



Review

Fused-ring metallabenzenes



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Contents

1. Introduction	152
2. Metallabenzenes with fused three-membered rings	152
2.1. Metallabenzothiirenes	152
2.1.1. Synthesis	153
2.1.2. Structure, bonding and spectroscopy	153
2.1.3. Reactions	153
2.2. Metallabenzoxiirenes	154
2.2.1. Synthesis	154
2.2.2. Structure, bonding and spectroscopy	154
2.2.3. Reactions	155
2.3. Metallabenzazirines	155
2.3.1. Synthesis	155
2.3.2. Structure, bonding and spectroscopy	155
2.3.3. Reactions	155
3. Metallabenzenes with fused five-membered rings	155
3.1. Metallabenzofurans	155
3.1.1. Synthesis	155
3.1.2. Structure, bonding and spectroscopy	157
3.1.3. Reactions	157
3.2. Metallabenzothiophenes	158
3.2.1. Synthesis	158
3.2.2. Structure, bonding and spectroscopy	158
3.3. Metallabenzothiazoles and metallabenzothiazolium cations	159
3.3.1. Synthesis	159
3.3.2. Structure, bonding and spectroscopy	160
3.3.3. Reactions	160
3.4. Metallabenzoxathioles	160
3.4.1. Synthesis	160
3.4.2. Structure, bonding and spectroscopy	161
4. Metallabenzenes with fused six-membered rings	161
4.1. Metallanaphthalenes	161
4.1.1. Synthesis	161
4.1.2. Structure, bonding and spectroscopy	162
4.1.3. Reactions	162
4.2. Ruthena- and osmabenzenes that incorporate 8-hydroxyquinolyl fused rings	163
4.2.1. Synthesis	163
4.2.2. Structure, bonding and spectroscopy	163
4.2.3. Reactions	163
4.3. Fused-ring metallabenzenes where π -electron delocalization within the fused ring is frustrated: "tethered" metallabenzenes	163
5. Polycyclic metallabenzenoids	163
5.1. A polycyclic metallabenzenoid that incorporates a fused thiazolidine ring	164
5.2. Polycyclic metallabenzenoids that incorporate fused metallapyridine or metallapyridyne rings	165
5.2.1. Synthesis and reactions	165

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6. Concluding remarks.....	165
Acknowledgements.....	166
References.....	166

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ABSTRACT

Metallabenzonoids that contain a ring fused to the basic metallabenzene core represent a rapidly emerging new sub-category of metallabenzenes. There are a very large number of possible variations in the size, composition, degree of saturation and substitution patterns of the fused rings, as well as different isomer possibilities. At present compounds that incorporate fused 3-, 5- or 6-membered rings are all known and these are covered in separate sections of this review. The syntheses, spectroscopic properties, structures and reactions of the fused-ring metallabenzenes are discussed. Preliminary indications based on these data suggest that when π -electron delocalization can extend over the fused rings, the six-membered metallacyclic rings of the metallabenzonoids retain aromatic character, but at reduced levels compared to the parent metallabenzenes. Appropriate theoretical studies are needed to provide more reliable information about the bonding in fused-ring metallabenzenes.

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1. Introduction

Metallabenzenes are now well established as a distinct class of organometallic compounds and since the first reported example appeared in 1982 [1] a considerable amount of information regarding the syntheses, reactions, structures, physical properties and bonding of these metallaaromatic compounds has been reported [2–6]. More recently it has become apparent that metallabenzonoids that incorporate a ring fused to the basic metallabenzene core represent a rapidly emerging new sub-category of metallabenzenes [6]. Currently, examples of these bicyclic compounds that incorporate fused 3-, 5- or 6-membered ring are all known. The general structures of reported fused-ring metallabenzenes are depicted in Chart 1.

Although this is an area that is still very much in its infancy, the number of members of this set of compounds is potentially very large indeed. For example, variations in the fused ring size (i.e. number of ring atoms), composition (i.e. heterocyclic or all-carbon), degree of saturation (i.e. unsaturated with fully delocalized π -bonding through to fully saturated), and substituents are all possible. In addition, there are a large number of isomer possibilities for these compounds. The position of the metal relative to the fused ring is one important consideration as the metal might either occupy one of the ring junction positions or be in a location remote from these. Clearly, isomerism resulting from the positions of the atoms and/or substituents within the fused rings themselves is also possible.

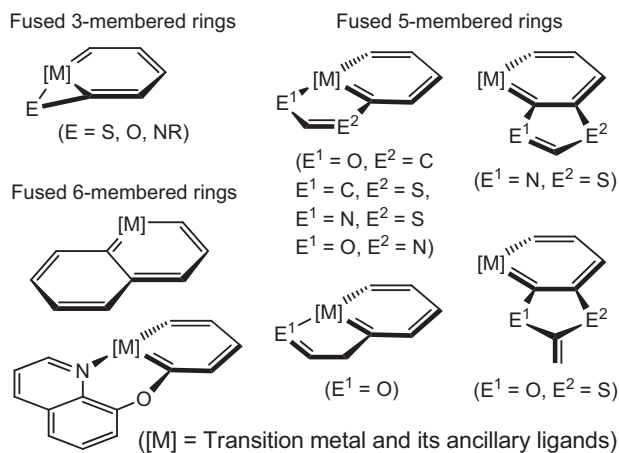


Chart 1. General structures of reported fused-ring metallabenzenes.

Unlike the situation for metallabenzenes where electron delocalisation and aromatic character have been well established, the same has not yet been confirmed for fused-ring metallabenzenes. The limited data currently available suggests that when it is possible to extend the π -electron delocalisation over the fused ring, this does occur at least to some degree. However, more extensive studies are needed to confirm and quantify this for each fused-ring scenario. Because of this uncertainty, the π -electrons of the metallabenzonoids are represented in the schemes and charts as localised double bonds (with the lone electron pairs on the heteroatoms implicit), although this should not be taken as implying an absence of electron delocalisation within these compounds or that this represents an accurate π -electron count [6].

It should be noted that there are a few examples in the literature of metallabenzenes that contain more than two fused rings [7,8]. Although not the primary focus of this review, these compounds are included in a separate polycyclic section at the end of this review.

This review is organised into sections according to the size of the fused ring (i.e. the number of fused-ring atoms). Other fused-ring properties such as composition and degree of saturation are addressed in sub-sections where appropriate. Simple substitution reactions of the ancillary ligands on the metal are not addressed in a separate section, although selected examples appear in some of the synthetic and reaction schemes. Proposed intermediates are labelled in the schemes with a number followed by an upper-case letter, e.g. 1A. The ring numbering schemes follow those used in the original reports. The literature is covered up to July, 2013.

2. Metallabenzenes with fused three-membered rings

A small number of metallabenzenes with fused 3-membered rings are known and one of the first metallabenzenes to be reported contained a fused ring of this type [1]. In all examples the metal is found at a ring junction and the atom or group that forms the fused ring (E, see Chart 1) is either S, O or NR. An alternative description of these compounds is as metallabenzenes with η^2 -C(E) functions, but here these compounds are considered as fused-ring metallabenzenes.

2.1. Metallabenzothiirenes

Metallabenzothiirenes are a class of metallabenzonoids comprised of a metallabenzene ring with a fused three-membered sulfur-containing ring (Chart 2). Metallabenzothiirenes are the metallacyclic analogues of benzothiirene, where a transition metal (with its ancillary ligands) replaces a ring junction carbon atom.

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