

## Review

# Half-sandwich late transition metal complexes based on functionalized carborane ligands



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## ABSTRACT

This review describes the recent progress on the research of half-sandwich late transition metal complexes with functionalized carborane ligands. Continuous study on preparation of different types of carborane-based late transition metal complexes is of great interest because of their rich coordination mode, novel reactivity and promising applications in a variety of important fields. The synthetic pathways used for the preparation of half-sandwich complexes with [SS], [PP], [NP], [PS], [CN], [CS] coordination modes are summarized. Diverse reactivities (metal–metal bonding formation, insertion reaction and B–H activation) and catalytic activities (hydrogenation, olefin polymerization, H<sub>2</sub> activation, asymmetric reduction and cross-coupling reaction) are also discussed in this article.

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## 1. Introduction

During the past few decades, interest in 1,2-dicarba-*closo*-dodecaborane ( $o\text{-C}_2\text{B}_{10}\text{H}_{12}$ ) and its derivatives, which possess rigid three-dimensional aromatic structures, greatly increased owing to their chemical and thermal stability [1–18]. The field of icosahedral carboranes has developed extensively since the first publications almost 50 years ago [19–22]. Carborane is an electron-deficient cage, and all the carbon and boron atoms in this icosahedral cage are hexa-coordinate to alleviate the electron deficiency. Both DFT calculations and experimental results show that the C–H bonds in the cage are weakly acidic, and the electron properties of the *closo*-carborane cage were explicitly elaborated by Mirkin and coworkers in 2011 [23]. So the deprotonation of the C–H bonds of this cage in the presence of strong bases (such as alkyllithium, potassium hydride and Grignard reagents) occurs smoothly, then the obtained carboranyl anion can subsequently react with diverse electrophilic reagents to give various types of substituted carboranyl ligands. Lots of reports on extremely air and moisture stable C, N–, C, P–, C, S–, N, P–, N, S–, P, P– and S, S-chelating *o*-carboranyl transition metal complexes suggest the metal center could be greatly stabilized by the bulky *o*-carborane cage in organometallic reactions [14]. Because of their unique physical and chemical properties, carborane derivatives have been utilized for the preparation of catalysts [24,25], energy materials [26], polymers [27,28], and a large number of unique coordination compounds [29–31]. Moreover, research of carboranes in the area of biomedicine chemistry often concentrated on their application in boron neutron capture therapy (BNCT), and in most cases they are very efficient for treating cancer by using this method [3].

Among the various types of reported carboranyl-based complexes, half-sandwich transition metal complexes based on substituted-carboranyl ligands are unique because of the particular electronic and steric properties of the half-sandwich moiety. Half-sandwich late transition metal complexes with  $\text{Cp}^\#$  unit ( $\text{Cp}^\# = \text{Cp}$  ( $\eta^5\text{-C}_5\text{H}_5$ );  $\text{Cp}^*$  ( $\eta^5\text{-C}_5\text{Me}_5$ );  $\text{Cp}'$  ( $\eta^5\text{-1,3-}^t\text{Bu}_2\text{C}_5\text{H}_3$ ); *p*-cymene ( $\eta^6\text{-1-Me-4-}^i\text{Pr-C}_6\text{H}_4$ )) attracted considerable attention because of their distinguishing features (Fig. 1): (i) the transition metal precursors [ $\text{Cp}^\#\text{MCl}_2$ ] ( $\text{M} = \text{Co}, \text{Ir}, \text{Rh}, \text{Ru}$ ) are easily synthesized with high yields by reactions of metal chlorides with conjugated ligands (such as arenes, cyclopentadiene, and their derivatives); (ii) The hemisphere of the metal center is perfectly shielded by the  $\text{Cp}^\#$  ligands, from which the complexity of the subsequent reactions is avoided; (iii) The redox property and solubility of these transition metal complexes is enhanced by introducing various types of substituents to cyclopentadienyl ring.

We have been interested in carborane-based transition metal complexes for many years, especially in the synthesis and application of organometallic complexes based on the functionalized carboranyl ligands. In this review, we summarize the recent progress on the synthesis, structure and reactivity of the half-sandwich late transition metal complexes containing

functionalized carboranyl ligands. Early transition metal complexes and rare earth metal analog were thoroughly studied and reviewed by Xie [32–35], thus this part will not be included in this paper. Moreover, the applications of carborane-based late transition metal complexes in catalysis will be discussed subsequently. (The unlabeled vertex of the polyhedral structures in the following schemes is a BH group, and the black dot of the carborane cage represents a carbon atom).

