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Review

Carbene ligands in diiron complexes ☆

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Abstract

The diiron frame $Fe_2Cp_2CO_2$ allows the coordination of a variety of carbene ligands, including heteroatom substituted (Fischer type) and alkylidenes, in both bridging and terminal coordination modes. Synthetic strategies have been devised for obtaining aminocarbenes and thiocarbenes, by nucleophilic addition on the corresponding bridging amino- and thio-carbyne cationic complexes $[Fe_2(\mu\text{-}CX)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (X = SMe, NMe_2, N(Me)Xyl), respectively. A more general approach to the synthesis of diiron complexes bridged by carbenes, exploits the electrophilic character of the sulphonium complex $[Fe_2\{\mu\text{-}C(CN)(SMe_2)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ and the *facile* displacement of the SMe_2 moiety by nucleophiles. These methods afford a large variety of heteroatom (N, P, O, S) substituted carbene complexes and also μ-alkylidenes.

Terminally bonded alkynyl methoxy carbene complexes have been obtained by the classical Fischer method, consisting in nucleophilic addition at a terminal CO, to generate an acyl intermediate, followed by oxygen atom methylation. The coordination to diiron cationic complexes makes the alkynylmethoxy carbene ligands very reactive towards the addition of nucleophiles, like amines and carbanions. These additions are regio- and stereoselective, occurring exclusively at the alkynyl moiety.

Finally, new multidentate and functionalized bridging ligands are described. They are anchored to the diiron frame through an aminocarbene, or an alkylidene binding end, or both. These ligands result from intramolecular couplings and rearrangements which involve the μ-aminocarbyne, the terminally bonded nitrile ligands and acetylides.

Keywords: Carbene; Carbyne; Diiron complexes; Bridging ligands

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Contents

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1. Introduction

Since the first tungsten(0) carbene complex reported by Fischer and Maasböl in [1], transition metal carbene complexes have experienced a rapid and enormous development which has been paralleled by applications in organic synthesis [2] and catalysis [3]. Both heteroatom stabilized carbenes (Fischer) and electrophilic (Schrock) [4] carbenes are considered among the most versatile organometallic reagents.

The overwhelming majority of carbene complexes are mononuclear and investigations concerning di- and polymetallic carbene complexes have been considerably more limited [5]. However, they represent an area of growing interest in the development of new reagents and catalysts because of the potential advantage of cooperative effects due to the presence of two, or more, metal atoms [6]. An additional reason which makes attractive the studies on dinuclear complexes derives from the possibility of favouring further coordination modes for the carbene ligands, which in turn, are expected to produce a considerable extension and modification of their reactivity. As an example, Sierra has recently reviewed [5] on the different mode, for a heteroatom substituted metal carbene (Fischer type carbenes) to join a second metal atom. As shown in Chart 1, the bond, which can be direct or mediated by an hydrocarbon chain, may occur through: (i) the carbene carbon (**I**); (ii) the heteroatom (**II**); (iii) the metal atom (**III**). In addition, carbenes can 'bridge' two metal atoms (**IV**), and Fischer carbenes may assume a further coordination mode (**V**) due to the heteroatom–metal interaction, which is believed to contribute significantly to their stability [7].

Bridging carbenes are usually more stable, and less reactive compared to the corresponding terminally coordinated species. Notwithstanding this, they have been intensively investigated, and in particular complexes bearing the bridging methylidene (μ-CH_2) have provided valuable organometallic models for investigating Fischer–Tropsch processes [8].

Herein we will briefly review our contribution in the field of the dinuclear complexes containing carbene ligands, both bridging and terminally coordinated.

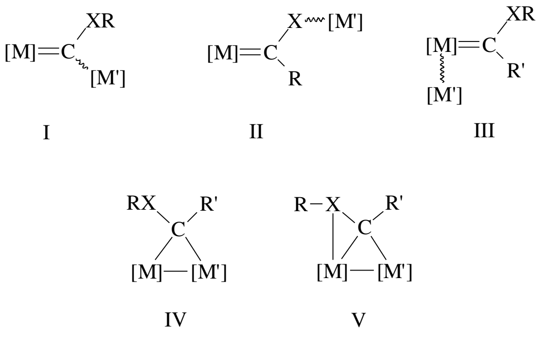


Chart 1.

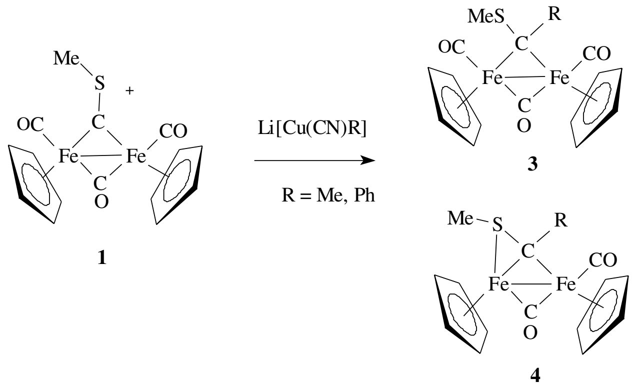
2. Dinuclear complexes with bridging Fischer carbene ligands

2.1. Synthesis from bridging carbyne complexes

Several methods have been devised for the synthesis of bridging carbenes; among them, the outstanding contributions of F.G.A. Stone have to be recognized [9] for his modular approach to the construction of clusters with bridging carbenes and carbynes, and the fruitful use of isolobal analogy concepts [10]. The reaction of mononuclear carbynes with appropriate metal containing nucleophiles or metal hydrides is still a useful route for synthesis of bridging carbene complexes [11]. Bridging carbynes are also good source of μ-carbenes: a significant example concern the bridging methylidyne complex $[Fe_2(\mu\text{-}CH)(\mu\text{-}CO)(CO)_2(Cp)_2]^+$, which has been studied in details over more than a decade by Casey et al. [12]. The relevant electrophilic character of the μ-CH ligand allows a large variety of nucleophilic additions at the bridging carbon, including the remarkable 'hydrocarbation' [13] and provide access to a variety of bridging carbene complexes.

Several years ago our attention was directed to related diiron complexes characterized by the presence of heteroatom substituted bridging carbyne ligands: the thiocarbyne $[Fe_2(\mu\text{-}CSMe)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1**) [14] and aminocarbyne $[Fe_2\{\mu\text{-}CN(Me)R\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (R = Me, CH_2Ph, Xyl) (**2**) [15]. Our aim was to find methods for generating Fischer type bridging thio- and amino-carbene complexes and to study their chemistry.

The thiocarbyne complex **1** undergoes addition at the bridging carbyne carbon by a variety of nucleophilic regents, including: $NaBH_4$ [16], cyanide [17], and several organocopper reagents [18] (Scheme 1). In all the cases,



Scheme 1.