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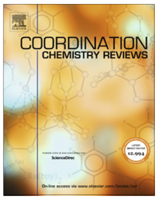

Review

# Non-heteroatom-substituted alkylidene complexes of groups 10 and 11

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ABSTRACT

This review aims to offer a detailed summary of the discoveries regarding non-heteroatom-substituted alkylidenes of group 10 and 11 metals that have appeared in the literature since the first isolable representative of this class was reported in 2002. Special attention is focused on synthetic and bonding aspects of well-defined species. The importance of this family of compounds in catalytic organic transformations is often mentioned and a number of references are provided. We stress, however, that it is not the main issue of this review, as this topic has received considerable attention in the current literature.

**Contents**

## 1. Introduction and scope

Transition metal complexes with carbene ligands have expanded over the years to constitute one of the most important families of organometallic compounds. Since the development of N-heterocyclic carbenes (NHCs) [1], and more recently of the also highly versatile cyclic(alkyl)(amino)carbenes (CAACs) [2], carbenes have been employed as ancillary ligands to provide thermodynamic and kinetic stability to countless transition metal complexes and reaction intermediates. These carbenes have become indispensable partners of *d* transition elements and main group metals alike, and perform an invaluable function in homogeneous catalysis [1,2].

Notwithstanding the importance of carbenes as spectator ligands, the vital role that transition metal carbenes play in modern chemistry rests largely on the extraordinarily rich and diverse reactivity of the $M{=}C$ bond, that allows their successful applications in diverse organic transformations whose importance cannot be overstated, not least in homogeneous catalytic olefin metathesis [3–10].

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*Abbreviations:* Mes, 2,4,6-trimethylphenyl; Xyl, 2,6-dimethylphenyl; *p*-Tol, 4-methylphenyl; Tf, trifluoromethylsulphonyl; EDA, ethyl diazoacetate.

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The explosive growth of the field has naturally given rise to extensive literature coverage. A comprehensive annual survey on the progress of metal–carbene chemistry is provided by Herndon in this Journal, with the latest, covering the year 2015, appearing in the second half of 2016 [11]. In this article we concentrate on carbenes of late transition metals. Complexes of Fe, Ru and Os with carbene ligands have been known for several decades. Similarly, a variety of carbene complexes of Group 9 elements have attracted considerable attention. In particular, we and other researchers have described a number of complexes of Ir(III) with carbenes of both the :CRR′ and :CRX types (X = heteroatom substituent) [12–15]. Accordingly, as detailed later, the aim of this review is to offer a concise summary of complexes of groups 10 and 11 metals with carbene ligands devoid of heteroatoms.

Before we discuss this chemistry in due detail, a word is perhaps necessary on the terminology we use in this review. The comments we will make in this regard will smoothly lead us to some, necessarily brief, considerations on the reactivity modes exhibited by the metal–carbene bond and on the bonding models supporting this chemistry.

The terms "carbene" and "alkylidene" are often used as synonymous by coordination and organometallic chemists. Even though both indicate an organic fragment that binds to a metal centre through a divalent 6-electron carbon atom, :C(R)R′, this causes confusion and creates ambiguity. The origin of the above terms is as follows.

In 1964, Fischer and Maasböl prepared the first transition metal carbene [16a], the tungsten complex $W(C(OMe)Me)(CO)_5$, that was soon followed by other related compounds [16b,c]. These complexes are 18-electron species in low oxidation states. They are reasonably stable and feature heteroatoms at the carbene atom, which generally exhibits electrophilic reactivity. Only four years later, Öfele reported a surprisingly stable chromium complex containing also a $Cr(CO)_5$ fragment, but bound to a cyclopropylidene unit, *i.e.* a carbene ligand with no heteroatoms [17]. Subsequently, Schrock discovered a new class of metal carbenes, exemplified by the 10-electron species $Ta(CHCMe_3)(CH_2CMe_3)_3$. In the series of complexes made by Schrock and coworkers [18], an early transition metal in high oxidation state, with 10–16 valence electrons, is bonded to a nucleophilic carbene carrying C or H substituents at the carbon atom. It soon became customary to name the two classes of metal carbenes as Fischer and Schrock carbenes, respectively.

