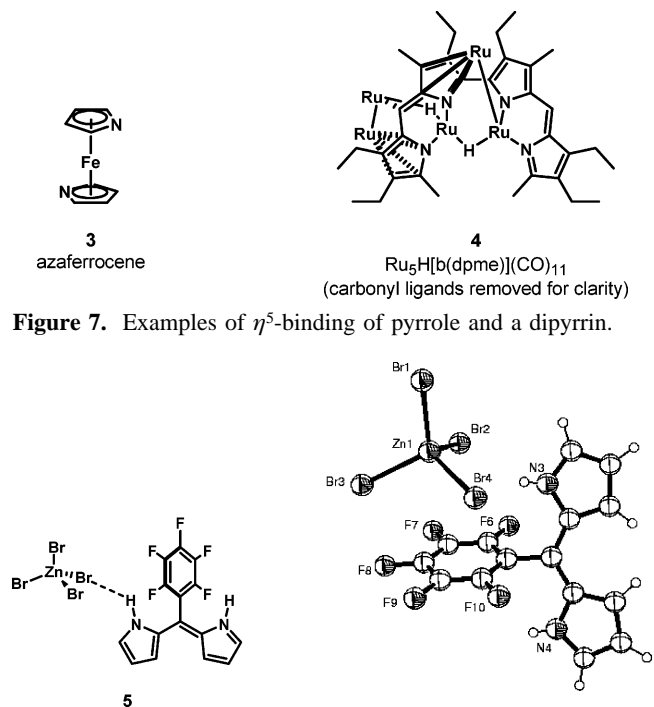


Figure 7. Examples of η^5 -binding of pyrrole and a dipyrin.

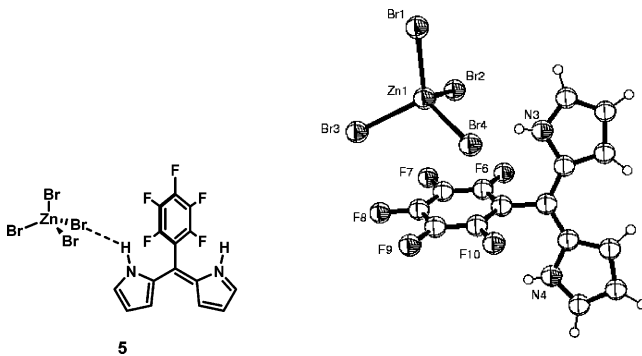


Figure 8. Rotation about the 5-position in dipyrins.

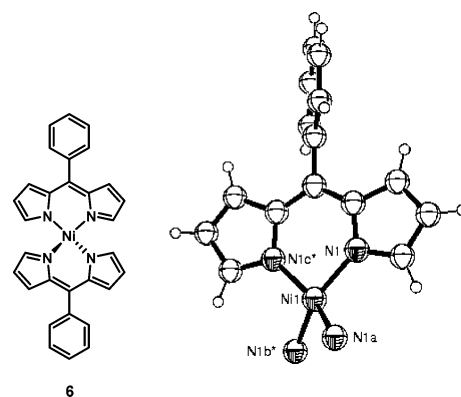


Figure 9. Tetrahedral coordination geometry in a nickel(II) dipyrinato complex (the structure has been truncated for clarity).

dipyrins formed supramolecular structures with tetrahalozinc anions (Figure 8).⁹²

The coordination geometry of metal complexes of dipyrins is influenced by the steric interactions between substituents at the 1,9-positions of multiple ligands brought into close proximity by complex formation.⁹³ Interactions between 1,9-substituents as small as hydrogen atoms result in the preferential formation of non-square-planar coordination geometry about the complexed metal ion. For example, nickel(II) (compound **6** in Figure 9) and copper(II) complexes of 5-phenyldipyrin adopt distorted tetrahedral coordination geometries, thus sterically accommodating the 1,9-substituents.²¹ This is not the typical coordination geometry adopted by copper(II) complexes, and interestingly, the nickel(II) complexes are low spin, enabling NMR spectra to be obtained of the resulting diamagnetic complexes. The cobalt(II) complex of 5-phenyldipyrin (**7**) was found to be difficult to isolate, and transformation to the octahedral tris(dipyrinato) cobalt(III) complex **9** was observed (Figure 10).⁶ Subsequently, such octahedral complexes were formed directly from cobalt(III) salts, and iron(III) complexes, such as compound **10** in Figure 11, were formed similarly. Use

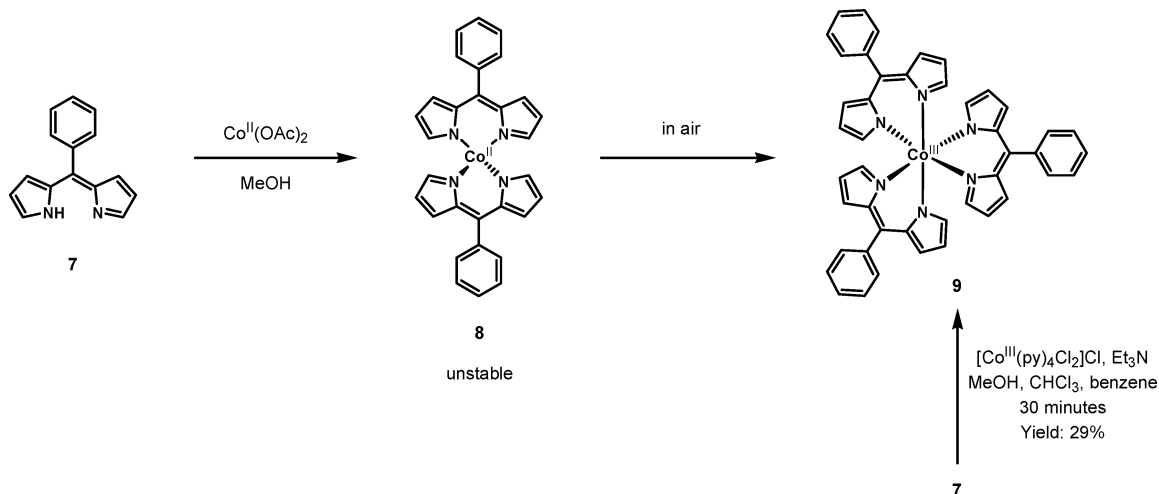


Figure 10. Formation of a stable octahedral cobalt(III) dipyrinato complex.

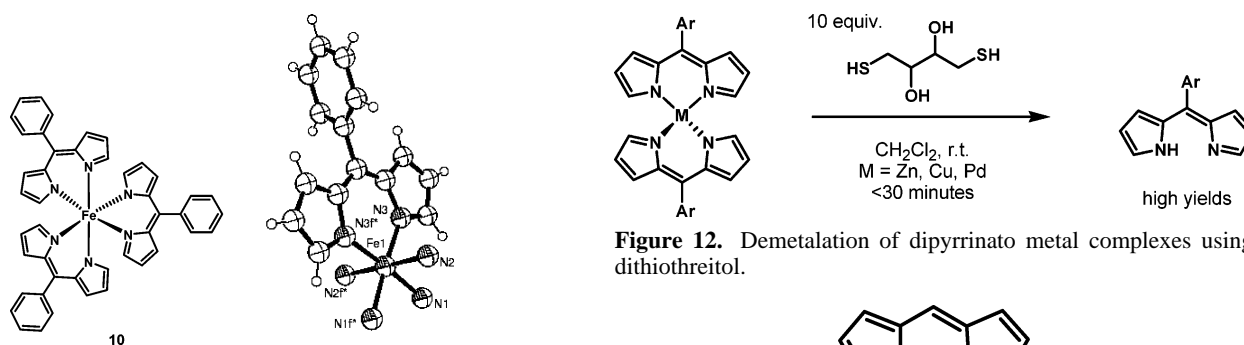


Figure 11. Octahedral coordination geometry in an iron(III) dipyrinato complex (the structure has been truncated for clarity).

of an excess of cobalt(III) salt resulted in mixtures, presumably due to formation of heteroleptic complexes.⁶ The relatively shielded chemical shift of the 1,9-hydrogen substituents in the ¹H NMR spectrum of cobalt(III) complex **9** is somewhat diagnostic for octahedral complexes of dipyrins, as a result of these atoms being shielded by two aryl dipyrinato systems. The octahedral iron(III) complex **10** has been studied using electrochemistry, and this report also includes an improved preparative procedure for **7**.⁸ The iron(III) complex exhibits quasireversible redox couples, indicative of a hard donor ligand environment. Such behavior serves to rationalize the observation that iron(II) complexes of dipyrins are unstable toward oxidation of the iron center.⁶ For further discussion of the electrochemical behavior of dipyrinato complexes, see section 3.2.2.

Demetalation of Homoleptic 5-Aryldipyrinato Complexes. It has been observed that treating rhodium(I) complexes of dipyrins with bromine or chlorine causes demetalation of the complexes, generating the hydrobromide or hydrochloride salts, respectively, of the dipyrin ligands.⁸⁶ Incomplete demetalation of the homoleptic 5-phenyldipyrinato zinc(II) complex was observed upon treatment with excess trifluoroacetic acid (TFA) or methanolic hydrochloric acid.⁴¹ This is somewhat surprising as many complexes are labile under acidic conditions. As shown in Figure 12, complete demetalation of a variety of dipyrinato complexes was achieved by treatment with dithiothreitol (DTT, threo-1,4-dimercapto-2,3-butanediol): use of ethylene glycol was unsatisfactory. Alternatively, reduction of the homoleptic 5-phenyldipyrinato zinc(II) complex with sodium borohydride gave the corresponding dipyrromethane,⁴¹ akin to the

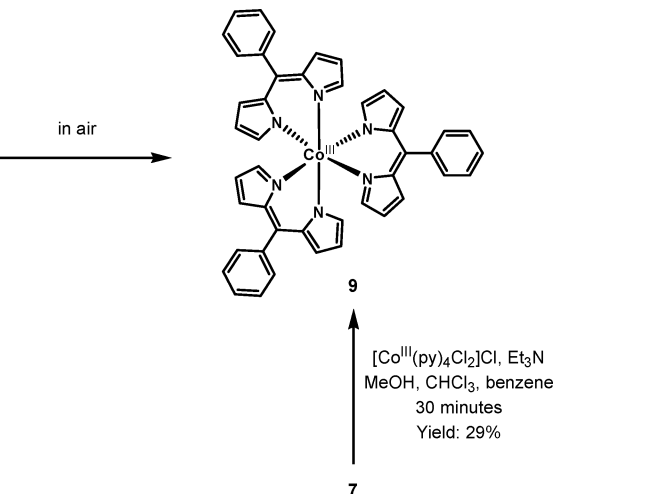


Figure 12. Demetalation of dipyrinato metal complexes using dithiothreitol.

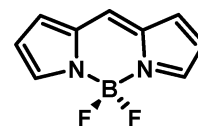


Figure 13. Basic structure of a borondifluoride dipyrinato complex.

well-documented reduction of dipyrins to give dipyrromethanes.⁹⁴ Furthermore, treatment of dimeric dipyrinato copper(II) complexes with potassium cyanide resulted in complete demetalation.^{42,85}

3.1.4. Dipyrinato Complexes of Boron

Borondifluoride complexes of dipyrins (Figure 13) were first reported in 1968.⁹⁵ Even in this earliest report the researchers described the intense fluorescence of complexes of this type, and this has become recognized as their most important property. The effect of molecular structure upon the spectroscopic properties of borondifluoride dipyrinato complexes has received a great deal of attention in the literature.^{46,52,96–101} In the early 1980s borondifluoride complexes of dipyrins were employed in experiments that utilized their intense fluorescence for the study of gas chromatographic processes.^{102,103} For these experiments movement of injected samples of a complex was monitored to determine the broadening of the sample band and the extent of their absorption onto glass column surfaces. Their generally high fluorescence quantum yields, with tunable emission maxima wavelengths and good photochemical stability, have led borondifluoride dipyrinato complexes to become highly popular for use in biological staining and dye laser applications, making them the most commercially important examples of dipyrinato complexes.

When searching for information regarding borondifluoride dipyrinato complexes it should be known that they are

commonly referred to as 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene dyes for most laser applications and BODIPY dyes for biological applications, as dubbed by the company Molecular Probes upon commercialization.¹⁰⁴ The correlations between structure and photophysical and lasing properties, such as values for absorbance maxima wavelengths, molar absorptivities, fluorescence wavelengths, fluorescence quantum yields, oscillator strengths, Stokes shifts, lifetimes, radiative and non-radiative deactivation rate constants, lasing wavenumbers and lasing efficiencies for a variety of representative borondifluoride dipyrinato complexes in different solvents and polymeric solid matrices, were recently reviewed.¹⁰⁵ Although clearly worthy of several reviews of their own, this review will only focus upon the new structures and applications that are being developed for borondifluoride dipyrinato complexes. Some references which report chemical modifications of borondifluoride dipyrinato complexes are mentioned in section 3.1.7.

The optical properties of borondifluoride dipyrinato complexes make them attractive for use in multichromophoric systems. As previously mentioned, methods for tuning the wavelength of fluorescence emission maxima are under constant scrutiny. Extending the conjugation in the dipyrinato ligand can shift the typical emission maximum of the borondifluoride complex as much as 170 nm to longer wavelength without compromising molar absorptivity or quantum yield of fluorescence.^{13,106,107} Light-harvesting arrays are macromolecules that are used to study the intramolecular transfer of energy from absorbed photons between multiple chromophores.¹⁰⁸ Borondifluoride dipyrinato complexes have been used as building units in the construction of light-harvesting arrays which utilize both through-space (non-conjugated linker) and through-bond (conjugated linker) energy-transfer mechanisms. Studies of energy-transfer cassettes involving through-bond energy transfer, in which the energy donor (the high-energy absorbing chromophore) and acceptor (the low-energy emitting chromophore) are two different borondifluoride complexes, have yielded promising results.¹⁰⁹ Later studies have used anthracene as the donor or the acceptor for the dipyrinato complex.²⁴ The triplet emitting state of the borondifluoride dipyrinato unit was observed for the first time from a complex contained within a ruthenium(II)-terpyridine energy-transfer cassette.¹¹⁰ The authors proposed that interactions between the ruthenium terpyridine chromophore and the dipyrinato complex allowed for this first observation of the phenomenon.¹¹⁰ For the purposes of developing multichromophoric compounds for studying photoinduced electron-transfer reactions, borondifluoride dipyrinato complexes have been attached to calix[4]arenes¹¹¹ but more commonly to metalloporphyrins and porphyrin derivatives.^{35,112–123} A further discussion of the application of dipyrinato complexes in light-harvesting arrays is presented in section 3.1.5.

Similar to other types of dipyrinato complexes, the design of typical borondifluoride dipyrinato complex structures was revolutionized¹²⁴ by the popularization of techniques for the synthesis of 5-aryl-substituted dipyrins.¹²⁵ Alternatively, fluorescent aza derivatives have been reported in which the methine group typically in the 5-position of the dipyrinato ligand has been replaced with a nitrogen atom.^{126,127} Another class of structural variation that has recently been investigated involves modifying the substituents of the chelated boron atom. In one example, a dipyrinato ligand was found to bind the central boron atom in a tetradentate manner through the

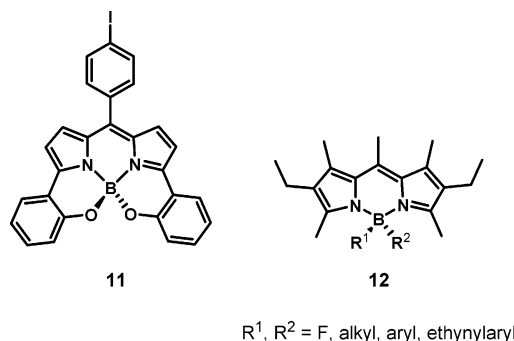


Figure 14. Boron substituent variations in dipyrinato complexes of boron.

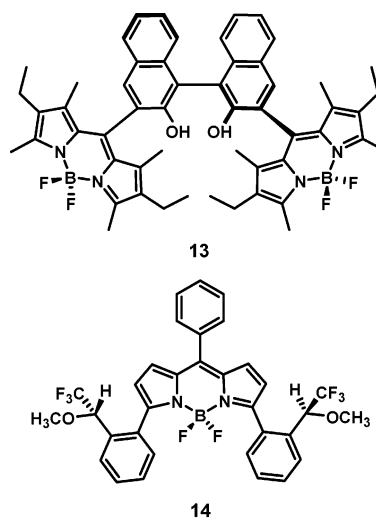


Figure 15. Chiral borondifluoride dipyrinato complexes.

dipyrinato nitrogen atoms as well as through the oxygen atoms of two phenolate substituents (compound **11** Figure 14).¹²⁸ Complex **11** was prepared as a racemic mixture of the helically chiral product.¹²⁸ This new type of highly rotationally constrained boron dipyrinato complex was shown to exhibit a fluorescence emission that was more intense, narrower, and significantly shifted to higher wavelength compared to borondifluoride derivatives.¹²⁸ In other reports, the fluorine substituents of the boron were replaced with a variety of alkyl, aromatic, and ethynylaromatic groups (**12** in Figure 14).^{129–132} This substitution was shown to cause desirable changes to the function of these molecules as fluorescent labels, minimizing fluorescence quenching of the dipyrinato complex upon conjugation to proteins and increasing the values of the Stokes shift between the lowest energy absorption band and the emission band.^{129,132} The terms “*F*-Bodipy” and “*E*-Bodipy” have been suggested to differentiate between borondifluoride dipyrinato complexes and complexes in which the fluorine atoms have been replaced by ethynyl substituents.¹³²

The synthesis of chiral borondifluoride dipyrinato complexes is a relatively unexplored area of research. In addition to the above-mentioned example of the helically chiral boron complex of the tetradentate dipyrinato ligand, there are only a few reports of such compounds in the literature. In one of these, enantiopure atropisomeric binaphthyl auxiliaries attached through the 5-position of the dipyrinato ligand were the source of chirality in a borondifluoride complex, **13** in Figure 15.^{133,134} Analysis of the rate of fluorescence quenching of the chiral borondifluoride dipyrinato complex **13** by amines revealed differential quenching by enantiomers of

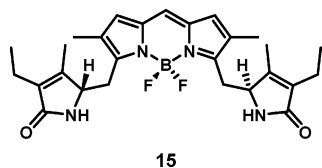


Figure 16. Chiral borondifluoride urobilin complex.

chiral amines.¹³⁴ It was proposed that the observed differential quenching rates could be exploited for chiral discriminations.