## 2. Half-sandwich late transition metal complexes with functionalized carboranyl ligands

### 2.1. 1,2-Dichalcogenolato-*o*-carborane

#### 2.1.1. Metal–metal bond formation

1,2-Dichalcogenolato-*o*-carborane [ $1,2\text{-E}_2\text{-(C}_2\text{B}_{10}\text{H}_{10})$ ] $^{2-}$  ( $\text{E} = \text{S}, \text{Se}$ ), which are easily prepared by the insertion of elemental chalcogen into the Li–C bonds of dilithium carborane  $\text{Li}_2(o\text{-C}_2\text{B}_{10}\text{H}_{10})$ , have raised considerable interests in their wide-ranging potential applications [36]. During the last decade a large number of late transition metal complexes based on this ligand have been reported, among which group 8 and 9 complexes are the most studied species, probably because of their easy preparation and high stability [37]. Model complexes  $\text{A Cp}^\#\text{M}[\text{C}_2\text{E}_2(\text{B}_{10}\text{H}_{10})]$  ( $\text{M} = \text{Co}(\text{Cp}), \text{Rh}(\text{Cp}^*, \text{Cp}'), \text{Ir}(\text{Cp}^*), \text{Ru}(p\text{-cymene})$ ;  $\text{E} = \text{S}, \text{Se}$ ) were furnished in almost quantitative yields by reactions of 1,2-dichalcogenolato-*o*-carborane ligands with half-sandwich metal precursors [38] (Scheme 1). Crystal structures of these complexes show that the  $\text{MC}_2\text{S}_2$  core is nearly planar. The unsaturated 16-electron complexes **A** can take up a two-electron donor (such as CO, pyridine (py), RCN, phosphine ligands) to give 18-electron saturated complexes **A'** with folded  $\text{MC}_2\text{S}_2$  five-membered ring.

Many multinuclear metal clusters containing direct M–M interactions are now well known and have numerous applications [39–42]. So far, several efficient routes, such as photochemical reactions and the exchange reaction between late transition metal precursors and metal hydrides, have been utilized to construct the M–M bonds [43]. The ancillary ligands in these complexes (such as Cl, CO and  $\text{Cp}^\#$ ) play an important role in stabilizing the M–M bonds. Herberhold and Jin's work on complex **A** suggests that this kind of species might be a good candidate for the construction of the multinuclear metal clusters with carborane cages through M–M bonds formation, owing to the electron deficiency at the metal center and strong coordination ability of chalcogen element. There are some other advantages of this species, for example, the solubility of the multinuclear metal clusters is remarkably increased by the combination of the high symmetric icosahedral carborane cage and the cyclopentadienyl ligands. Extensive explorations indicate that direct M–M bonds formation between group 8 or 9 (Ru, Co, Rh, Ir) metals and transition metals (Mo, W, Fe, Co, Rh, Ir) can be accomplished successfully by using the building block **A** and low oxidation state electron rich transition metal precursors (such as  $[\text{M}(\text{cod})\text{Cl}]_2$ ,  $[\text{M}(\text{cod})(\mu\text{-OMe})_2]_2$ ,  $\text{cod} = 1,5\text{-cyclooctadiene}$ ,  $\text{M} = \text{Ir}, \text{Rh}$ ;  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ ;  $\text{Ni}(\text{cod})_2$ ;  $\text{M}(\text{CO})_3(\text{py})_3$ ,  $\text{py} = \text{pyridine}$ ,  $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Fe}(\text{CO})_5$ ;  $\text{Co}_2(\text{CO})_8$ ; etc.) as starting material. Thus a series of *bi*-, *tri*- and *tetra*-nuclear *homo*- and *hetero*-metal clusters are obtained by taking advantage of the electron deficiency on the metal center and the strong assisting potential of the ancillary ligands [13,14,44–52] (Fig. 1). Among various types of multinuclear clusters presented in Fig. 2, *tri*-nuclear cluster with [ $\text{Cp}^*(\text{Ir}_2\text{Mo})$ ] skeleton (**H**) shows an excellent third-order nonlinear optical properties. The achievements obtained in this field are highlighted because of their potential application in the development of novel optical materials with particular physical and chemical properties [53].

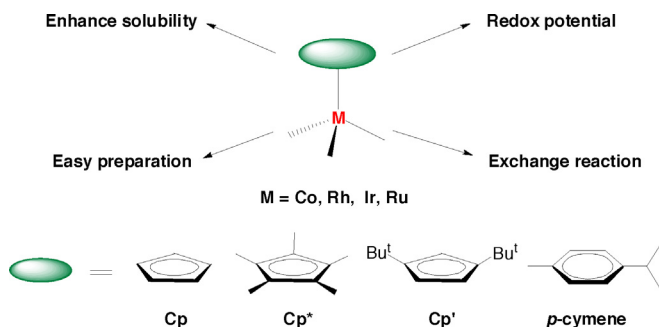


Fig. 1. Structure features of half-sandwich moiety.

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