In the following years many compounds of general formula $L_nM = CRR'$, where R and R′ are H, alkyl or aryl, were prepared and named alkylidenes as derivatives of alkyls [19], regardless of their nucleophilic or electrophilic reactivity. In this way, it became common practice to use the term "alkylidene" when referring to complexes with H, alkyl or aryl substituents on the carbon, and "carbene" to refer to species with one or two heteroatom substituents [20a]. But this was not uniformly accepted by researchers in the field. Many utilized "carbene" and "alkylidene" for Fischer and Schrock complexes, respectively, whereas others employed only "carbene" or only "alkylidene", for all metal carbenes, or even used the two terms interchangeably. The nomenclature committee of the IUPAC recommended that carbene should be reserved for describing the free ligand, naming all transition metal complexes of carbenes as substituted alkylidenes [21]. As it is evident nowadays, these recommendations have not been standard practice among transition metal carbene chemists. However in his recent book [22a], Bochmann states that *the systematic term "alkylidenes" is now applied to all types of carbenes*. Moreover, the expression *alkylidene complexes in low oxidation states* is employed as equivalent to Fischer carbenes, while *alkylidene complexes in high oxidation states* ($d^0$) is meant to describe Schrock carbenes [22a].

The real distinction between the two families of carbene complexes resides doubtless in the nucleophilic or electrophilic reactivity they may display [22]. As lucidly compiled and discussed by Roper some 30 years ago [20], similar to other chemical reactions, those of coordinated carbenes are influenced by frontier orbital-controlled and charge-controlled factors [23]. Thus, despite the $M^{\delta+}$–$C^{\delta-}$ polarity of the metal–carbene bond that may be suggestive of nucleophilic behaviour, the reactions of Fischer carbenes (e.g. $Cr(=CXY)(CO)_5$) with nucleophiles are frontier-orbital controlled. Hence, electron density transfer from the HOMO of the nucleophile to the carbene complex LUMO, that resides largely on $C_\alpha$, disrupts the usually reduced π interaction found in these complexes and converts the metal–carbene bond into a metal-alkyl one. Conversely, when the metal–carbene bond has high π character as in Schrock carbenes, electrophilic attack at the carbene carbon atom is expected, particularly when this atom is most negatively charged and when the π bonding orbital has strong carbon-$p_\pi$ character [20b].

An alternative interpretation of carbene reactivity based on quantum-mechanic calculations was offered by Hall in 1984 [24]. In this approach the electrophilic or nucleophilic reactivity of the M=C bond can be explained with the aid of different bonding schemes (Fig. 1). Using the isolobal analogy, 18-electron metal carbenes may be viewed as arising from the bonding of singlet metal and singlet carbene fragments, *i.e.* from donor–acceptor σ and π interactions (Fig. 1a) [20,22]. Clearly, the resulting dative covalent bonds [25] would be akin to those in M–CO linkages, such that for the singlet-bonding, donor–acceptor metal carbene scheme, electrophilic reactivity can reasonably be expected. Moreover, singlet electronic states would be favoured by strong π acceptors at the metal and by heteroatom substituents on the carbene, which increase the HOMO–LUMO gap in the carbene ligand [20].

In contrast, nucleophilic, often electron-deficient metal carbenes, can be electronically associated with triplet electronic states of their metal and carbene building units (Fig. 1b), resulting in the formation of two normal covalent bonds [25], and in olefinic-like, *i.e.* nucleophilic, reactivity of the M=C bond. In this case, triplet states can be foreseen for metal fragments that lack strong π acceptor ligands, as well as for carbenes bearing only hydrogen or hydrocarbyl substituents, particularly alkyl groups. Naturally,

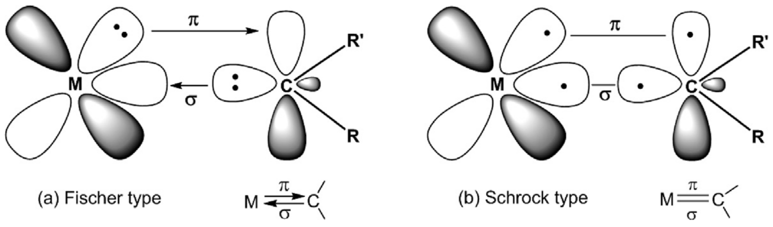

**Fig. 1.** Bonding situations in metal complexes with carbene ligands [22]. (a) Singlet metal and singlet carbene fragments proposed for low oxidation state Fischer carbenes. (b) The triplet metal and carbene building blocks in high oxidation state alkylidene complexes (Schrock carbenes).

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