In another report regarding chiral borondifluoride dipyrinato complexes, aryl substituents bearing a stereogenic center serve as the source of chirality at either the 5- or 1,9-positions of the dipyrinato ligand.¹³⁵ The enantiomerically pure compounds, such as **14** (Figure 15), prepared in this study were found to exhibit relatively low circular dichroism and specific rotation ($[\alpha]^{20}_D$) values, compared to homochiral borondifluoride urobilin (Figure 16) complexes such as **15**.¹³⁶

The two new general areas of application for borondifluoride dipyrinato complexes most commonly discussed in the literature are as components of energy-transfer cassettes and light-harvesting arrays, discussed previously, and as fluorescent molecular sensors. Several examples have been reported involving biomolecular labeling by covalent attachment through an amide bond to a protein^{129,137,138} or oligonucleotide^{139–141} of interest. Generally, in molecular sensors the borondifluoride dipyrinato unit is covalently bound to a functional group that specifically targets an analyte. Binding of the analyte produces a measurable change in the spectroscopic properties of the borondifluoride dipyrinato fluorophore. Examples of this strategy include the use of pyridine substituents on borondifluoride dipyrinato complexes for sensing zinc(II) ions,^{36,37,142} zinc(II)bipyridyl substituents for sensing anions,¹⁴³ calix[4]arene substituents for sensing calcium(II) ions,¹⁴⁴ hydroxyl-quinoline substituents for sensing mercury(II) ions,¹⁴⁵ benzo crown ether substituents for sensing sodium(I) and potassium(I) ions,¹⁴⁶ aza-

crown ether substituents for sensing sodium(I) and calcium(II),¹⁴⁷ an oligothioether substituent for sensing copper(II),¹⁴⁸ a 1,2-diaminophenyl substituent that serves as a probe for nitric oxide,¹⁴⁹ and a phenylboronic acid substituent for sensing monosaccharides.¹⁵⁰ There have been several borondifluoride dipyrinato complexes developed for sensing pH. The dipyrinato substituent that undergoes chemical changes with changing pH includes a dimethylaminophenyl group,^{20,151,152} a phenol,¹⁵³ and a calix[4]arene.¹⁵⁴

3.1.5. Supramolecular Dipyrinato Metal Complexes

In the quest for efficient light-harvesting systems and linear arrays capable of efficiently transferring the energy from absorbed photons through multiple chromophores, as mentioned in section 3.1.4, dipyrins have been used as auxiliary pigments and linkers in multiporphyrin structures. Typically, porphyrins have strong absorption profiles in the blue region, but weak absorption throughout the rest of the visible spectrum limits their potential usefulness in light-harvesting arrays.⁴¹ Incorporation of auxiliary pigments that absorb in complementary regions has the potential to increase the efficiency of the light-harvesting array in porphyrin–zinc(II) dipyrinato–porphyrin triads such as **16** in Figure 17.⁴¹ In essence, the dipyrinato metal complex links the two porphyrin units together and simultaneously provides essential light-collection capabilities. Fluorescence studies have

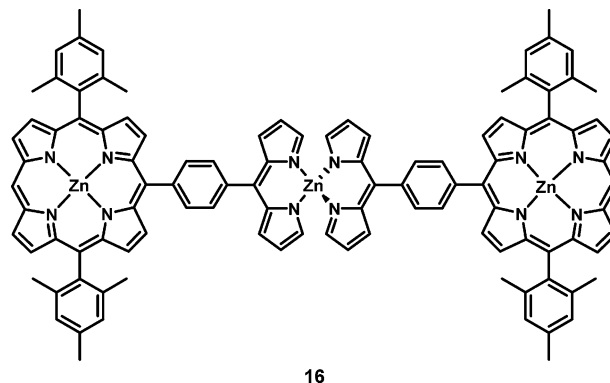


Figure 17. Porphyrin–zinc(II) dipyrinato–porphyrin light-harvesting triad.

indicated efficient energy transfer from the dipyrinato moiety to the porphyrin, making such triads promising leads in the quest for efficient light-harvesting systems.⁴¹ The ready self-assembly of homoleptic dipyrinato complexes, and thus the linking role of the unit, renders such complexes advantageous over borondifluoride dipyrinato complexes despite the longer excited-state decay of the latter. However, it is interesting to note that triads linked via dimeric dipyrinato zinc(II) complexes were found to be unstable to silica, and decomposition to the corresponding free-base ensued.⁴¹ Furthermore, it was postulated from results of electrochemical studies that oxidation of both porphyrin–dipyrinato zinc(II)–porphyrin triads and homoleptic dipyrinato zinc(II) complexes leads to demetalation.⁴¹ One approach⁴¹ used to prepare such triads involved the Suzuki coupling of 5-(4-iodophenyl)dipyrinato palladium(II) and a porphyrin appended with a boronic ester at a meso position (for more information, see section 3.1.7). Analogous arrays involve borondifluoride dipyrinato–porphyrin–borondifluoride dipyrinato triads such as **18a** (Figure 18) or the corresponding rhodium(I) complex **18b**.¹⁵⁵

A system involving a borondifluoride dipyrinato–porphyrin–porphyrin architecture, **19** in Figure 19, was reported as a suitable building block for incorporation into light-harvesting arrays designed as linear coordination polymers.⁴⁴ Self-assembly of this system resulted from the affinity of imidazoles for zinc(II)porphyrins, and so an imidazole-appended porphyrin and a borondifluoride dipyrinato complex-appended zinc(II)porphyrin strapped with a phenanthroline unit were brought into close proximity. The borondifluoride dipyrinato moiety absorbs energy which efficiently migrates to the porphyrin units. This self-assembled approach to light-harvesting arrays presents an attractive synthetic alternative to the use of covalent bonds to link appropriate absorbers and emitters. During attempts to form corroles, a phlorin–dipyrinato conjugate was isolated as a low-yield side product from the condensation/oxidation of perfluorinated benzaldehyde and 5-mesityldipyrin.¹⁵⁶

Multichromophoric systems containing ruthenium(II) tris(bipyridyl) complexes and borondifluoride dipyrinato units (Figure 20) allow electron-rich metal centers, effective energy-absorbing dipyrinato complexes, and electron-accepting bipyridyl ligands to be united in a single structure (**20**).⁴³ The twisted nature of the structure, courtesy of methyl substituents on the dipyrinato units, renders the dipyrinato and bipyridyl chromophores non-planar, and so conjugation of the two is prevented. As well as efficient intercomponent energy-transfer processes and rich reversible redox behavior, the complexes exhibit phosphorescence assigned to the

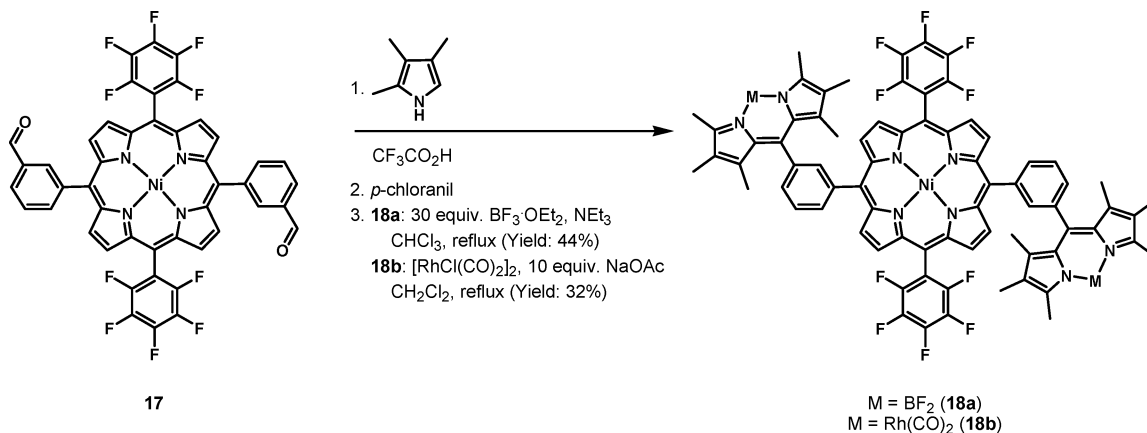


Figure 18. Dipyrin complex–porphyrin–dipyrin complex triad.

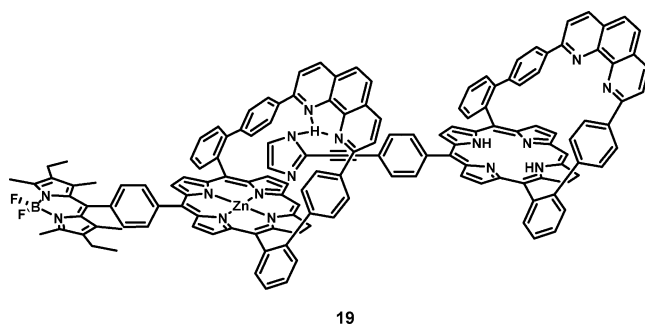


Figure 19. Borondifluoride dipyrinato–porphyrin–porphyrin triad.

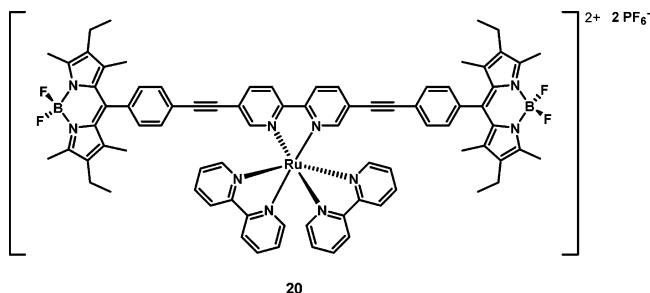


Figure 20. Borondifluoride dipyrinato–ruthenium(II) tris(bipyridyl) multichromophoric system.

borondifluoride dipyrinato units. The latter is believed to be an effective decay process due to the presence of the heavy ruthenium(II) center surrounded by bipyridyl ligands.

Trimeric dipyrinato cobalt(III) and iron(III) complexes of 5-(4-pyridyl)dipyrin self-assemble into heterometallic–organic frameworks in the presence of silver(I) salts.^{67,68} X-ray crystallography reveals that each silver(I) ion is coordinated to three pyridyl ligands in the extended framework as shown for **21** in Figure 21.⁶⁸ Given their facile synthesis, use of dipyrinato ligands within such networks allows the possibility to tune optical, magnetic, and fluorescent properties within the framework as well as develop porous materials with interesting photophysical properties. Furthermore, the octahedral coordination geometry of central metal ions provides an opportunity to create homochiral extended solids.^{68,157}

3.1.6. Heteroleptic Dipyrinato Complexes

With the steric requirements of 1,9-substituents forcing tetrahedral or octahedral coordination geometry in homoleptic dipyrinato complexes, heteroleptic (those bearing two or

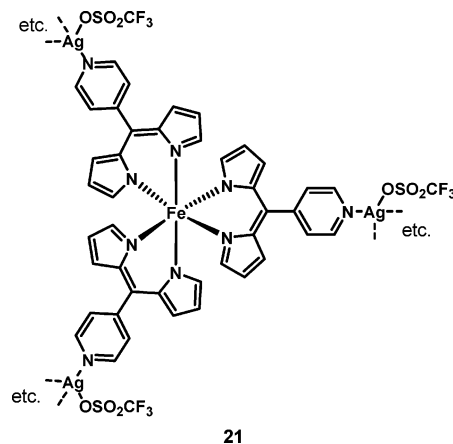


Figure 21. Silver(I)–iron(III) dipyrinato coordination polymers.

more different ligands on a metal center) complexes of dipyrins facilitate formation of square-planar coordination geometry. For example, a bridged dimeric complex **23** and the heteroleptic complex **24** were proposed for the products formed from dipyrin **22** and palladium(II) (Figure 22).¹¹ The structure of heteroleptic **24** was later confirmed by X-ray analysis, with the dipyrinato unit coordinated as a mono-anionic bidentate ligand and the dipyrin coordinated as a neutral unidentate ligand.⁸⁷ With mercury(II) the constitution of the complex depended upon the salt used; mercury(II) nitrate gave a homoleptic dipyrinato mercury(II) complex with **22**, and mercury(II) chloride gave a heteroleptic chlorodipyrinato mercury(II) complex.¹¹

Heteroleptic complexes of rhodium(I) were reported to form upon reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with dipyrins in the presence of sodium acetate.⁸⁶ The complexes contained a bidentate dipyrinato ligand and two CO ligands. Treatment of the rhodium(I) complexes with either bromine or chlorine returned the HBr/HCl salts of the original dipyrins, as mentioned previously. The octahedral heteroleptic chromium(III) complex **26** was formed upon reacting chromium(II)-acetate with dipyrin **25** (Figure 23). In-situ oxidation of the chromium(II) ion gave the appropriate oxidation state to accommodate the 1,9-dimethyl groups of the dipyrinato ligand in an octahedral geometry.⁶³ It has also been reported that use of an excess of cobalt(III) salt in the complexation of 5-aryl dipyrins resulted in inseparable mixtures, presumably due to formation of heteroleptic complexes.⁶

A recent resurgence in interest in heteroleptic dipyrinato complexes has stemmed from the discovery that such complexes are useful in the construction of extended

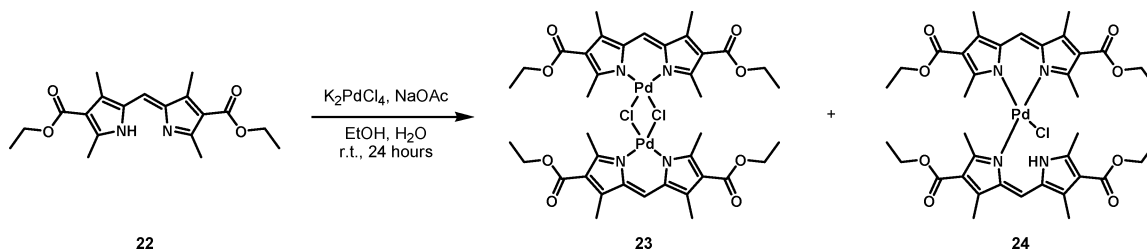


Figure 22. Formation of bridged dimer and heteroleptic palladium(II) dipyrinato complexes.

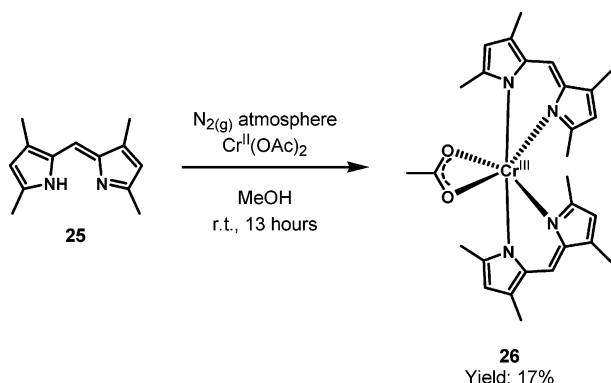


Figure 23. Formation of a heteroleptic chromium(III) dipyrinato complex.

networks and coordinative polymers. Homoleptic complexes of copper(II) are often formed when 0.4 equiv of the metal salt are used in the complexation reaction.⁸² Heteroleptic complexes are more likely to be formed in the presence of stoichiometric amounts (or excess) of metal salt, as expected. Acetylacetonato ligands (acac) and the hexafluoro derivative (hfacac) make excellent ancillary ligands for heteroleptic dipyrinato complexes, as the steric encumbrances near the metal center are minimal (unlike that for the 1,9-substituents of dipyrins).¹⁵⁸ Heteroleptic complexes of this type can accommodate square-planar coordination geometry, as for copper(II) and palladium(II),¹¹ and this coordination is responsible for many of the extended networks reported. For example, **27** formed the discrete heteroleptic complex **28** with copper(II), but the pyridyl derivative **29** formed the heteroleptic complex **30** (Figure 24).

The discrete head-to-tail cyclic dimer **32** is formed upon reaction of one equivalent of $Cu(hfacac)_2$ with two equivalents of 5-[3-(methylthio)phenyl]dipyrin, formed in situ from the corresponding dipyrromethane (**31** in Figure 25).⁸¹ The dimer is held together by two weak sulfur–copper(II) interactions between the thioether moiety of one dipyrinato ligand and the copper(II) center bound to the other dipyrinato ligand. The isomeric dipyrin **33** (Figure 26) gives extended helical copper(II) coordination polymers upon reaction with $Cu(hfacac)_2$, whereby the thioether moiety weakly binds to the axial position of a square-pyramidal copper(II) center in a neighboring unit. The trifluoromethyl groups are oriented in the solid state with self-aggregation, reminiscent of phase separation in fluoroalkanes. This interaction is extremely important to the stability of the polymer as complexation of copper(II) acetylacetonate with **33** gave a heteroleptic complex that decomposed during isolation to give the homoleptic dipyrinato complex. Such disproportionation is common between solution and solid-state dipyrin chemistry.¹⁵⁹ Fluorine–fluorine interactions also dominated the tendency of 5-quinoline-substituted dipyrins to self-assemble into extended heteroleptic coord-

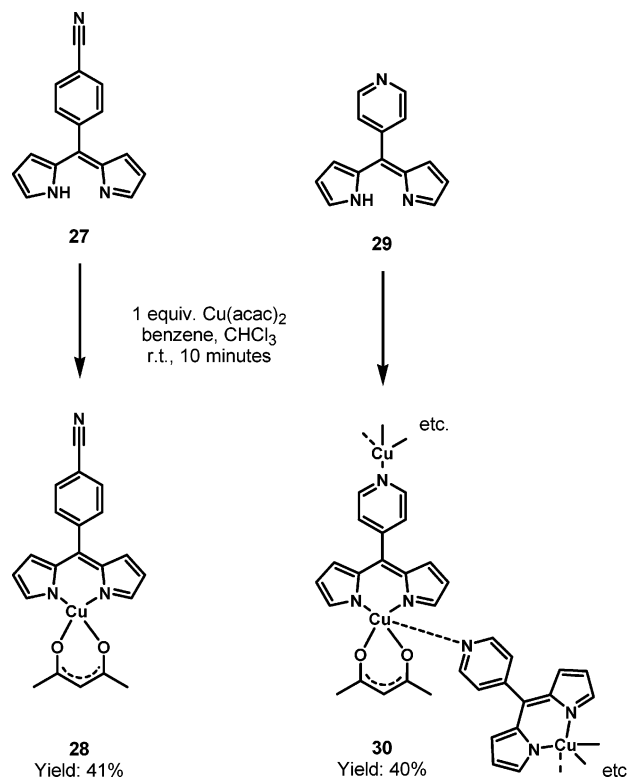


Figure 24. Heteroleptic copper(II) dipyrinato complexes.

