



Metallafurans and their synthetic chemistry

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Abstract Based on isolobal analogy, the definition of metallafuran was described and its synthetic chemistry was briefly summarized. In the structure of furan, when one of CH groups was replaced by an isolobal metal fragment ML_n ($M = \text{metal}$; $L = \text{ligand}$), the corresponding organometallic complex was called metallafuran, which should be two possible isomers called α -metallafuran (metal fragment at α -carbon of original furan) and β -metallafuran (metal fragment at β -carbon of original furan). As an organometallic complex, α -metallafuran has two resonant forms: one can be viewed as carbonyl coordinated vinyl metal complex and the other can be viewed as alkoxymetal carbene. Therefore, α -metallafuran was also called chelated vinyl ketone metal complex or oxametallacyclopentadiene in the early literatures. For synthesis of metallafurans, α -metallafurans were very common and easily prepared, for example, from alkynes insertion into acyl metal complexes and so on. While there were rare examples reported for β -metallafurans. In this mini review,

the synthetic chemistry of metallafuran was mainly focused on its formation mechanism.

Keywords Metallafuran · Aromaticity · Metallaaromatics · Synthesis · Mechanism

1 Introduction

According to Hoffmann's concept [1], if the symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in molecular fragments are similar, they can be described as isolobal molecular fragments. Based on isolobal principle (now formally known as isolobal analogy), one can predict the bonding and reactivity of lesser-known compound from that of better-known isolobal compound. A good example of isolobal analogy was the prediction of metallabenzenes, a type of novel transition metal containing six-membered ring aromatic compounds [2], in which one of CH groups was replaced by isolobal metal fragment. From then on, it brought the quick development of metalla-aromatic chemistry [3, 4]. For example, the first synthesis of metallabenzene was reported by Roper and co-workers [5] in 1982 and metallabenzynes was prepared by Jia and co-workers [6] in 2001. In 2013, the novel metallapetalenes and their derivatives were reported by Zhu et al. [7, 8]. Among these examples, isolobal analogy has been proved to be a powerful strategy to understand the bonding and reactivity of these kinds of novel organometallic complexes. Now, isolobal analogy can even be used to predict or design new molecules with unique functions and properties. Meanwhile, many hetero-atom containing aromatic compounds [9] have interesting functions and properties.

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Therefore, the metal containing aromatic heterocyclic complexes could be very interesting compounds. The simplest aromatic heterocyclic compound is furan. Following this direction, if one of CH groups in furan is replaced by an isolobal metal fragment (ML_n , M = metal; L = ligand), it can give metallafuran (Fig. 1), which should be two possible isomers called α -metallafuran and β -metallafuran.

As an organometallic complex, α -metallafuran has two resonant forms **A** and **B** (Fig. 1). In general, if the structure of α -metallafuran was mainly contributed from the resonant form **B**, it was also called chelated vinyl ketone or oxametallacyclopentadiene, which has been widely studied much earlier before the concept of isolobal analogy in the literature. In this limited review, we try to trace back the synthesis of α - and β -metallafurans of single five-membered ring with non-cluster substructure selected from the Cambridge Structural Database, CSD version 5.36 (February 2015). The fused metallafurans and some metallafurans are not included due to be well summarized in references [10, 11].

2 Synthesis of α -metallafuran

2.1 Alkyne insertion into acyl complexes

2.1.1 Reactions of alkyne with carbonyl metal alkyl complexes

The report on synthesis of α -metallafuran can be traced back to the early development of organometallic chemistry in 1960s. For example, treatment of carbonyl metal alkyl complex $RMn(CO)_5$ (**1a**, R = H; **1b**, R = Me; **1c**, R = Ph) with alkynes ($R'C\equiv CR''$) can give the five-membered ring complex **2** (**2a**, R = H; **2b**, R = Me; **2c**, R = Ph) [12, 13]. As shown in Scheme 1, the insertion of CO into metal-alkyl bond via migratory insertion gave a metal acyl intermediate $(CO)_4MnCOR$ and then the coordination of alkynes gave complex **3**. Complex **3** underwent insertion of coordinated alkyne to give 16e complex **4**. Finally, the coordination of C=O group to the metal center produced stable five-membered ring complex **2**.

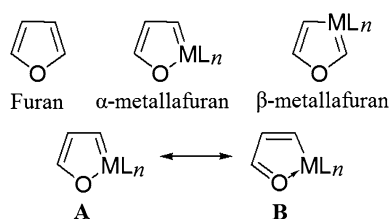
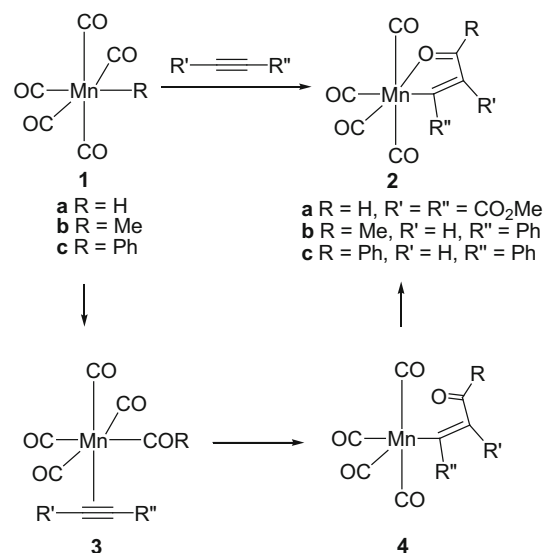


Fig. 1 Structures of furan and metallafurans



Scheme 1 Proposed mechanism for the formation of α -metallafuran **2**

Complex **2** was characterized by IR and elemental analysis. For example, the absorption of C=O group in the five-membered metal ring of **2a** was located at $1,591\text{ cm}^{-1}$, which was less than the normal absorption of C=O group in organic compounds [14]. It indicates that complex **2a** can be viewed as α -metallafuran, despite it was called chelated vinyl ketone complex at that time.

Similarly, other metal containing α -metallafurans can be prepared from the corresponding metal carbonyl complexes with the insertion of alkyne followed by the coordination of C=O group. For example, the molybdenum [15], tungsten [16] and rhodium [17] containing α -metallafurans **6**, **8** and **10** were prepared from the reaction of complexes **5**, **7** and **9** with alkynes respectively (Scheme 2). Among them, the structures of complexes **8** and **10a** have been confirmed by single-crystal X-ray diffraction. The distances of M–C1, C1–C2, C2–C3, C3–O and M–O bonds in the metal ring are summarized in Table S1 (online). For example, the distances of W–C1, C1–C2, C2–C3 and C3–O and W–O for **8** were 2.148(2), 1.386(4), 1.378(4), 1.290(3) and 2.108(2) Å respectively. The result shows that the ring structure of complex **8** is delocalized.

2.1.2 Reactions of alkyne with metal acyl complexes

Obviously, the metal acyl complex (L_nMnCOR) can also react with alkynes directly to give the α -metallafuran via the same mechanism. For instant, treatment of complex **11** with alkyne gave complex **12** as a yellow solid in 20%–40% yield (Scheme 3) [18]. In this reaction, the coordinated acetonitrile of complex **11** dissociated first to

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