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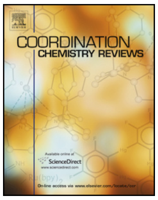

Review

Recent development in the chemistry of transition metal-containing metallabenzenes and metallabenzynes

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Contents

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ABSTRACT

Transition metal-containing metallabenzenes and metallabenzynes are organometallic compounds derived from formal replacement of a CH group or a C atom in benzene and benzyne by an isolobal transition metal fragment. The chemistry of these interesting metallaaromatics has received considerable attention in recent years. A number of such complexes have been obtained from various synthetic routes.

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Interesting chemical properties of these complexes have also been reported. This review summarizes recent progress in the synthesis and reactivity of metallabenzenes and metallabenzynes.

1. Introduction

Aromaticity has fascinated chemists for over a century and is still attracting considerable current attention. The archetypical aromatic compound is benzene. Formal replacement of a CH group in benzene by an isolobal hetero atom/group can give heterocyclic aromatic compounds. In the past, many such compounds with a main-group element/group have been synthesized. Six-membered heterocyclic aromatic compounds are now well documented [1] for species with hetero atoms/groups such as O^+, S^+, Se^+, Te^+, N, P [2], As [3], Sb [3], Bi [3], SiR [4,5], SnR [6], BR^- [7] and GaR^- [8].

Recently, there has been much interest in the chemistry of transition metal-containing metallabenzenes, metallaaromatics derived from formal replacement of a CH group in benzene by an isolobal transition metal fragment. These complexes are interesting because they may display both aromatic and organometallic properties. Transition metal-containing metallabenzenes were first predicted theoretically by Thorn and Hoffman in 1979 [9]. The first stable transition metal-containing metallabenzenes were reported by Elliott et al. in 1982 [10]. Since then, the chemistry of transition metal-containing metallabenzenes has attracted considerable attention both experimentally and theoretically. The early advances in the chemistry of transition metal-containing metallabenzenes have been reviewed by Bleeke in 2001 [11], He et al. in 2004 [12], Wright in 2006 [13] and Landorf and Haley in 2006 [14]. There are also two short accounts on the chemistry of iridabenzenes, one appeared in 1991 [15] and the other one in 2007 [16].

Compounds closely related to metallabenzenes are metallabenzynes [17], which can be thought as compounds formed by formal replacement of a C atom or a CH group in benzyne with an isolobal transition metal fragment. The first stable transition metal-containing metallabenzyne was reported in 2001 [18]. The early progress in the chemistry of metallabenzynes has been summarized in a short account (in 2004) [19], in a review article on the chemistry of metallabenzenes (in 2006) [14] and in a review article on the chemistry of osmium carbyne complexes (in 2007) [20].

Further advances in the chemistry of metallabenzenes and metallabenzynes have been achieved in recent years. In this work, we will summarize recent (mainly from 2006 on) progress in the chemistry of metallabenzenes and metallabenzynes, especially their synthesis and chemical properties.

We recognize that there has also been much interest in the chemistry of other transitionmetal-containing metallaaromatics. For example, substantial progress has also been made in the chemistry of heteroatom-containing metallaaromatics, compounds with a transition metal fragment and other heteroatoms or groups [16,21] including metallathiabenzenes [22], metallapyridines [23], metallapyryliums [24], metallathiophenes [25], metallafurans [26], metallapyrroles [27], metallaindolizine [28], azametallahelicenes [29], metallabenzimidazolium [30], metallapyrimido[2,1-*a*]isoindoles [31], metalladithiolenes [32] and aromatic transition metal clusters [33]. The chemistry of these compounds, although highly interesting, will not be covered here due to the limitation of the scope of this review.

2. Chemistry of metallabenzenes

2.1. Synthetic routes to construct metallabenzene rings

A number of new metallabenzenes have been synthesized in recent years by various synthetic routes. In this section, the strategies to construct the metallabenzene ring are discussed. Metallabenzenes made from modification of the substituent of the metallabenzene ring or from ligand substitution reactions will be described in the section concerning reactivities of metallabenzenes.

2.1.1. Coupling of thiocarbonyl ligandwithalkynes

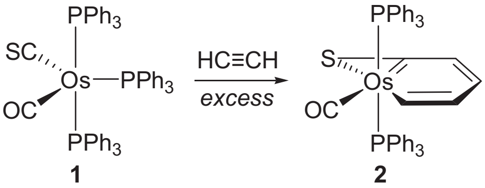
The first stable metallabenzene, osmabenzene **2**, was obtained from the reaction of the osmiumthiocarbonyl complex **1** with excess of ethyne (Scheme 1) [10].

The chemistry has recently been successfully extended to prepare iridabenzenes. For example, treatment of the cationic thiocarbonyl complex $[Ir(CS)(MeCN)(PPh_3)_2]OTf$ (**3**) sequentially with ethyne and LiCl produced the neutral iridacyclopentadiene complex **4**, which in turn reacted with methyl triflate and LiCl to give the neutral iridabenzene $Ir\{C_5H_4(SMe)\}Cl_2(PPh_3)_2$ (**5**) [34]. In the absence of LiCl, complex **3** reacted with ethyne to give the cationic iridacyclopentadiene complex **6**, which underwent amigratory insertion reaction involving the thiocarbonyl ligand to form the cationic iridabenzene **7** (Scheme 2) [35].

2.1.2. Reaction of lithiated 3-vinyl-1-cyclopropenes with metal halide complexes and thermal reactions of benzvalene complexes

Reactions of lithiated 3-vinyl-1-cyclopropenes with metal halide complexes provide another route to metallabenzenes. The first metallabenzene synthesized with the strategy is the iridabenzene **10**, which was produced from the reaction of (*Z*)-1,2-diphenyl-3-(2-lithioethenyl)-1-cyclopropene (**8**) with $IrCl(CO)(PPh_3)_2$ (**9**) (Scheme 3) [36]. The chemistry has been extended to prepare a series of iridabenzenes through the reactions of (*Z*)-1,2-diphenyl-3-(2-lithioethenyl)-1-cyclopropene (**8**) [37,38] or (*Z*)-1-alkyl-2-phenyl-3-(2-lithioethenyl)-1-cyclopropenes [39] with complexes $IrCl(CO)(PR_3)_2$ ($PR_3 = PPh_3$, PMe_3, PMe_2Ph, PEt_3, $PMePh_2$, $P(p\text{-}MeOPh)_3$, P^iBu_3).

The latest development in the synthesis of iridabenzenes with this methodology involves the use of $SiMe_3$ functionalized derivatives (Scheme 4) [40,41]. (Z)-1-Phenyl-2-(trimethylsilyl)-3-(2-lithioethenyl)-1-cyclopropene (**11**) reacted with $IrCl(CO)(PPh_3)_2$ (**9**) to give the iridabenzene **13** along with the iridabenzvalene complex **12** and the cyclopentadienyl complex **14**. When heated at 75 °C, the iridabenzvalene **12** can be converted to the iridabenzene



Scheme 1. Synthesis of the first stable metallabenzene [10].