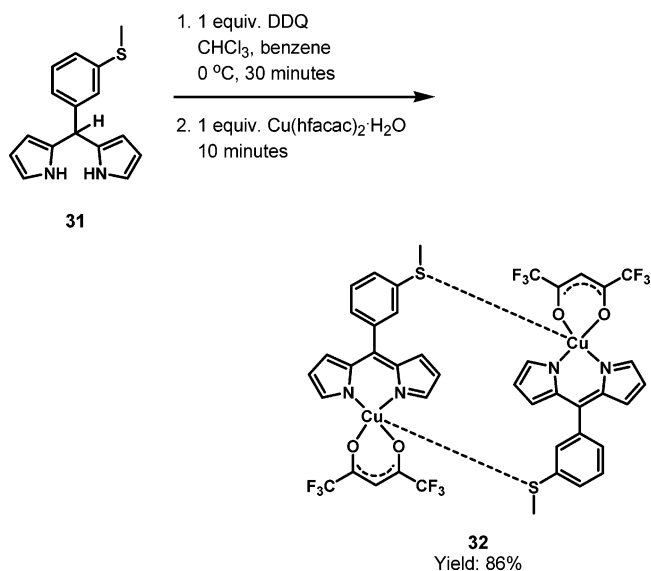
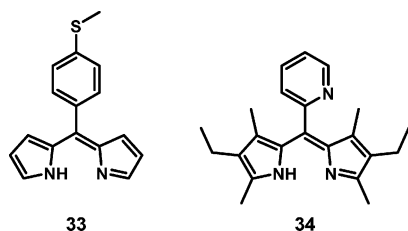


Figure 25. Heteroleptic head-to-tail copper(II) dipyrinato(hfacac) complex dimer.

dination polymers.¹⁶⁰ Another discrete heteroleptic head-to-tail cyclic dimer, $Zn_2(dipyrinato)_2Cl_2$, was formed when 5-pyridyl-substituted dipyrin (**34**) was reacted with zinc(II) chloride. The dimer was found to be held together by each

**Figure 26.** 5-Aryl dipyrriins.

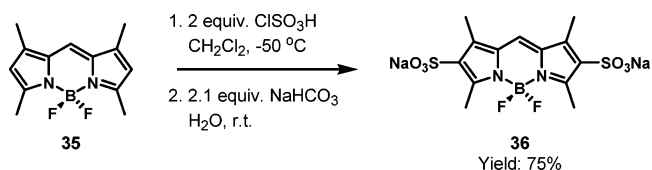
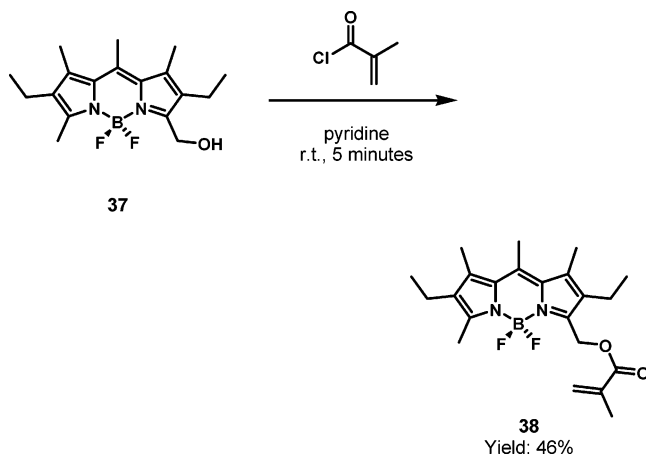
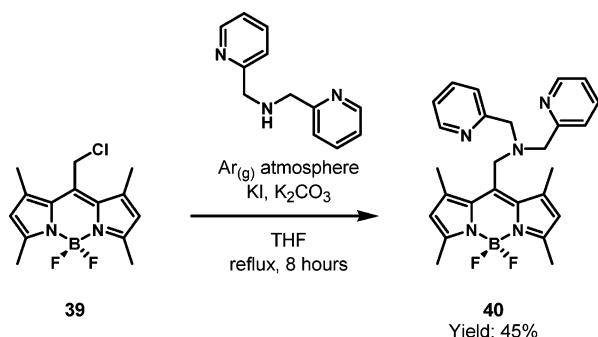
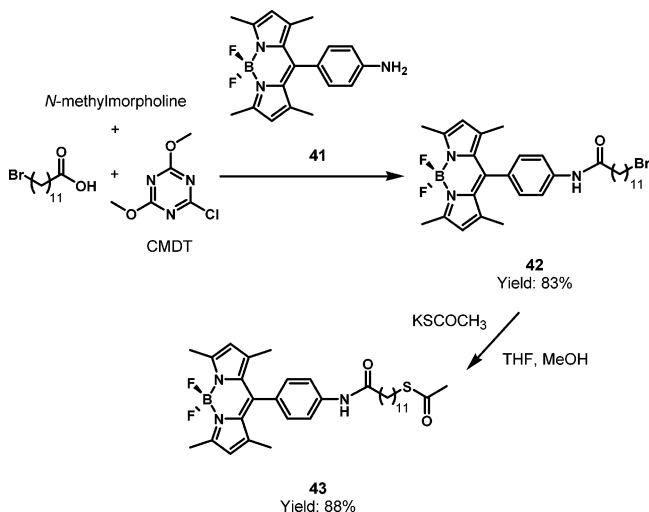
tetrahedral zinc(II) being coordinated to one bidentate dipyrriinato ligand and the pyridyl moiety of the other dipyrriinato ligand.¹⁶¹

This work has been extended to include dipyrriins substituted in the 5-position by aryl rings with appended 4-methanoate, 4-amido, and 4-nitro groups, and the magnetic and thermal properties of complexes formed from such ligands have been studied.¹⁶² Upon formation of square-planar heteroleptic complexes containing copper(II), the amido and nitro groups enabled formation of polymeric chains in the solid state through hydrogen bonding and coordinative contacts, respectively. The ester functional group has been used to immobilize a dipyrriin onto Wang resin, and subsequent reaction with stoichiometric amounts of copper(II) acetylacetonate gave immobilized heteroleptic Zn-(dipyrriinato)(acac) complexes. An interesting feature of such immobilized complexes lies in the ability of the swollen polymer to react reversibly with pyridine.

A variety of studies involving solutions of dipyrriins and their complexes have been reported.^{49,159,163,164} The solid-state structure and structure in solution of dipyrriinato complexes often vary, and a heteroleptic complex probably precedes formation of the homoleptic complex. Absorption spectroscopy solution studies involving complexation of dipyrriins and copper(II) chloride or zinc(II) acetate have been reported to exhibit an isosbestic point, whereas those involving copper(II) acetate do not.¹⁶⁴ Job plots revealed stoichiometric ratios between 1:1 and 2:1 [dipyrriinato:Cu(II)], and isolation of complexes gave both homoleptic dipyrriinato complexes and heteroleptic acetato dipyrriinato complexes. A serious complication arising from the somewhat broad absorption profile for the dipyrriinato unit, as well as overlapping signals for ligand, homoleptic, and heteroleptic complexes, lies in the analysis of electronic absorption spectra corresponding to complexation reactions. With a number of heteroleptic species being possible along the reaction pathway, ¹H NMR spectroscopy has emerged as a useful technique for following the progress of complexation reactions.¹⁵⁹

3.1.7. Chemical Manipulations of Dipyrriinato Complexes

Performing chemical manipulations to elaborate and modify dipyrriinato metal complexes is an underdeveloped area of research. In these reactions the metal ion to which the dipyrriinato ligand is complexed serves as a protecting group for the nitrogen atoms of the corresponding free-base dipyrriins. Strongly acidic and/or reductive conditions are

**Figure 27.** Sulfonation of dipyrriinato complex.**Figure 28.** Esterification of a dipyrriinato complex substituted with an alcohol.**Figure 29.** Manipulation of a dipyrriinato 5 substituent.**Figure 30.** Use of an amide coupling reagent with an amine-substituted borondifluoride dipyrriinato complex.

known to decomplex the metal ion, that is deprotect the dipyrriin nitrogen atoms, so these conditions are usually avoided during chemical manipulations of the dipyrriinato ligand. The majority of the known reactions fall within three general categories: substitutions, functional-group interconversions, and metal-catalyzed cross-coupling reactions.

Substitution reactions will be considered first. Sulfonation reactions of borondifluoride dipyrriinato complexes in attempts to prepare water-soluble fluorescent probes and LASER dyes, as shown in Figure 27, were the first reported successful substitutions of metal dipyrriinato complexes.^{165,166} The increased nucleophilicity of the 2,8-positions over the

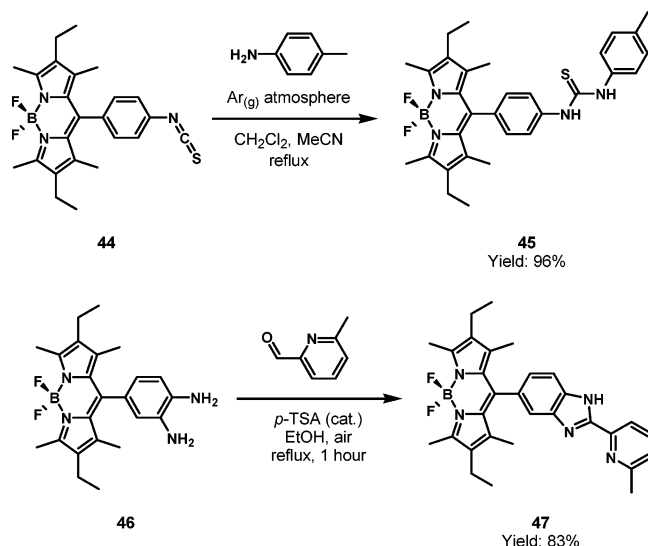


Figure 31. Derivatization of 5-substituted amino-aromatic dipyrinato complexes.

5-position within complex **35** results in selective substitution with sulfonate groups to give disulfonate **36** in acceptable yields.

Other examples of substitution reactions include those in which the derivatization transformation occurs at a substituent on the dipyrin ring. One example of this, shown in Figure 28, is the esterification of the hydroxy group within dipyrinato complex **37** with an acrylate to give **38**, appropriately substituted for subsequent polymerization reactions.¹⁶⁷

Another example is substitution of the alkyl chloride within dipyrinato complex **39** with an amine to form the tertiary amine **40**, as shown in Figure 29.¹⁴²

It has been demonstrated that borondifluoride dipyrinato complexes are compatible for use with the amide coupling reagent 2-chloro-4,6-dimethoxy-1,3,5-triazine (CMDT). The 5-aniline substituent within **41** (Figure 30) was used to prepare amide **42**, which was then thio-alkylated to give **43**.¹¹⁶

It has also been demonstrated that primary amino groups present on 5-aryl substituents of borondifluoride dipyrinato

complexes can be quantitatively transformed into isocyanate or isothiocyanate groups (as in **44**), which can subsequently undergo transformations to give ureas and thioureas (as in **45**), respectively, by reaction with amines.⁴⁰ In addition, diamino-substituted 5-aryl substituents (as in **46**) can be transformed into polyimine derivatives (as in **47**).⁴⁰ Some of these reactions are illustrated in Figure 31.

Difficulties have been reported for efforts to dehydrogenate rings attached to dipyrins, attempted with the hope of increasing conjugation to the dipyrin rings.^{107,168} Two examples of dehydrogenations involving borondifluoride dipyrinato complexes are shown in Figure 32. In the first example borondifluoride complex **48** was reacted with 10 mol equiv of DDQ in an attempt to dehydrogenate the 1,2-butadiyl substituents and give compound **50**.¹⁶⁸ However, the ketone derivative **49** was the only product isolated, formed via a proposed mechanism of hydride abstraction, subsequent trapping of the carbocation with water, followed by oxidation.¹⁶⁸ In the second example DDQ is used in an attempt to prepare boron difluoride complex **53** by dehydrogenation of the methylene groups in compound **51**.¹⁰⁷ A product, **52**, was obtained in which one side of **51** had undergone dehydrogenation. Increasing the number of molar equivalents of DDQ failed to provide the desired product, and increasing the temperature of the reaction resulted in decomposition of the starting material.¹⁰⁷ Computational modeling of the reaction to dehydrogenate **51** to give **52** and then **53** revealed that the activation energy required to transform **52** to **53** was prohibitively high as a result of the strong steric interactions created between the hydrogen atoms of the aryl rings and the fluorine atoms when the dipyrin ligand of the product is made planar upon dehydrogenation.¹⁰⁷

Oxidations of methyl groups on the dipyrin rings of borondifluoride dipyrinato complexes can be performed as shown in Figure 33.^{167,168} In one example of this reaction the 1-methyl group of the dipyrinato complex **54** was oxidized to a formyl group using DDQ.¹⁶⁸ The resulting aldehyde (**55**) was reduced to the corresponding alcohol, **56**, by hydrogenation, with formation of two side products: dipyrromethane **57** and regenerated **54**.^{167,168} Alternately,

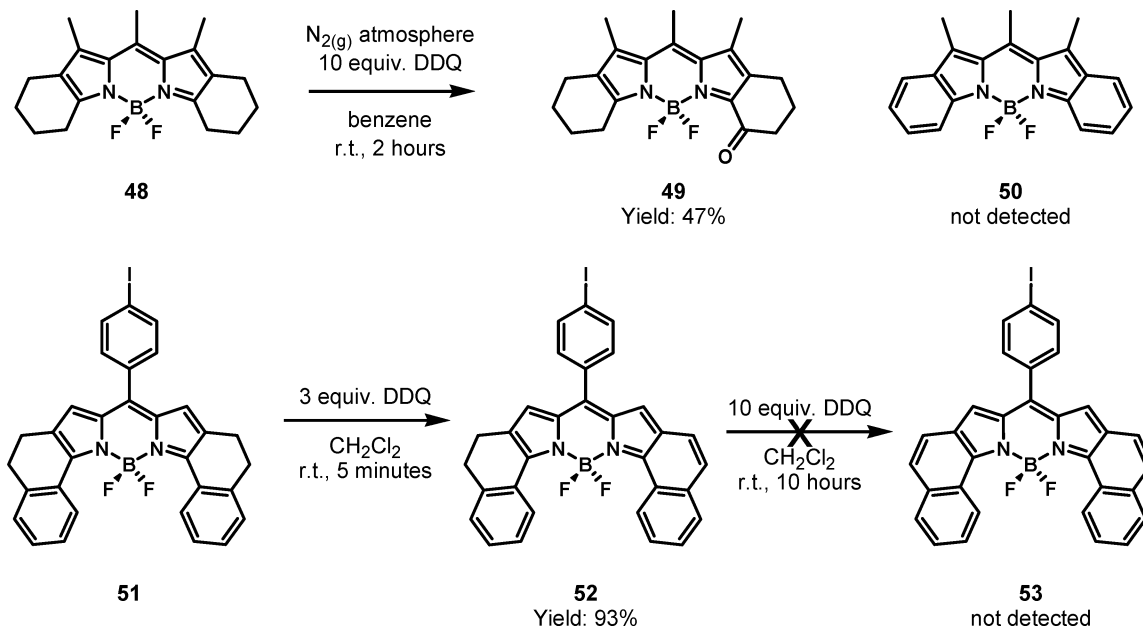


Figure 32. Dehydrogenations of dipyrin substituents.

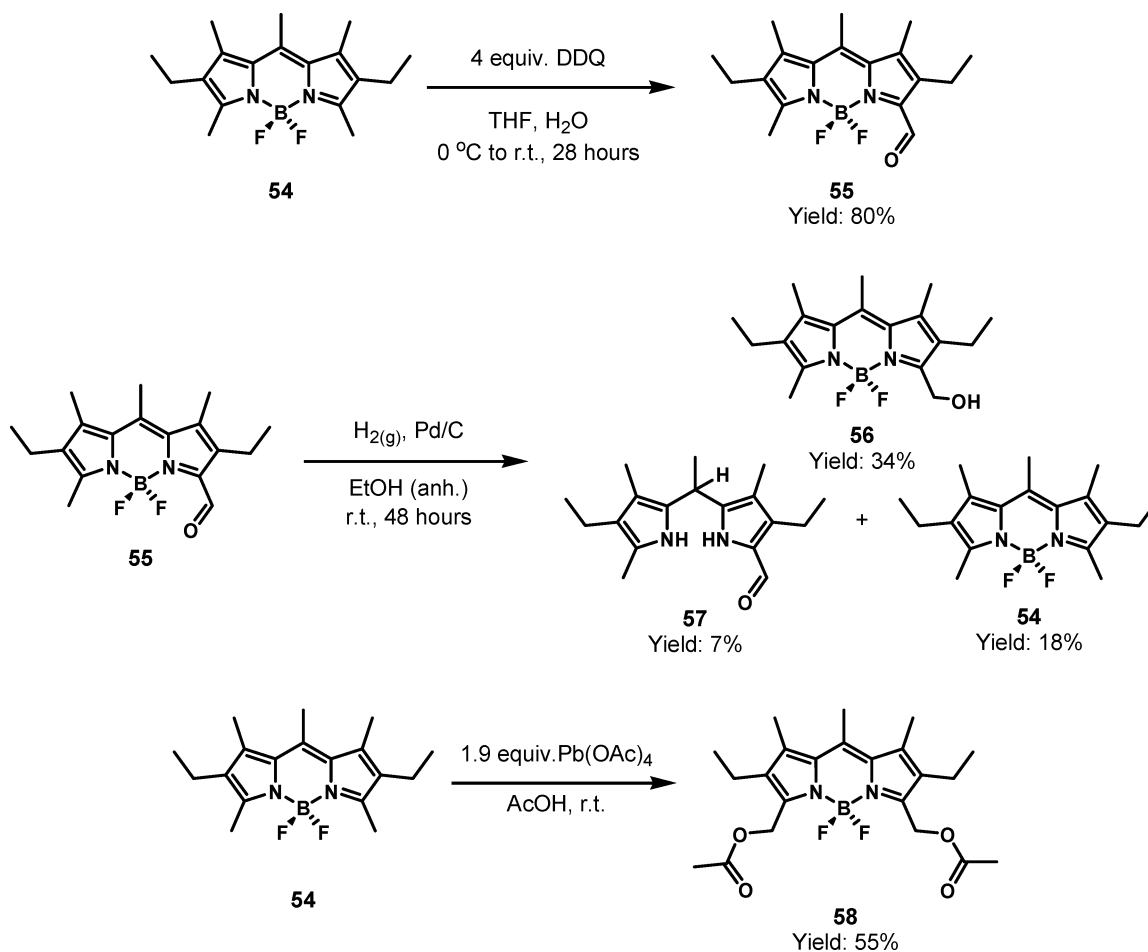


Figure 33. Examples of 1-methyl oxidations and reductions in dipyrinato complexes.

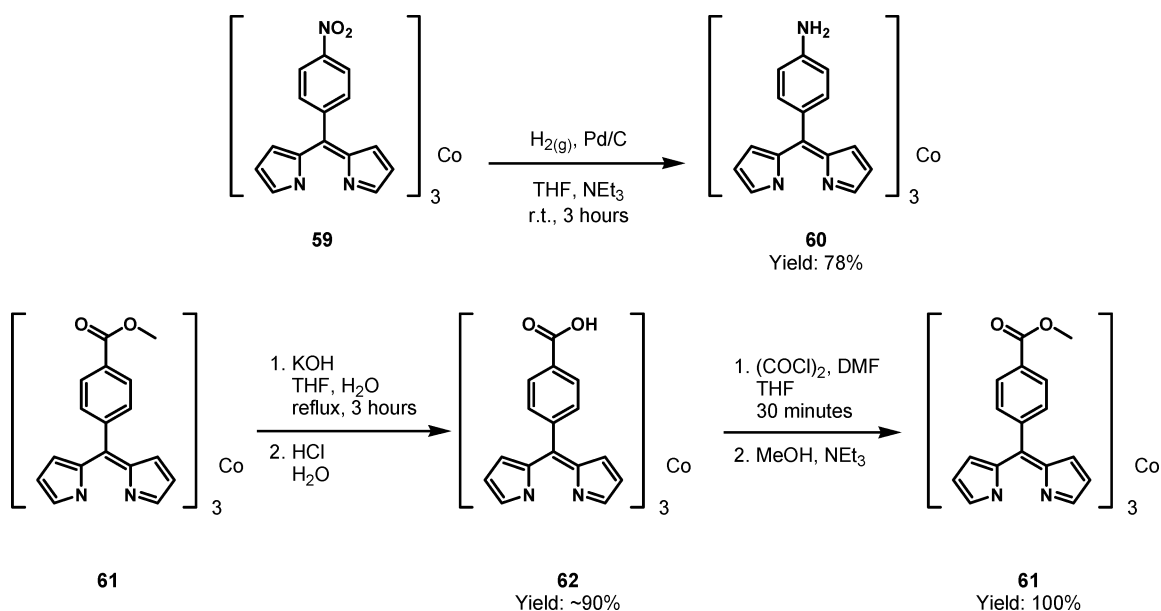


Figure 34. Manipulation of nitro and methyl carboxylate functional groups on aryl rings of 5-substituted dipyrinato complexes.

methyl substituents have been shown to undergo oxidation by lead tetraacetate exemplified by the transformation of dipyrinato complex **54** into **58**, a reaction traditionally used for oxidation of α -methyl groups of pyrroles.¹⁶⁸

Manipulations of functional groups on 5-aryl substituents of complexed dipyrinato ligands are also known: for example, hydrogenation of the nitro group of cobalt(III)

complex **59** to yield an amine, **60** (Figure 34).^{6,40,116} In an interesting demonstration of the ability to perform manipulations of the functional groups present in dipyrinato metal complexes the methyl ester of **61** (Figure 34) was saponified and then reformed through a series of organic procedures.⁶

A particularly interesting example of the chemistry of dipyrinato complexes chemistry is the retro-Diels–Alder

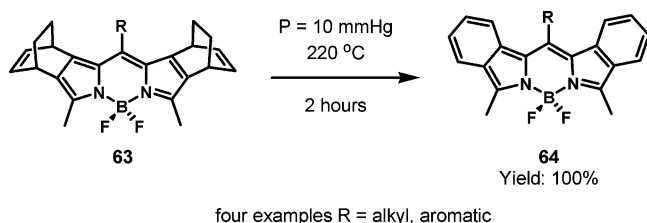


Figure 35. Retro-Diels–Alder reaction performed upon a substituted borondifluoride dipyrinato complex.

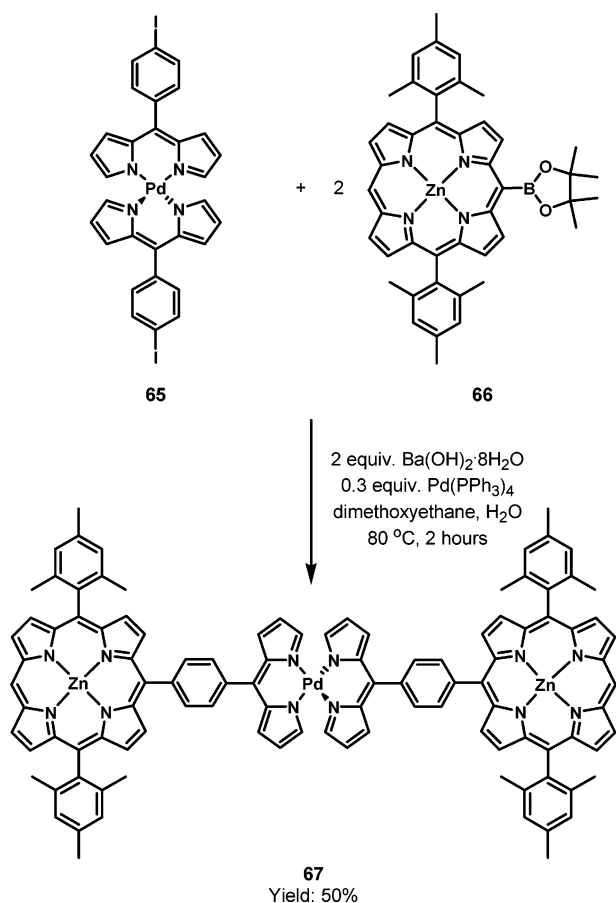


Figure 36. Suzuki cross-coupling reaction involving a palladium(II) dipyrinato complex.

reaction to prepare the benzo-fused borondifluoride dipyrinato product **64**, as shown in Figure 35.¹⁶⁹ The reactant dipyrinato complex **63** was prepared by condensation of two equivalents of the corresponding tricyclic pyrrole precursor with one equivalent of an alkyl or aryl acid chloride, followed by subsequent boron complexation.

The final, and by far the largest, category of chemical transformations that are performed upon dipyrinato complexes are the metal-catalyzed cross-coupling reactions. Palladium-catalyzed Suzuki couplings are poisoned by free-base dipyrrens and zinc(II) and copper(II) complexes of dipyrrens, and this was attributed to the sequestration of palladium from the catalyst.⁴¹ The corresponding palladium(II) dipyrinato complex **65** is compatible with Suzuki coupling as shown in Figure 36, a method used for the synthesis of the porphyrin–zinc(II) dipyrinato–porphyrin triad **16** (Figure 17) via the palladium(II) dipyrinato precursor **67**.⁴¹

Macromolecular light-harvesting arrays are commonly prepared by the coupling of borondifluoride dipyrinato units with porphyrins by means of the Sonagashira reac-

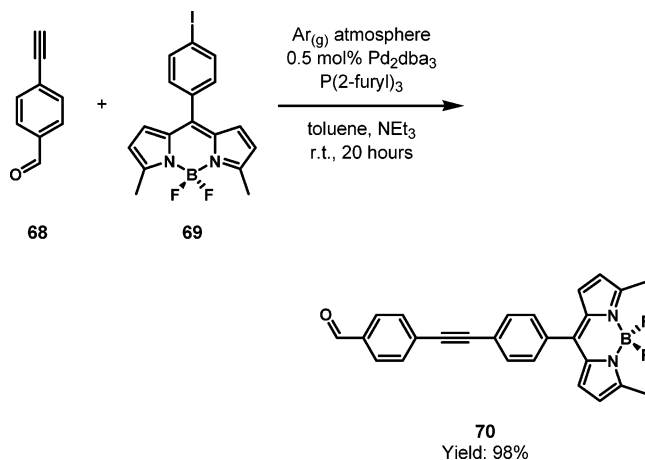


Figure 37. Sonagashira reaction involving a dipyrinato complex.

tion^{38,39,42,109,113,119,129,170} or modifications thereof.^{114,119} An example of the application of borondifluoride dipyrinato complexes in the Sonagashira reaction is shown in Figure 37 in which an alkyne, **68**, is coupled to 5-(4-iodophenyl)dipyrinato complex **69** to yield **70**, the precursor to a borondifluoride dipyrinato–porphyrin light-harvesting array.¹¹³

The brevity of this summary illustrates the lack of information regarding chemical elaboration of dipyrinato complexes and demonstrates that present knowledge is mostly based upon manipulations of dipyrinato complexes of borondifluoride. This reflects the great interest in modification of these complexes to fine tune their optical properties or attach selective binding receptors as mentioned in section 3.1.4. Dipyrinato complexes tend to be more crystalline and have superior chromatographic properties to dipyrrens because the former are generally less polar, more highly visible due to their intense colors, more stable, and less prone to trailing on silica stationary phases. For these reasons it would be advantageous to develop a more diverse repertoire of reactions that could be used to perform modifications of dipyrinato complexes.

3.2. Properties

The significance of dipyrinato metal complexes in the study of coordination chemistry became apparent not long after their initial discovery. The steric interactions between 1,9-substituents of the dipyrrens,¹¹ even those as small as hydrogen atoms, were found to distort the geometry of coordination about the metal ions, as discussed in section 3.1.3. As such, even those metal(II) ions for which square planarity is usually the preferred geometry were found to adopt pseudotetrahedral coordination geometry.^{171,172} These deviations from theory prompted extensive studies of properties such as conductivities,¹⁷³ magnetic susceptibility,^{64,66,73,76} ligand-field parameters,^{64,75,79} X-ray crystal structures,^{62,76,87,171,172} and spectroscopic behavior from absorption spectra,^{61,64,66,73–77,79,83,87} X-ray powder spectra,^{73,77} IR spectra,^{61,64,66,74,75,77,83} ¹H NMR spectra,^{61,76,83,86,87,174} and ESR spectra^{77,80} for a wide variety of dipyrinato metal complexes, as previously summarized.⁴⁶

The complexation process of dipyrrens has recently been studied using several spectroscopic techniques. Absorption spectroscopy, calorimetry, and ¹H NMR spectroscopy were used to prove the existence of heteroleptic dipyrinato metal complexes as intermediates in the complexation of metal ions

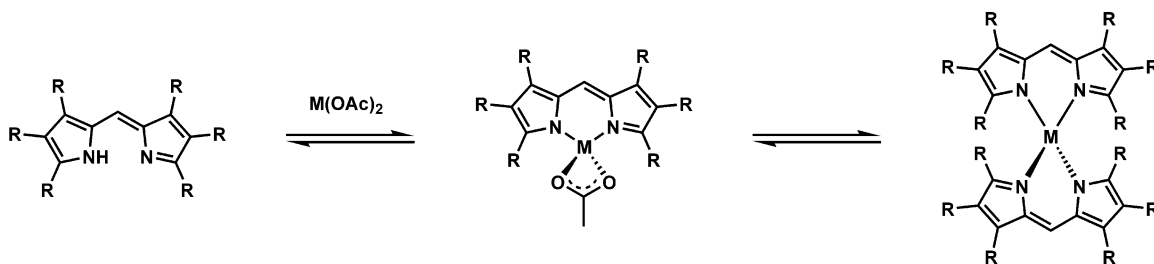


Figure 38. Formation of homoleptic dipyrinato metal complexes through a heteroleptic intermediate.

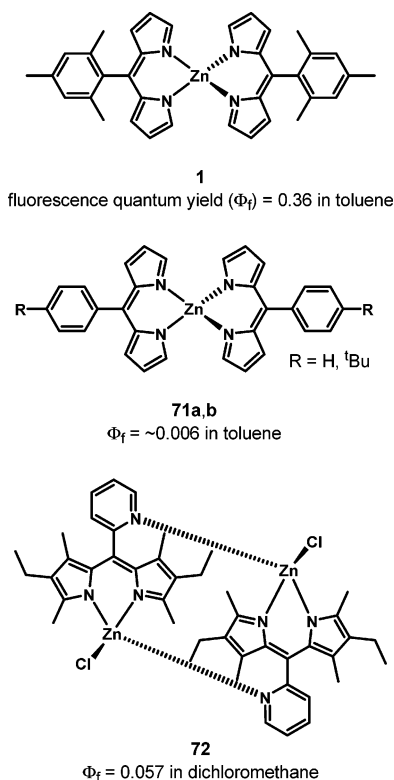


Figure 39. Fluorescent and nonfluorescent zinc(II) dipyrinato complexes.

by dipyrins to form homoleptic complexes as seen in Figure 38 and discussed in section 3.1.6.^{159,175} Some thermodynamic data, including equilibrium constants, have been reported^{48,163,176–178} for the dipyrin complexation process, although the calculations did not account for the existence of the heteroleptic intermediates that were observed by others. However, more recent publications do confirm the observation of the heteroleptic intermediates.^{179,180} The studies reveal that the equilibria can be shifted toward formation of homoleptic dipyrin complexes by a number of factors including the basicity of the medium¹⁷⁵ and the coordination ability of the metal salt anion^{175,180} (i.e., metal chlorides do not form heteroleptic dipyrin complexes as readily as metal acetates, acetylacetonates, or valinates).

3.2.1. Fluorescent Dipyrinato Metal Complexes

Homoleptic dipyrinato metal complexes were long thought to be non-fluorescent, in contrast to their highly fluorescent boron–dipyrinato analogues. In 2004 it was reported that the zinc(II) dipyrinato complex **1** in Figure 39, prepared from 5-mesityldipyrin, was highly fluorescent with a multi-nanosecond singlet excited-state lifetime:⁸⁴ 5-phenyl and 5-(4-*tert*-butylphenyl) substitution results in very weak emitters with rapidly deactivating excited-state lifetimes as

seen for compounds **71a** and **71b**. Presumably the 2,6-methyl groups of the mesityl group within **1** prohibit internal rotation, and so steric constraints drastically enhance the excited-state lifetime of complexes involving 5-mesityldipyrinato ligands. Such properties are of interest in applications whereby intense absorption and fluorescence attributes in the visible region are desirable. Furthermore, the ability of dipyrins to self-assemble makes them attractive synthetic linking tools for such applications (see section 3.1.5). Homoleptic gallium(III) and indium(III) analogues of **1** exhibit less intense fluorescence.⁸⁵ Another example of increased fluorescence resulting from inhibition of the rotation of an aryl group in the dipyrin 5-position involves a 5-(2-pyridyl)dipyrinato ligand which forms a head-to-tail cyclic dimer, **72** in Figure 39, upon complexation with zinc(II) chloride.¹⁶¹ The heteroleptic dimer contains two tridentate ligands, two zinc(II) centers, and two coordinated chloride ions. The pyridyl moiety occupies a tetrahedral zinc(II) binding site, and so rotation of the pyridyl group, relative to the dipyrinato unit, is prohibited.

3.2.2. Electrochemical Studies of Dipyrinato Complexes

Electrochemical studies of dipyrinato complexes have shown consistent behavior for ligand-centered oxidations and reductions with some affects due to molecular structure. The redox behavior of free-base dipyrins has been investigated^{99,181–183} and shown to be similar when compared to that of their protonated forms, although with somewhat lower oxidation potentials, which can be rationalized by the reduced electron availability in the protonated systems.¹⁸³ The electrochemical properties of dipyrinato complexes exhibit differences that are related to the identity of the complexed metal ions.^{181,182,184} For dipyrins with aromatic substituents in the 5-position, the Hammett constants for the various aromatic substituents have been shown to directly correlate to the redox potentials of the corresponding nickel(II) dipyrinato complex.¹⁸¹

Nickel(II),¹⁸¹ copper(II),^{182,184} and palladium(II)¹⁸⁴ complexes of 5-aryl-1,1'-bis(dipyrin)s exhibit two reversible redox couples, although observation of the second reduction is limited by the electrolytic discharge limit.¹⁸¹ Iron(III) complexes of 5-aryl dipyrins display one quasireversible one-electron oxidation that is not greatly affected by the substituents of the 5-aryl group.^{8,42} Zinc(II) complexes of 5-aryl dipyrins have been shown to undergo two highly irreversible one-electron oxidations.⁴¹ The irreversibility of the oxidations is attributed to demetalation of the complex upon formation of the mono- or dication in solution.⁴¹ The electrochemical behavior of borondifluoride dipyrinato complexes is routinely measured as part of their characterization,^{20,24,37,39,40,43,107,110,113,116,121,123,130–133,146,149,169,185,186} and such information is often used to calculate HOMO–LUMO gaps for energy diagrams.^{43,181} Generally, borondifluoride dipyrinato complexes have been shown to undergo one

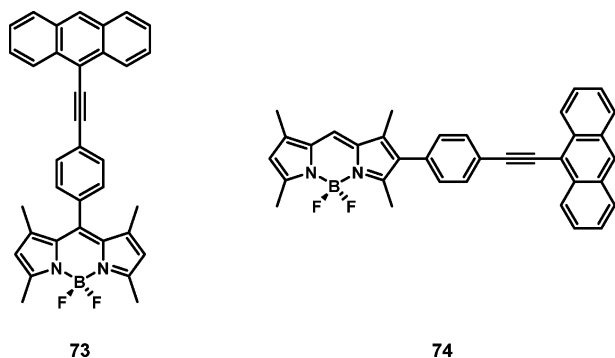


Figure 40. Differently substituted borondifluoride dipyrinato complexes with similar redox behaviors.



Figure 41. Three possible configurations for calix[4]phyrin(1.1.1.1)s.

reversible one-electron oxidation and one reversible one-electron reduction,¹³² although scanning with cyclic voltammetry at more positive and negative potentials than are routinely used has revealed additional irreversible redox reactions.¹²¹ Substitution with electron-donating groups and functional groups that increase conjugation has been found to stabilize the radical cation formed upon oxidation during the electrochemical studies and therefore make the oxidation potential of borondifluoride dipyrinato complexes substituted in this manner less positive. Alternately, substitution with electron-withdrawing groups has been found to make the oxidation potential more positive.^{38,40,43,106,146,149} The site of substitution of conjugated groups on the dipyrin structure has been shown to have little effect upon the redox potentials of borondifluoride dipyrinato complexes;^{24,106} indeed, compounds **73** and **74** (Figure 40) have effectively the same redox profile.²⁴ Some borondifluoride complexes of 5-pyridyl dipyrins have been shown to possess electrochemical properties that are in exception to those of typical complexes when measured in dichloromethane.³⁸ This observation, which has been attributed to reaction of the radical cation formed upon oxidation with the solvent, can be eliminated by recording the cyclic voltammograms in acetonitrile.³⁸ In compounds that contain more than one borondifluoride

dipyrinato unit it has been observed that the units undergo reduction at different potentials, indicating that the units do not interact with each other.^{43,110}

4. Related Dipyrin Structures

4.1. Calix[4]phyrin(1.1.1.1)s

The calix[4]phyrin(1.1.1.1)s, also known as *trans*-porphodimethenes, 5,15-porphodimethenes, or α,γ -dihydroporphyrins, are a popular class of cyclic bis(dipyrin)s. A review from 2001 presents a well-written history of porphomethenes and porphodimethenes.¹⁸⁷ Calix[4]phyrin(1.1.1.1)s differ structurally from porphyrins by the sp^3 hybridization of two opposing meso positions, which results in a loss of the macrocyclic aromaticity and gives them a non-planar structure of two dipyrins bound together in a macrocycle. Like other dipyrins, they have the ability to form complexes with a wide variety of metal ions.

For molecules in which the two substituents at each of the sp^3 -hybridized meso-like centers are not equivalent calix[4]phyrin(1.1.1.1)s can, with the assumption of tautomerization involving exchange of a hydrogen atom between the two nitrogens of each dipyrin unit, form with three different configurations (Figure 41): *anti*, *syn-equatorial*, and *syn-axial*. Solid-state data has shown that *syn-axial* is generally the configuration of the major products of calix[4]phyrin(1.1.1.1) syntheses.

The existence of calix[4]phyrin(1.1.1.1)s was first proposed based upon spectroscopic data collected during the process of oxidizing calix[4]pyrroles (porphyrinogens) to porphyrins¹⁸⁸ and during the reduction of porphyrins.^{189–191} Support for their proposed structure was provided through isolation of a zinc(II) complex of a calix[4]phyrin(1.1.1.1) during porphyrin synthesis¹⁹² and by a variety of metal complexes obtained through reductive alkylation of metallo-octaethylporphyrins.^{193–196}

Historically the substituents of the sp^3 -hybridized carbon atoms included at least one hydrogen atom, which generally made the *trans*-porphodimethenes unstable because they could dehydrogenate to form porphyrins¹⁹³ or rearrange to form chlorins.^{194,196} Diversification of the methods for calix[4]phyrin(1.1.1.1) synthesis have allowed for placement of two substituents at each of the sp^3 -hybridized meso-like centers, making the molecules more resistant to oxidation and rearrangement. Most synthetic pathways to *trans*-porphodimethenes produce products in which the two sp^3 -hybridized meso-like centers bear the same substituents. These methods include the following: (1) photoreduction

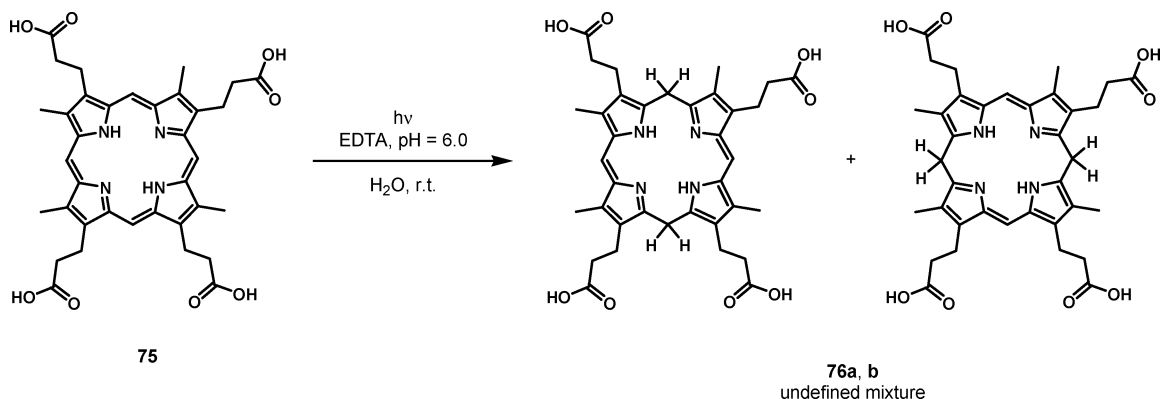


Figure 42. Calix[4]phyrin(1.1.1.1) synthesis by photoreduction of porphyrins.

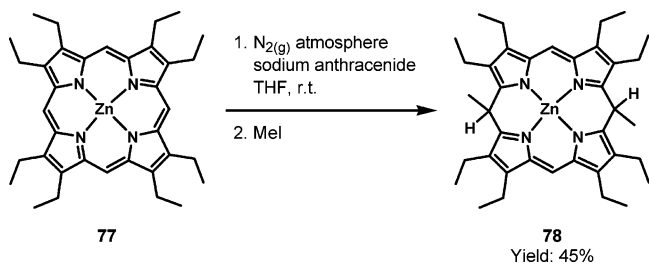


Figure 43. Calix[4]phyrin(1.1.1.1) synthesis by reductive *meso*-alkylation of porphyrins.

of porphyrins (Figure 42),¹⁸⁹ (2) reductive *meso*-alkylation of porphyrins (Figure 43),¹⁹⁷ (3) oxidation of calix[4]pyrroles (Figure 44),¹⁹² (4) dealkylation of calix[4]pyrroles (Figure 45),¹⁹⁸ and (5) acid-catalyzed condensation of pyrrolic compounds with carbonyl-containing molecules, followed by oxidation as appropriate. The fifth category of calix[4]phyrin(1.1.1.1) synthesis includes the methods most commonly used by current researchers. Many variations of this strategy have been examined,^{199–201} as shown in Figure 46. The first variation of this method involves condensation of a 1,9-diformyl dipyrromethane with a 1,9-diunsubstituted dipyrromethane to yield a calix[4]phyrin(1.1.1.1) in which the two dipyrin halves may be substituted differently. The second and third variations are closely related and differ by the order in which the components of the final product are installed. Variation 2 involves a 5-aryl dipyrromethane intermediate, while variation 3 incurs the dipyrromethane that results from condensation of acetone with two equivalents of pyrrole. In both cases the sp^3 -hybridized *meso*-like centers are generated from condensation of 2-unsubstituted pyrroles with ketones, while the *meso* centers (5-aryl) are derived from aldehydes.

A one-pot variation of the acid-catalyzed condensation of pyrrole with carbonyl-containing compounds to yield calix[4]phyrin(1.1.1.1)s has been examined, as shown in Figure 47.²⁰² In this example it was reported that reaction of benzaldehyde, 3 mol equiv of pivalaldehyde, and 4 mol equiv of pyrrole, using TFA as a catalyst, followed by oxidation with DDQ yielded the calix[4]phyrin(1.1.1.1) **84** in approximately 1% yield.

An interesting synthesis of a calix[4]phyrin(1.1.1.1) **87** containing two different non-hydrogen substituents at both of the sp^3 -hybridized *meso* centers from the reaction of acenaphthenequinone (**86**) with 5-mesityldipyrromethane (**85**) is shown in Figure 48.²⁰³ In this example structural data of the solid-state material showed that the usual preference of calix[4]phyrin(1.1.1.1)s for the *syn*-axial configuration was not followed; however, ¹H NMR spectra of the two isomers in solution show significant motion in the structure.²⁰³

Most of the methods for synthesizing calix[4]phyrin(1.1.1.1) derivatives provide products in which the two sp^3 -hybridized *meso*-like centers bear the same substituents. Asymmetrically substituted *trans*-porphodimethenes are most efficiently synthesized by MacDonald-type condensations of

dipyrromethenes, thus providing modular control over the substitution patterns of the products.^{199,204}

Advances in the synthesis of calix[4]phyrin(1.1.1.1) derivatives stabilized toward oxidation by the presence of *meso*-alkyl or -aryl substituents greatly increased research interest in these molecules. In addition to their application in the synthesis of macrocyclic tetrapyrroles, their promise as receptors for sensing molecules is also of interest. It has been demonstrated that the calix[4]phyrin(1.1.1.1) **88** bearing ferrocenyl units at the *meso* positions (Figure 49) could be used to sense exogenic electron-rich anionic species, such as chloride ions, in solution because these species cause the voltammetric properties of the pyrrolic compound to change.²⁰⁵

4.2. Complexes of Bis(dipyrin)s

Molecules in which two dipyrins are attached together are termed bis(dipyrin)s. Figure 50 shows some of the structural variety in this class of molecules that arises from the position of attachment between the dipyrin units and the nature of the linker between the two dipyrins, although in many cases there is no linker at all and the dipyrins are directly bonded to each other. A bis(dipyrin) that contains a 1,1'-methylene linker is referred to as a biladiene-*ac* (Figure 50).⁵ The metal complexes of bis(dipyrin)s are known to adopt an assortment of molecular structures and different metal-to-ligand ratios depending on a number of factors including the conformational preference of the bis(dipyrinato) ligand and the coordination preference of the metal ion.

Bis(dipyrin)s were originally synthesized with the intended use as precursors to macrocyclic tetrapyrroles and strapped porphyrins. This review will recount the history of bis(dipyrin)s from the point of the first reported synthesis of a metal complex of such a molecule. In 1939 Hans Fischer published a report including two different 1:1 metal-to-ligand ratio (ML)-type palladium(II) complexes of 1,1'-bis(dipyrin)s.²⁰⁶ The metal complexes **90a** and **90b** were prepared, as shown in Figure 51, by reacting 1,9-dibromodipyrins **89a** and **89b** with palladium on calcium carbonate as a source of palladium(II) ions, and it was demonstrated that the non-metalated 1,1'-bis(dipyrin)s could be generated by treatment of the complexes with mineral acids.

Twenty years later, in attempts to synthesize macrocyclic tetrapyrroles, Fischer's previous results were reproduced using a different palladium source.²⁰⁷ It was shown that one of the palladium(II) complexes of a 1,1'-bis(dipyrin) (**90a**) could be cyclized by reacting with formaldehyde to yield the corresponding 10-oxacorrole palladium complex **91**, as shown in Figure 52. The oxidative cyclization of 1,1'-bis(dipyrinato) metal complexes would remain employed for many more decades as a technique for preparation of porphyrinoids.^{208–214}

Work with bis(dipyrin)s continued through the 1960s and focused upon the synthesis of nickel(II) complexes of

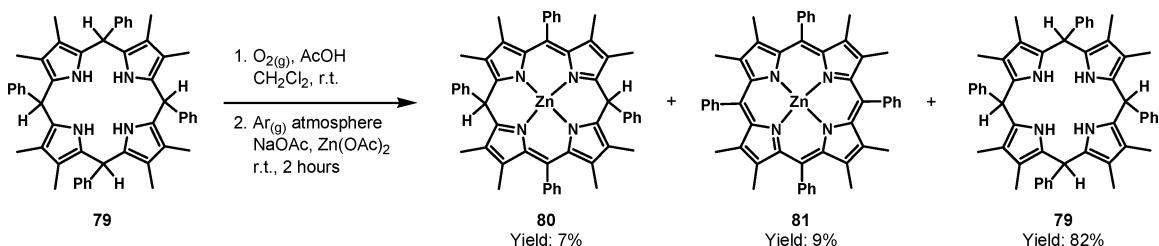


Figure 44. Calix[4]phyrin(1.1.1.1) synthesis by oxidation of calix[4]pyrroles.

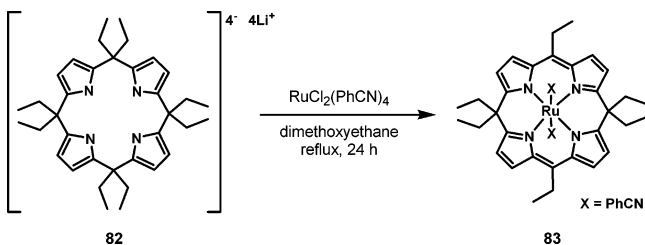
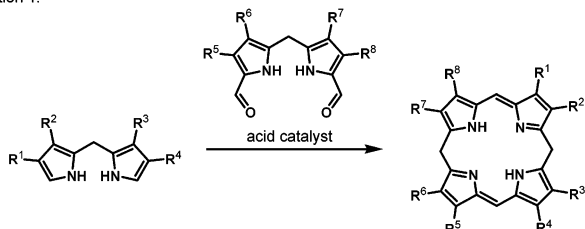
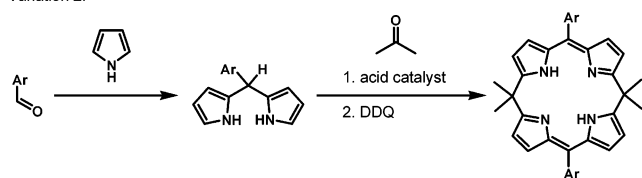


Figure 45. Calix[4]phyrin(1.1.1.1) synthesis by dealkylation of calix[4]pyrroles.

Variation 1:



Variation 2:



Variation 3:

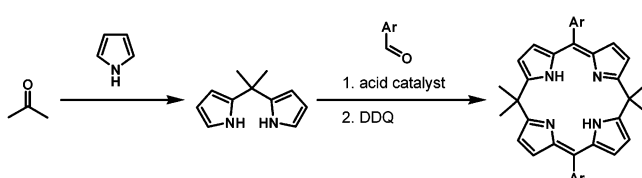


Figure 46. Variations upon the acid-catalyzed condensation of pyrrolic compounds with carbonyl-containing molecules to yield calix[4]phyrin(1.1.1.1)s.

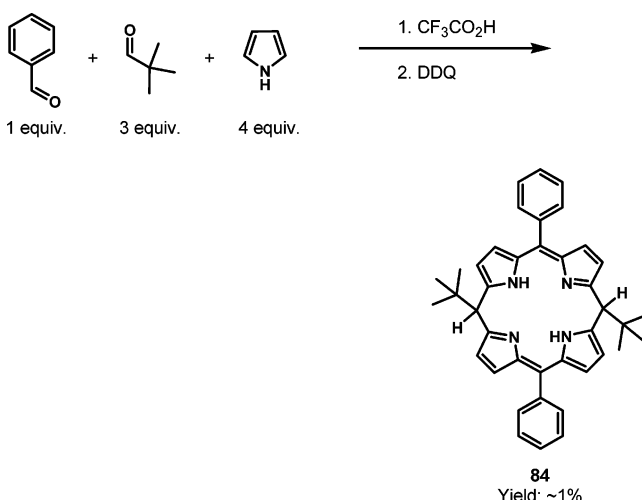


Figure 47. One-pot variation of the acid-catalyzed condensation of pyrrolic compounds with carbonyl-containing molecules to yield calix[4]phyrin(1.1.1.1)s.

corroles such as **94** seen in Figure 53 and 1,19-disubstituted tetrahydrocorrins such as **95a** and **95b**.^{215–219} In the process of investigating these goals, many discoveries were made regarding the factors affecting formation of bis(dipyrinato) metal complexes. Different metal ions were used including cobalt(II), copper(II), and zinc(II), linkers of different lengths

and steric bulk were employed, and the complexation conditions, most importantly solvent, were varied. These experiments regarding the synthesis of corrole metal complexes saw the isolation of the first 2:2 ligand-to-metal ratio dimeric dinuclear complexes such as **98** in Figure 54 by performing the metal complexation reaction using methanol as a solvent rather than ethanol, the latter of which had been used previously to yield the monomeric product **96**.^{218,219}

In the late 1960s and early 1970s it was shown that when the complexation reactions of bis(dipyrin)s were conducted in methanol, cobalt(II) and zinc(II) metal ions yielded dimeric products such as **100a** and **100b** (Figure 55) while nickel(II) and copper(II) produced monomeric complexes such as **101a** and **101b**.^{220,221} It was observed that cobalt(II) and zinc(II) complexes of 1,1'-bis(dipyrin)s deviate very little from perfect tetrahedral coordination geometries, whereas nickel(II) and copper(II) tend to form distorted square-planar dipyrinato complexes.^{220,221}

The reported use of bis(dipyrin)s in the synthesis of cyclic tetrapyrroles includes the metal complex (**102**) of a bis(dipyrin) that was not linked through the 1,1' positions (Figure 56).²²² This example of a rare copper(II) 3,3'-bis(dipyrinato) complex was employed in the synthesis of a strapped porphyrin **103**. For the proceeding 20 years there were few reports of bis(dipyrinato) metal complexes. In 1980 the crystallographic evidence of the dinuclear double-helical structures, suggested^{221,223} around 20 years earlier for dimeric bis(dipyrinato) complexes, was provided during a survey of the cyclization reactivity of 1,1'-bis(dipyrinato) metal complexes.^{224,225} The zinc(II) dinuclear double-helical complex (**105**) was shown by X-ray crystallography to exist in a dinuclear double-helical form that exhibits severe twisting about the helical axis (Figure 57).

The schematic diagrams in Figure 58 depict the possible structures of bis(dipyrinato) metal complexes that give rise to helical and non-helical molecules. Mononuclear ML bis(dipyrinato) complexes in which the two dipyrinato units are both bound in a bidentate manner to a single metal ion are helical. The helicity arises from the arrangement of the two dipyrinato units attached to one metal center approximately perpendicular to each other in the tetrahedrally coordinated structure. Similar to homoleptic dimeric dipyrinato metal complexes (see section 3.2), the steric demands of the substituents in the 1,9-positions of the bis(dipyrinato) ligand force the dipyrinato units binding the same metal ion to be out of plane with each other, resulting in a helical twist of the ligand. It is possible to imagine helical and non-helical arrangements of bis(dipyrinato) ligands in M_2L_2 complexes, as shown in Figure 58, although there have been no reports of non-helical complexes of this type. Helicity has become one of the impetuses behind the modern renaissance of bis(dipyrinato) metal complex research.

Nearly 20 years after the first crystal structure of a dinuclear double-helical bis(dipyrinato) complex was published, helical bis(dipyrinato) metal complexes returned to the literature. An investigation into the effect of ligand design upon the structure of bis(dipyrinato) metal complexes showed that by varying the length of alkyl linkers between the dipyrinato units of both 1,1'- and 2,2'-bis(dipyrin)s a variety of complexes of differing nuclearity could be prepared.^{226–228} One of these reports included the solved crystal structure of an interesting helical molecular triangle with a metal-to-ligand ratio of 3:3, compound **106** in Figures 59 and 60.²²⁷ A variety of double-helical dinuclear 2,2'-bis-

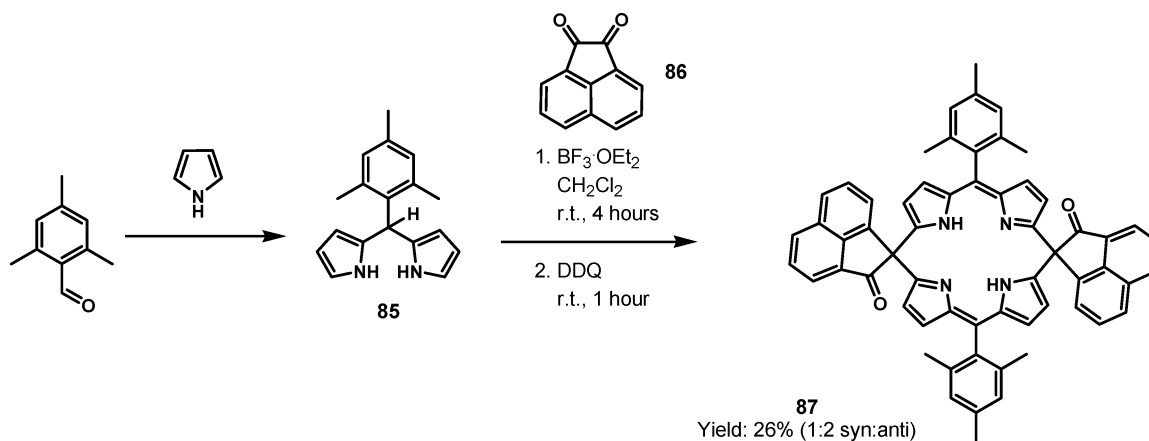


Figure 48. Synthesis of calix[4]phyrin(1.1.1.1) using acenaphthenequinone.

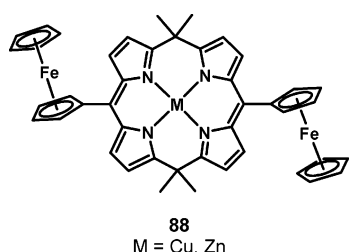


Figure 49. Calix[4]phyrin(1.1.1.1) for sensing anions.

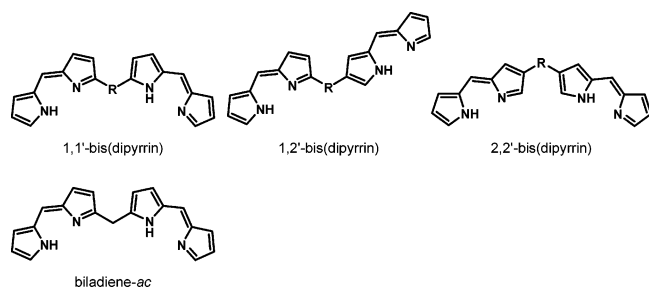


Figure 50. Structural variations of bis(dipyrin)s.

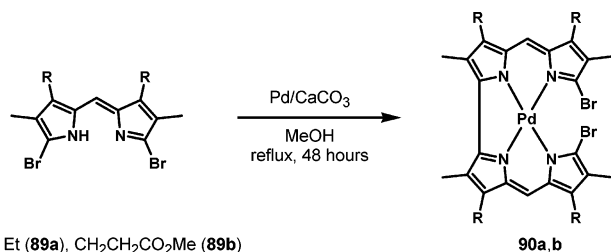


Figure 51. First reported preparation of an isolated bis(dipyrinato) metal complex.

(dipyrinato) metal complexes^{229–232} (**108** and **110** in Figure 60) and a zinc(II) 1,2'-bis(dipyrinato) molecular rectangle (**111** in Figure 61) were also reported.²³³ The demonstrated

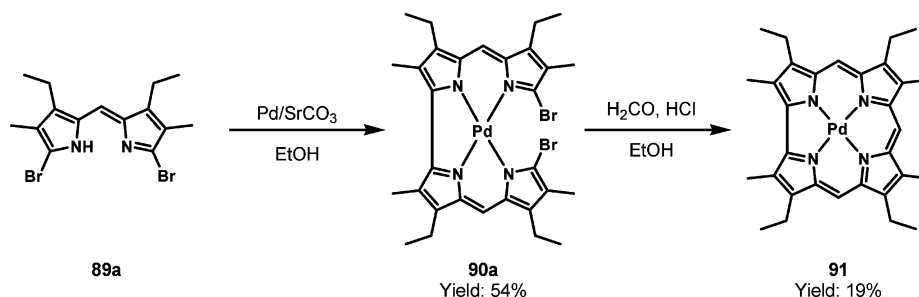


Figure 52. Cyclization of palladium(II) bis(dipyrinato) complexes.

ability to control the shape of bis(dipyrinato) metal complexes created interest in their potential as a new kind of supramolecular building block. The helicity of many of the complexes also offered a different kind of potential, that of chirality.

4.2.1. Nonracemic Helical Bis(dipyrinato) Metal Complexes

In the absence of any chiral influence helical bis(dipyrinato) metal complexes form as a racemic mixture of enantiomeric *M* (left) and *P* (right) helices.²³⁴ Chiral templating by incorporation of chiral groups in bis(dipyrinato) ligands has been presented as a method for inducing stereoselectivity in the complexation process.^{7,235,236} Initial studies were conducted upon dinuclear double-helical zinc(II) complexes of 2,2'-bis(dipyrin)s that were appended with homochiral terminal point chiral amides or esters.²³⁶ Circular dichroism of the pseudoenantiomeric *M* and *P* helicates such as **112** in Figure 62, resolved by chiral HPLC, showed low stereoselectivity for formation of the two helices.^{235,236} Further research achieved very high stereoselectivity, as shown by HPLC, ¹H NMR spectroscopy, circular dichroism, and X-ray structure analysis, by changing the design of the ligand to that of a bis(dipyrinato) structure (**113**) in which the two dipyrinato units were connected in 2,2' manner by a homochiral spacer.⁷

The chiral HPLC resolution of *M* and *P* enantiomers of the mononuclear nickel(II) 1,1'-bis(dipyrinato) complex **114** (Figure 63) has been reported as part of work directed toward chiral analogues of catalytically active metalloporphyrins:^{181,237} copper(II) and palladium(II) analogues were also reported.¹⁸⁴ The effect of 1,9-substituents upon the degree of helicity, as measured from X-ray structures and the angle between the planes of the two dipyrinato units, was surveyed as well as the stability of the helical chirality to racemization by heating in solution. The handedness of the helices was

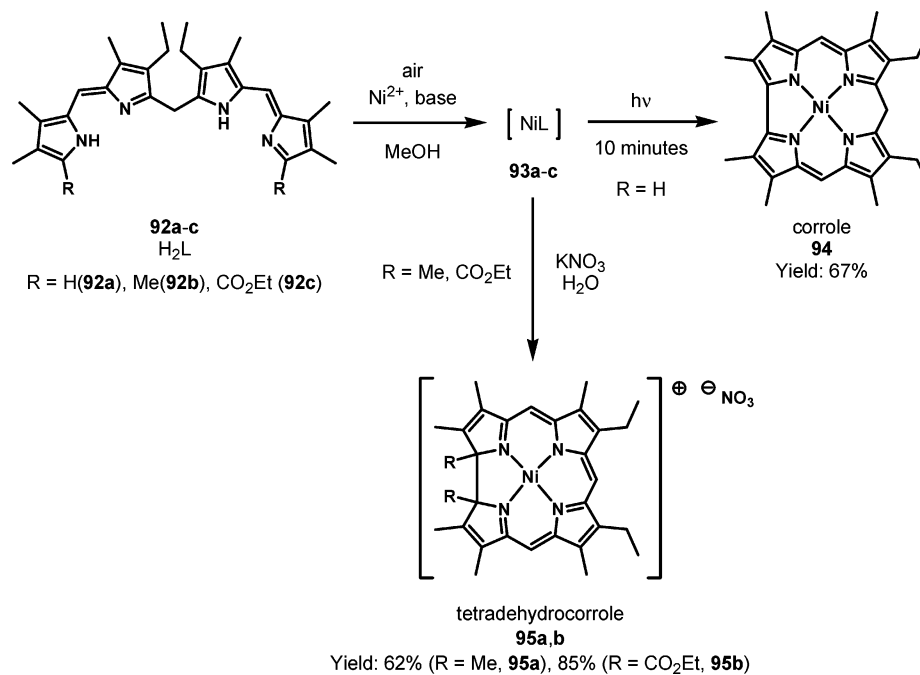


Figure 53. Further studies involving bis(dipyrrinato) metal complexes.

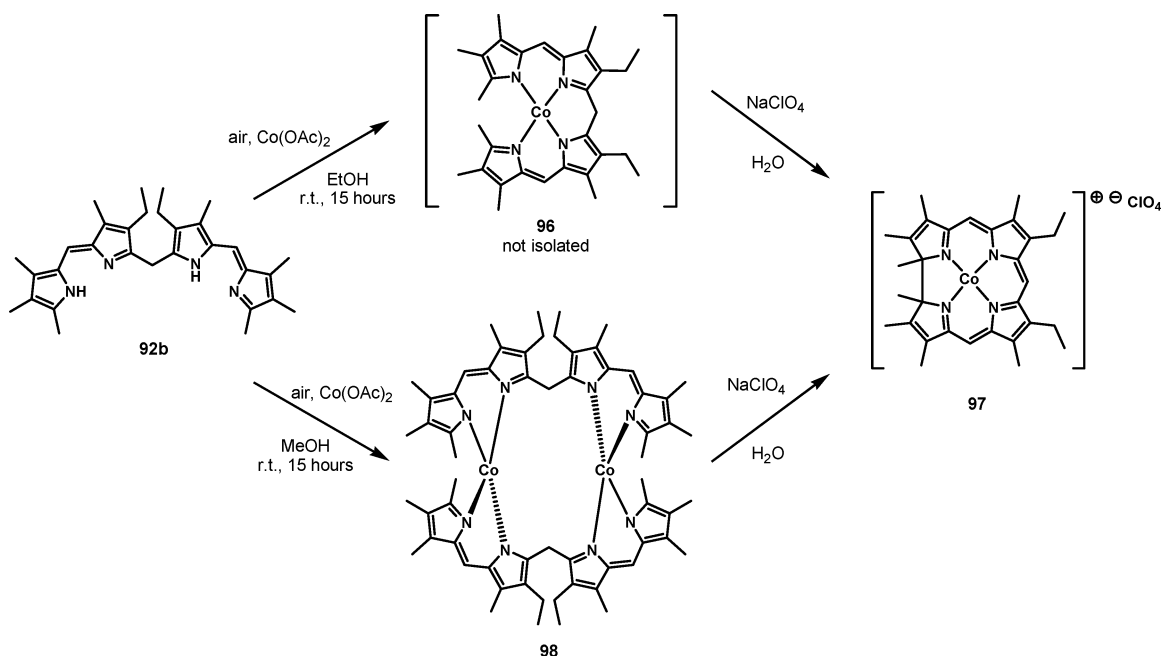


Figure 54. Preparation of dimeric bis(dipyrrinato) metal complexes.

found to be very stable, even at high temperatures.¹⁸¹ Thorough electrochemical studies of the metal complexes were also conducted.

Many of the 1,1'-bis(dipyrrinato) ligands that were used in this research were from a new class of 5-substituted bis(dipyrrin)s for which new synthetic methods were developed (Figure 64).^{238,239} Condensation of two equivalents of a 2-unsubstituted pyrrole with one equivalent of a diaroylpyrrole **115** was achieved by heating the mixture in the presence of phosphorus(V) oxychloride. Another method for synthesizing 5-substituted bis(dipyrrin)s by biaryl coupling of nickel(II) dipyrrinato complexes (**117**) was recently reported to give **118**, and **119** upon treatment with mineral acid.¹⁸² As is the case with dipyrrins, 5-substitution increases

the number of points of elaboration in the bis(dipyrrinato) ligand.

The preparation of a series of earlier transition metal ion complexes expanded the list of known coordination geometries available to bis(dipyrrin)s.^{91,184,240,241} A rhodium(I) cluster complex (**4**, shown previously in Figure 7) is the only example of non- κ^2 bonding of a metal ion by a bis(dipyrrin).⁹¹ This led to an investigation which showed that the rhodium reagents used in the preparation of bis(dipyrrinato) rhodium complexes affected the structure of the product in terms of the metal-to-ligand ratio.²⁴² Cyclization of manganese(II), nickel(II), copper(II), rhodium(I), and palladium(II) bis(dipyrrinato) complexes to form tetrapyrrolic macrocycles was also demonstrated.²⁴²⁻²⁴⁴

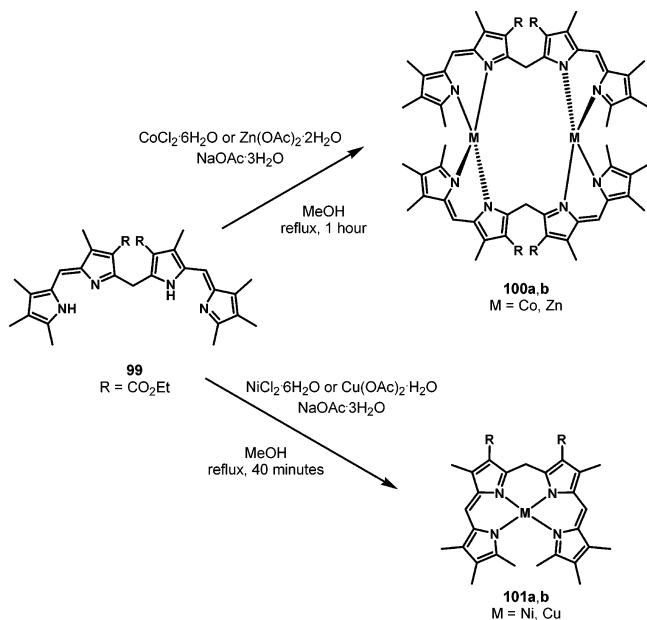


Figure 55. Bis(dipyrrinato) metal complex formation.

4.3. Propentdyopent Complexes

The propentdyopents (Figure 65) are a class of naturally occurring oxygenated dipyrin molecules found in urine. Some examples of metal complexes of propentdyopents are known, for example, copper(II),²⁴⁵ cobalt(II),²⁴⁶ and zinc(II) complexes.^{247,248} A copper(II) complex (**121**) of tetraethylpropentdyopent was formed by the slow air oxidation of the copper(II) octaethylbilindione complex (**120**) (Figure 66) and characterized by X-ray crystallography.²⁴⁵ The analogous cobalt(II) complex, for which an X-ray crystal structure was also obtained, was prepared in moderate yield by photooxidation of the cobalt(II) complex of octaethylformylbiliverdin.²⁴⁶ The propentdyopent metal complexes were shown to exhibit similar complexation geometries to those of dipyrrinato metal complexes.

4.4. Tripyrrin and Tripyrrinone Complexes

The tripyrrins have been described as “the structural link between porphyrins and dipyrins”.²⁴⁹ Tripyrrins are not to be confused with 5,15-dihydrotripyrins,⁵ although the latter are frequently called the former in the literature (Figure 67).

Tripyrrin anions bind metal dications to form metal(II) (tripyrrin)X complexes, where X is a monoanionic donor ligand.^{250,251} The ability of the tripyrrin ligand to form complexes with a variety of metals in their 2+ oxidation state was demonstrated by the synthesis of cobalt(II), nickel(II), copper(II), zinc(II), and palladium(II) complexes such as **122a–e** in Figure 68.^{250,251} Initial investigations of the solid-state structure of a palladium(II) tripyrrin complex showed a helical distortion from planarity for the tripyrrin as a result of the steric interactions between terminal pyrrolic ring substituents and the donor ligand (X) coordinated to the metal center,²⁴⁹ and further studies showed that this helical structure was not, however, the only solid-state structure exhibited for molecules of this type.²⁵² Palladium(II) tripyrrin complexes have also been observed to possess a planar ligand structure with a tetrahedrally distorted palladium center.²⁵² The two different structures are thought to equilibrate rapidly at room temperature.²⁵²

Several studies of the structures of tripyrrin metal complexes revealed that the nature of the donor ligand (X) had an effect upon the geometry and reactivity of the metal-ion center. A series of nickel(II) (tripyrrin)X complexes demonstrated that the coordination geometry about the nickel(II) center varied between four- and five-coordinate, the fifth coordination site being occupied by solvent or bidentate binding of the X ligand, depending upon whether this ligand was chloride, bromide, iodide, oxalate, or nitrate.^{251,253} It is possible to obtain stable five-coordinate palladium(II) complexes from reaction of palladium(II) (tripyrrin)X with certain Lewis bases^{254,255} and carbene complexes from the reaction with diazoalkanes²⁵⁵ when X is the weakly coordinating anion tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr^{F}).

Electrochemical studies of the tripyrrin metal complexes showed that the cobalt(II), nickel(II), zinc(II), and palladium(II) complexes **122a,b,d,e** (Figure 68) undergo one ligand-centered oxidation and two ligand-centered reductions. For the copper(II) complex (**122c**) a one-electron reduction of the metal center occurred.²⁵⁶

As for the tripyrrins, there are relatively few reports concerning metal complexes of tripyrrinones (Figure 69). There have been some reports regarding the cation transport ability of some tripyrrinones and other oligopyrrolic compounds.^{46,257} Recently the synthesis of nickel(II), copper(II), zinc(II), palladium(II), and platinum(II) complexes of tripyrrinones by oxidation of *N*-confused tetraphenyl porphyrin has been reported.^{258,259} Solid-state structures for these molecules revealed that the oxygen atom of a carbonyl substituent was also bound to the central metal ion in addition to the three nitrogen atoms of the tripyrrinone ligand. Previously, metal-ion titration experiments for tripyrrinone ligands in which an unexpected coordination mode was revealed had been reported.¹⁶⁴ In addition to the expected chelation of the metal ion by three nitrogen atoms of a dideprotonated tripyrrinone ligand, a particular zinc(II) complex (**123**) displayed tautomerization of the lactam to the hydroxyimino form for binding the zinc(II) ion as a monodeprotonated ligand, as shown in Figure 70.¹⁶⁴

Although structurally there are fundamental differences between the tripyrrin, tripyrrinone, and dipyrin, further research into the behavior of tripyrrins and tripyrrinones will undoubtedly contribute to the understanding of dipyrins.

4.5. Bilene-*b* Complexes

A specific class of dipyrins is the 1,19-dideoxybilene-*b*, also known as bilene-*b* or tetrapyrrene. These molecules possess a structure like that of a dipyrin, as seen in Figure 71, with two pyrroles attached through sp^3 -hybridized methylene linkers at either end.

These molecules have been most popular for their use in the synthesis of porphyrins,^{260–264} chlorins,^{265,266} and tetrahydrocorrins.^{267,268} The 1,19-dimethyl-derivatives, sometimes formed in situ, have also been used to synthesize metalloporphyrins by cyclization in the presence of metal ions.^{269–298} From the earliest of these metal cyclization reactions it was discovered that bilene-*b* analogues form homoleptic metal complexes.²⁷² This work was extended to investigate the metal-complex geometries of dipyrins through a study upon bilene-*b* metal complexes such as compound **72**: it was shown that they displayed complexation behavior similar to that of 1,9-sterically hindered dipyrins (Figure 72).^{272,299}

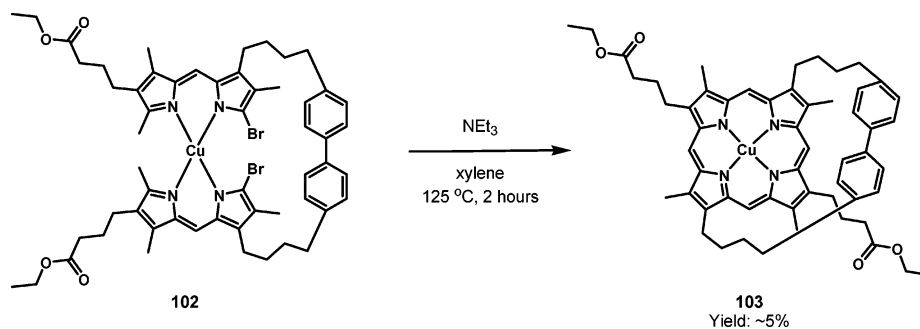


Figure 56. Copper(II) 3,3'-bis(dipyrrinato) complex used in porphyrin synthesis.

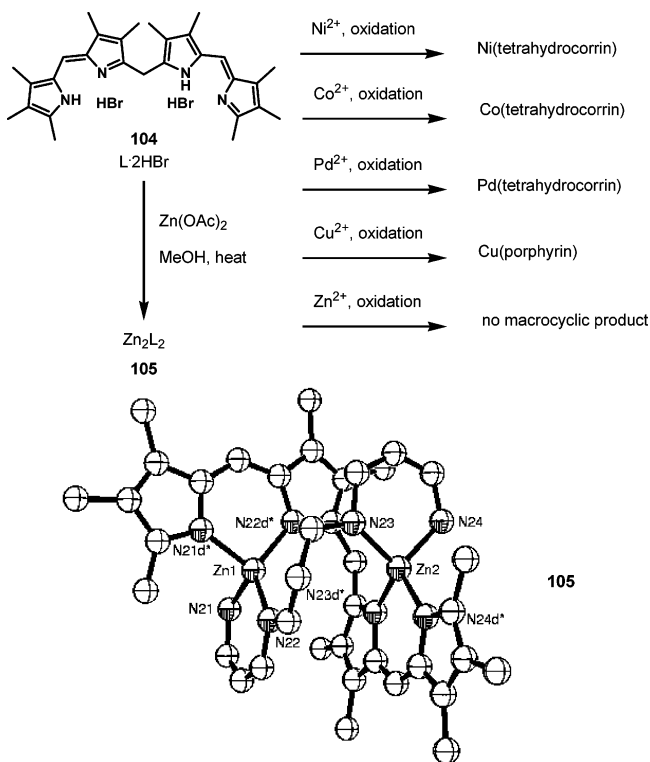


Figure 57. Survey of bis(dipyrrinato) metal complex cyclization chemistry including the solid-state structure of a dinuclear, double-helical zinc(II) bis(dipyrrinato) metal complex (the structure has been truncated for clarity).

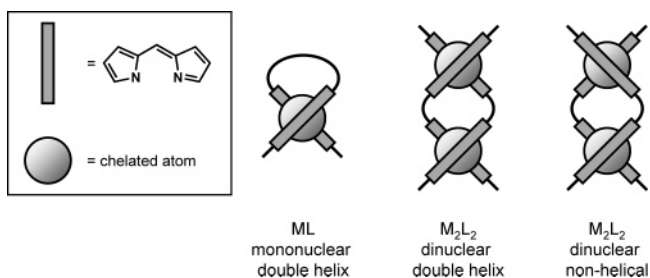


Figure 58. Schematic diagram of helical and nonhelical bis(dipyrrinato) metal complexes.

4.6. Complexes of Bilindiones, Biladienones, and Their Derivatives

Ligands based upon naturally occurring linear tetrapyrroles are known to function as tetradentate ligands in the formation of metal complexes with structures that resemble those of bis(dipyrrinato) metal complexes. Bilin-1,19-diones, like biliverdin-IX α (**125** in Figure 73), are the linear tetrapyrroles most widely studied in this regard. Although there had been

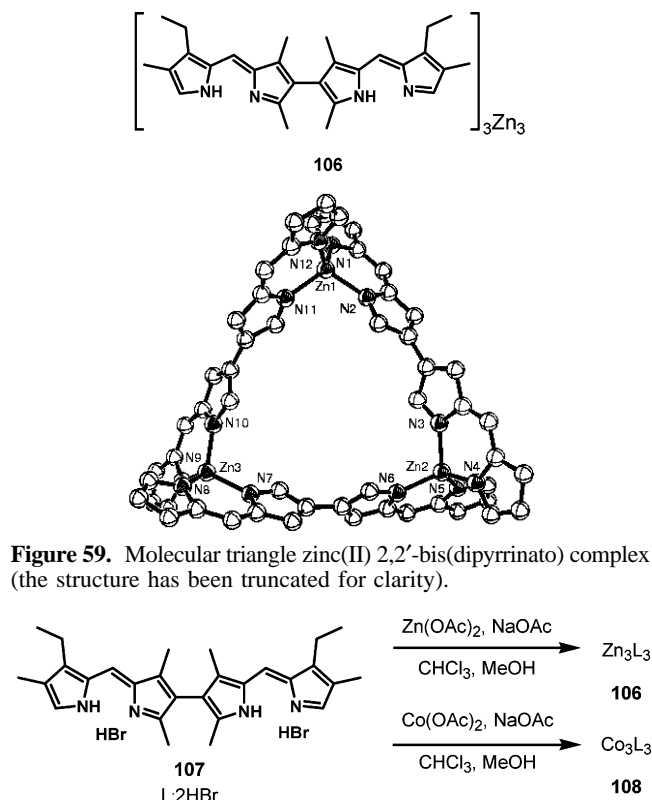
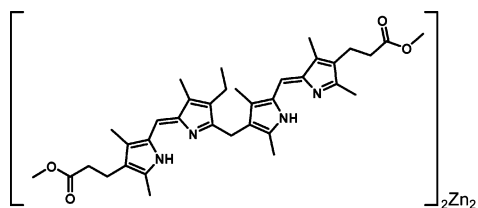


Figure 59. Molecular triangle zinc(II) 2,2'-bis(dipyrrinato) complex (the structure has been truncated for clarity).

Figure 60. Oligomers of bis(dipyrrinato) metal complexes.

some earlier reports regarding the synthesis of metal complexes of bilindione derivatives,³⁰⁰ interest in ligands of this type became more pronounced with the discovery in 1976 that octaethyl-19-formylbilin-1-one (**126**) forms zinc(II) complexes (Figure 74).³⁰¹

Analysis of the X-ray crystal structures of the zinc(II) octaethylformylbilinone products showed that two complexes with different stoichiometries and structures existed. A complex with 1:1 ligand-to-zinc(II) stoichiometry, in which the zinc(II) ion also binds to an aqua ligand, showed a deviation from planarity, resulting in helicity. The 2:2 complex was shown to exist as a dinuclear double helix, which had not been observed before for such systems. The



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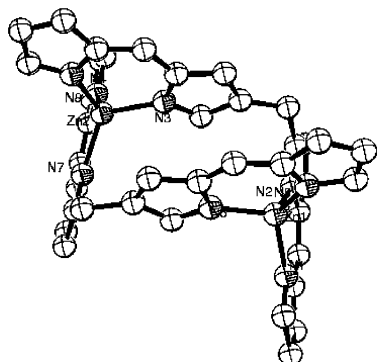
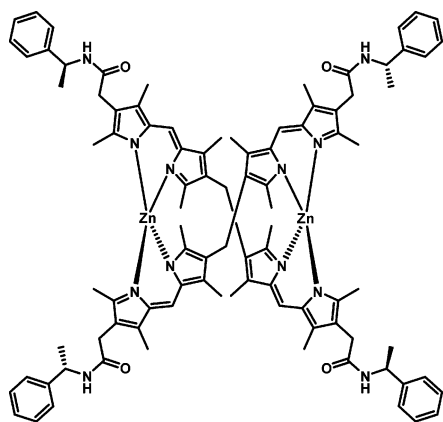
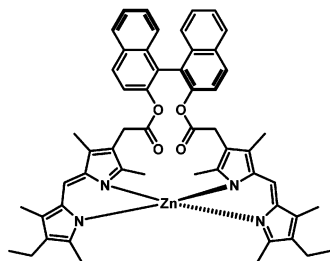


Figure 61. Molecular rectangle zinc(II) 1,2'-bis(dipyrinato) complex (the structure has been truncated for clarity).



112
d.r. = 54:46 (*P:M*)
for complex formation

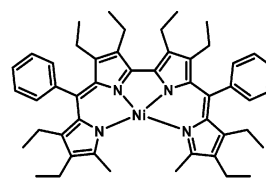


113
d.r. = 1:~99 (*P:M*)
for complex formation

Figure 62. Nonracemic zinc(II) bis(dipyrinato) complexes.

formation of 1:1 stoichiometry metal (magnesium(II), zinc(II), copper(II), nickel(II), iron(III)) complexes of bilin-1,19-dione derivatives formed by photooxidation of metalloporphyrins has also been reported.^{302–305}

Interest in the demonstrated helicity of metal complexes of bilindione derivatives resulted in further studies in the late 1970s, revealing X-ray crystal structure data for a “severely distorted” square-planar nickel(II)³⁰⁶ and boron-



114

M and *P* resolved by HPLC

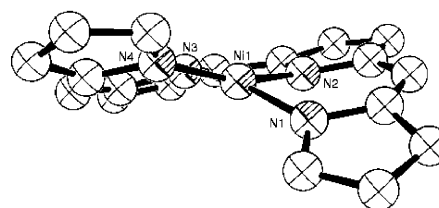


Figure 63. Helical nickel(II) 1,1'-bis(dipyrinato) complex (the structure has been truncated for clarity).

difluoride (in which the bilindione is bidentate)³⁰⁷ complexes of octaethylbilin-1,19-dione (**127** in Figure 75). The structural data for these molecules show that regardless of the preferred geometry of the central chelated atom, the oxygen atoms in the 1,19-positions of the bilindione ligand force the complexes to assume a helical twist.

Iron complexes of biliverdin IX α have been implied as intermediates in the degradative oxidation of heme (**128**) by the enzyme heme oxygenase, which is shown in Figure 76. The instability of iron complexes of bilindiones has hampered studies of the apparent nucleophilic attack of verdohemochrome (**129**) by hydroxide in the formation of biliverdin IX α . This instability led researchers to prepare analogues using various metal ions and ring substituents, beginning in the late 1980s.^{308–310} A series of metal complexes using octaethylbilin-1,19-dione as a ligand was prepared by oxidation of the corresponding octaethylporphyrin complex or complexation of octaethylbilin-1,19-dione with an appropriate metal salt. Several metal ions were employed to prepare a series of octaethylbilin-1,19-dione complexes that included interchangeable monomeric and dimeric iron(III)³¹⁰ or manganese(III)³¹¹ (involving the oxygen atoms binding the metal ion), distorted square-planar copper(II),²⁴⁵ distorted square-planar cobalt(II),^{311,312} square-planar nickel(II),³¹³ and distorted square-planar palladium(II).^{313–315} Thorough characterization of these compounds revealed that they possess unusual electronic structures, which often exhibit significant ligand radical character.³¹⁶ A study using density functional theory for the purpose of analyzing the molecular and electronic structure of some biliverdin complexes provided insight into the spin distributions of these molecules.³¹⁷

In addition, monomeric copper(II), nickel(II), and cobalt(II) complexes (**131a–c**) of octaethyl-19-formylbilin-1-one³¹⁸ have been prepared by photooxidation of the magnesium(II) complex (**130**) of octaethylporphyrin as seen in Figure 77 and the monomeric copper(II)³¹⁹ complex of tetraphenylketobiliverdin by photooxidation of the magnesium(II) complex of tetraphenylporphyrin. A higher yielding method for the preparation of complexes of this type using *m*-chloroperoxybenzoic acid was also reported.³²⁰

Comparisons for biochemical transformation of verdohemochrome by hydrolysis into biliverdin IX α were performed by studying ring-opening reactions (Figure 78) of metallo-5-oxaporphyrins (**132a–c**) with nucleophiles such as hydroxide,³²¹ alkoxides,^{316,321,322} amides,³²³ thiolates,³²³ and

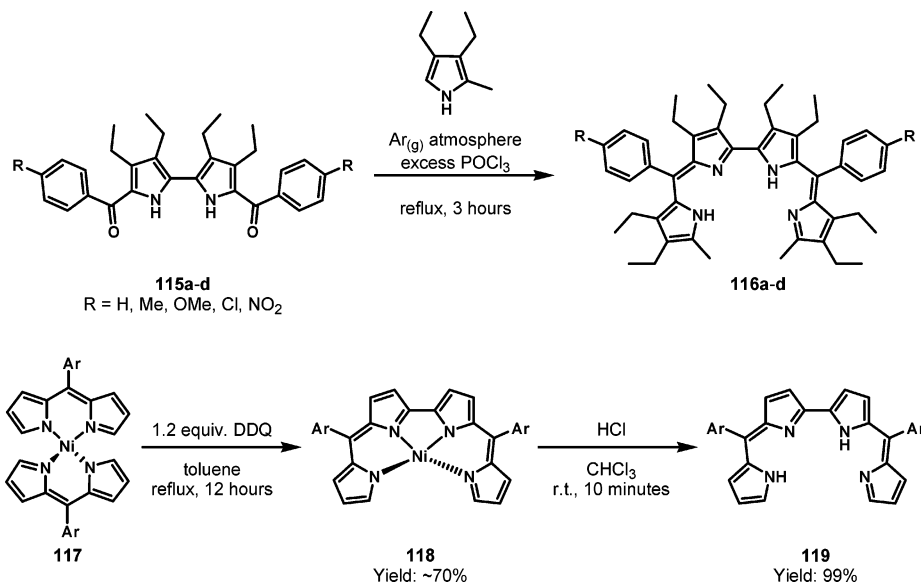


Figure 64. Syntheses of 1,1'-bis(dipyrrin)s without linkers.

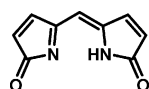


Figure 65. General structure of a propentdyopent.

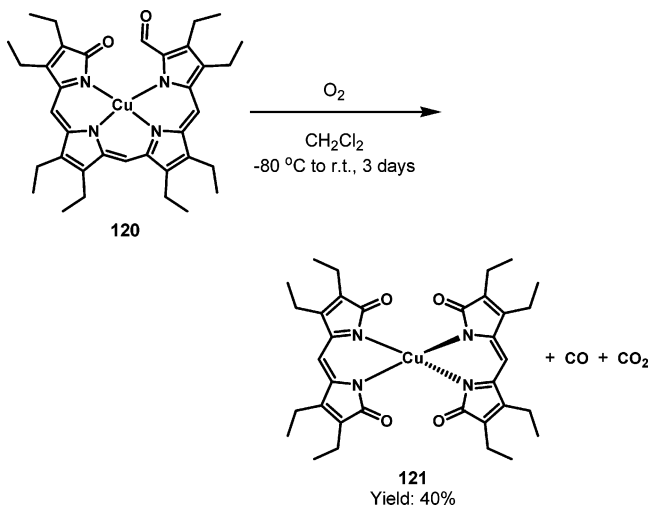


Figure 66. Oxidation of copper(II) octaethylbilindione.

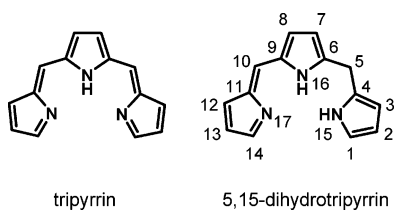


Figure 67. Structures of tripyrrin and 5,15-dihydrotripyrrin.

cyanide,³²⁴ thus forming substituted linear bilindione derivatives (**133**).

The control of helical chirality in zinc(II) complexes of 19-alkoxybilin-1-ones (**134**) (Figure 79) by induction from point chirality has been investigated.³²⁵ The source of the point chirality involved auxiliaries attached to the ligands at the 19-oxygen or amines and amino acid esters that acted as ligands on the zinc(II) center. A thorough analysis of the interactions of these two sources of point chirality with the zinc(II) bilinone structures to induce helical chirality, as

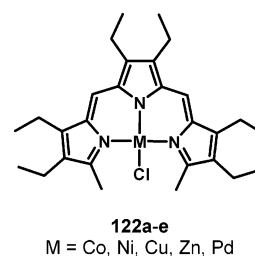


Figure 68. Structures of the tripyrrin metal complexes analyzed electrochemically.

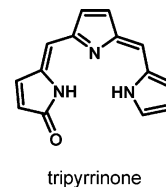


Figure 69. General structure of a tripyrrinone.

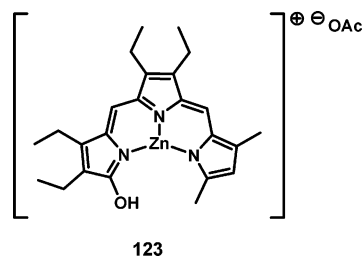


Figure 70. Zinc(II) hydroxyimino tripyrrinone complex.

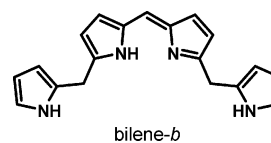


Figure 71. General structure of a bilene-*b*.

determined by circular dichroism and ¹H NMR spectroscopy, included consideration of the effects from solvent,³²⁶ temperature,³²⁷ the presence of aromatic rings in the chiral auxiliary,³²⁷ the connection of two zinc(II) bilinone units by one chiral auxiliary,³²⁸ influences from helicity of one zinc-

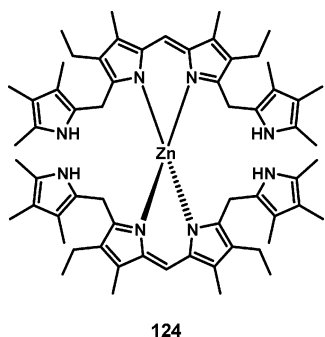


Figure 72. Structure of a zinc(II) bilene-*b* complex.

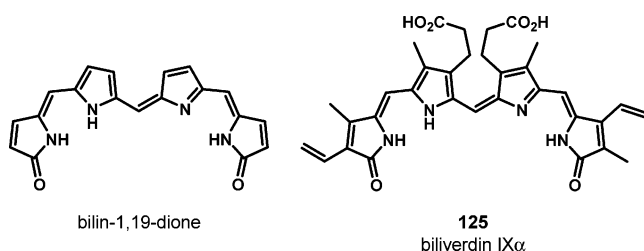


Figure 73. General structure of a bilin-1,19-dione, and structure of biliverdin IXα.

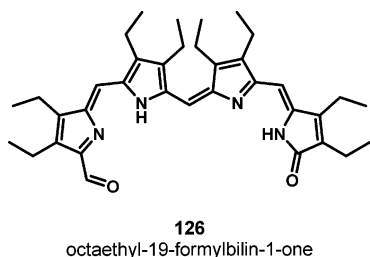


Figure 74. Structure of octaethyl-19-formylbilin-1-one.

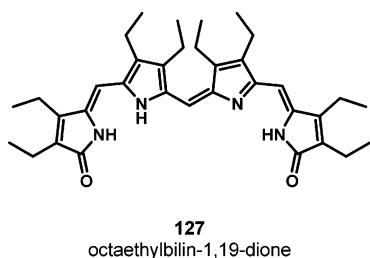


Figure 75. Structure of octaethylbilin-1,19-dione.

(II) bilinone unit upon another,^{329,330} and the absolute configuration of the amino acid esters.^{325,331}

In one study the concurrent induction of helical chirality by two sources of point chirality was examined. The molecules used in this study were of the structure **135** seen

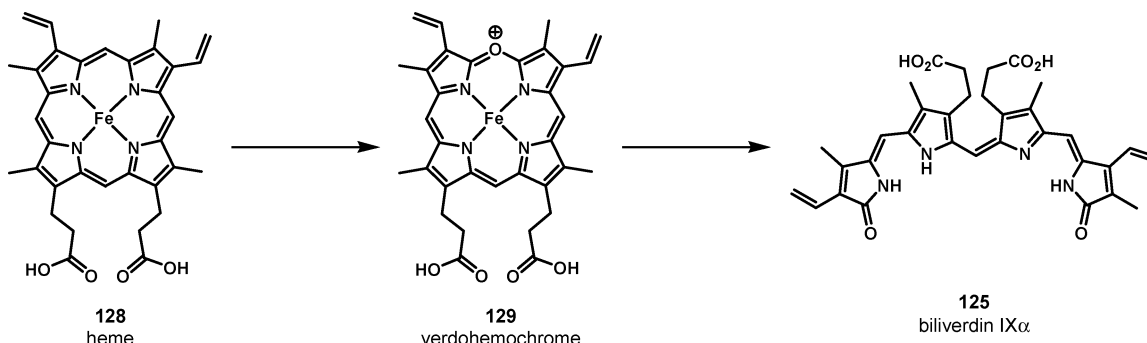


Figure 76. Degradative oxidation of heme by heme-oxygenase.

in Figure 80 with two zinc(II) bilinone units connected by a homochiral cyclohexanediol linker. When the cyclohexanediol unit was of (*R,R*) chirality the zinc(II) bilinone units induced (*P,P*) helical chirality, and when the cyclohexanediol unit was (*S,S*) the zinc(II) bilinone units adopted (*M,M*) helicity, with the sense of the helicity being determined by circular dichroism.³²⁸ Introduction of homochiral amino acid esters and amines failed to change the helicity of the zinc(II) bilinone complexes, but the complexes did exhibit different binding constants between enantiomers of amino acid esters and amines.³²⁸

A few reports concerning metal complexes of biladien-*ac*-10-ones (Figure 81) reveal that the complexation behavior of these ligands is highly similar to that of bis(dipyrin)s. In this line of research the preparation of complexes of 1:1 metal-to-ligand ratio for cobalt(II), nickel(II), copper(II), and palladium(II)³³² and both 1:1 and 2:2 ratio complexes for zinc(II), cadmium(II), and mercury(II) has been reported.³³³ The metal complexation behavior of biladien-*bc*-5-ones, which resembles that of tripyrins, has also been discussed.³³²

Prodigiosin (**136**) is a tripyrrolic red pigment synthesized by the bacterium *Serratia marcescens*. Containing both a dipyrin and a pyrrole, prodigiosin is known to form complexes with metal cations. For example, zinc(II)^{334–336} and cobalt(II)³³⁵ have been shown to form homoleptic prodigiosin complexes **137a** and **137b** as shown in Figure 82. Attempts to isolate a copper complex of prodigiosin resulted in isolation of the oxidized complex **138**, as shown in Figure 83.³³⁶ Prodigiosin exhibits a variety of biological effects, including immunosuppressive characteristics and cytotoxicity.^{337–339}

4.7. Iminopyrrole Complexes

Iminopyrroles, also known as pyrrole-2-aldimines,³⁴⁰ pyrrole-carboxaldehydes,³⁴¹ pyrrole-2-carbaldehydes,³⁴² pyrrole-2-ylalkeneamines,³⁴³ pyrrole-2-imines,³⁴⁴ pyrrolylimines,³⁴⁵ pyrrolide-imines,³⁴⁶ and pyrrolylaldimines,³⁴⁷ are a class of molecules of interest because they have shown some similarities to dipyrins in terms of their metal complexation behavior. Although the structures of dipyrins and iminopyrroles are significantly different since there are three carbon atoms between the chelating nitrogens in dipyrins and only two carbons between the nitrogens of iminopyrroles, the analogy between the structures of their metal complexes is apparent.

The first metal complex of an iminopyrrole was reported in 1937.³⁴⁸ Beginning from this earliest report, variation in the number of binding sites in the iminopyrrole ligands has been a focus of experimentation. Condensation of pyrrole-2-carboxaldehyde with amines or diamines yields bidentate

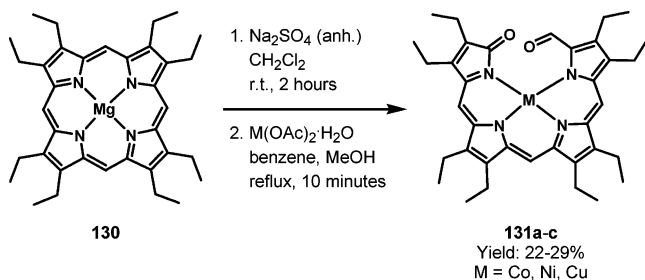


Figure 77. Photooxidation of the magnesium(II) complex of octaethylporphyrin.

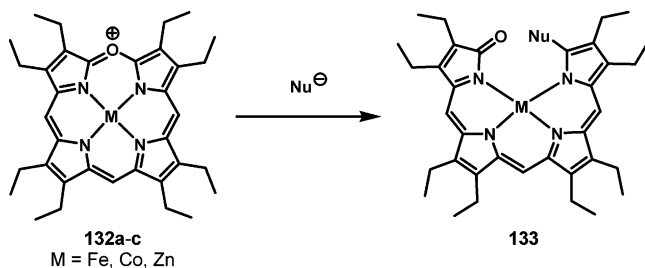


Figure 78. Ring-opening reaction of metallo-5-oxaporphyrin with nucleophile.

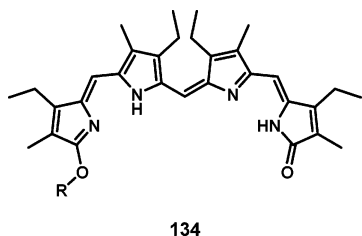


Figure 79. Structure of a 19-alkoxybilin-1-one.

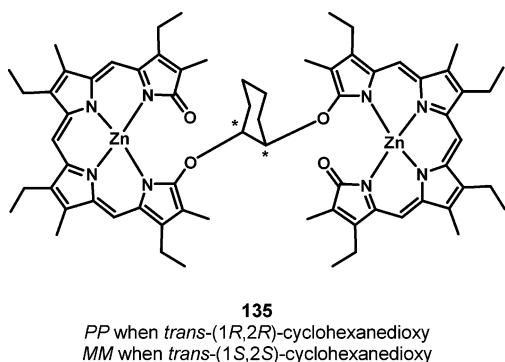


Figure 80. Chiral zinc(II) bilinone complexes.

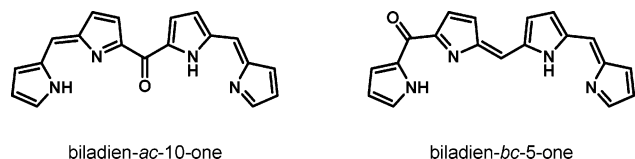


Figure 81. Structures of biladien-*ac*-10-one and biladien-*bc*-5-one.

or tetradentate ligands, respectively. Similar to dipyrins, bidentate iminopyrroles usually form 2:1 ligand-to-metal ratio complexes with metal(II) ions and 3:1 with metal(III) ions. Also similar to dipyrins, tetradentate iminopyrroles (bis(iminopyrrole)s)³⁴⁹ can form complexes of 1:1 stoichiometry with M(II) ions as well as 2:2 complexes, the latter of which have exhibited dinuclear double-helical structures.^{350–359} Other known molecular structures that bis(iminopyrrole)s

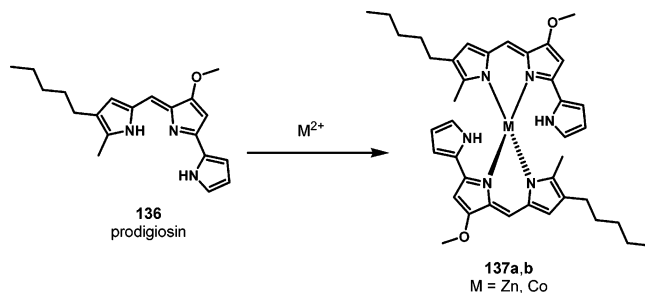


Figure 82. Formation of metal-ion complexes of prodigiosin.

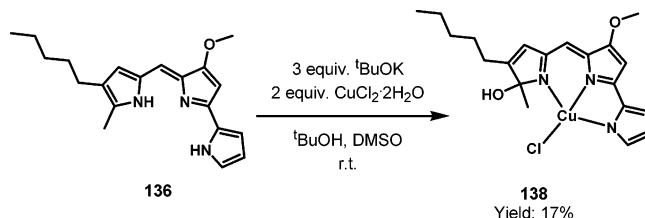


Figure 83. Oxidation upon formation of copper(II) complex of prodigiosin.

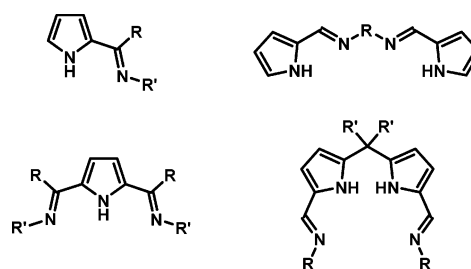


Figure 84. Structural variations of iminopyrroles.

have been shown to form include dinuclear dimeric rectangles,^{352,360} trinuclear trimeric triangles,³⁵⁶ tetranuclear tetrameric squares,^{356,361} and network polymers.^{352,362,363} Recently a new variation in bis(iminopyrrole) structure has been reported in which a dipyrromethane forms the linker between the two bidentate units in the molecule.^{354,355,364} The generalized structures of typical iminopyrroles and bis(iminopyrrole)s are shown in Figure 84.

A wider variety of metal ions have been employed in the synthesis of iminopyrrole complexes than have been reported for dipyrins. These metal ions include lithium(I),³⁶⁴ sodium(I),³⁶⁵ magnesium(II),^{347,351} aluminum(III),^{347,365} potassium(I),³⁶⁴ titanium(IV),^{366–368} yttrium(III),³⁶⁹ zirconium(II), zirconium(IV),^{365,370,371} ruthenium(II),³⁷² palladium(II),³⁷³ silver(I),^{350,360,362,363} samarium(II),³⁷⁴ hafnium(IV),³⁶⁵ mixed valence osmium(II/III),³⁴⁵ iridium(I),³⁴⁴ and mercury(II).^{361,375,376} Much of the variation in metal ions is attributable to efforts to develop iminopyrrole complexes as catalysts for hydrogenation,³⁷⁷ dinitrogen activation,³⁷⁴ and polymerization.^{346,347,365–371,378}

5. Conclusions

Dipyrins and metal complexes of dipyrins display interesting structures and possess many exciting and useful physical properties. There are several routes to the synthesis of dipyrins, each accommodating different structures depending on the overall symmetry or dissymmetry and the degree of substitution of the desired molecule. Dipyrins are known to form both homoleptic and heteroleptic complexes of a varied, but by no means exhaustive, list of metal ions. By far the most popular form of dipyrinato complexes is

the commercialized borondifluoride derivatives known as the BODIPYs. These compounds have been widely developed as fluorescent labels and probes for biological and ion-sensing applications. Dipyrinato complexes are being more frequently used in the design of supramolecular architectures ranging in size and application from energy-transfer cassettes to coordination polymers. There are a large number of structural variations of dipyrins such as calix[4]pyrroline-(1.1.1)s, tripyrins, oxygenated linear oligopyrroles, and iminopyrroles that are also known to form metal complexes. The research that has been conducted into the characterization and applications of these related compounds can be used to further understanding of the metal complexes of dipyrins.

There are many aspects of dipyrin chemistry that remain to be researched in detail. Our goal in writing this review is to highlight known dipyrin chemistry to demonstrate that these structures hold great potential for application in many areas of chemical research. We also aim to highlight areas that are poorly understood about dipyrins in order to recognize potential avenues of research and acknowledge how much work remains to be conducted in these areas.

6. Acknowledgment

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