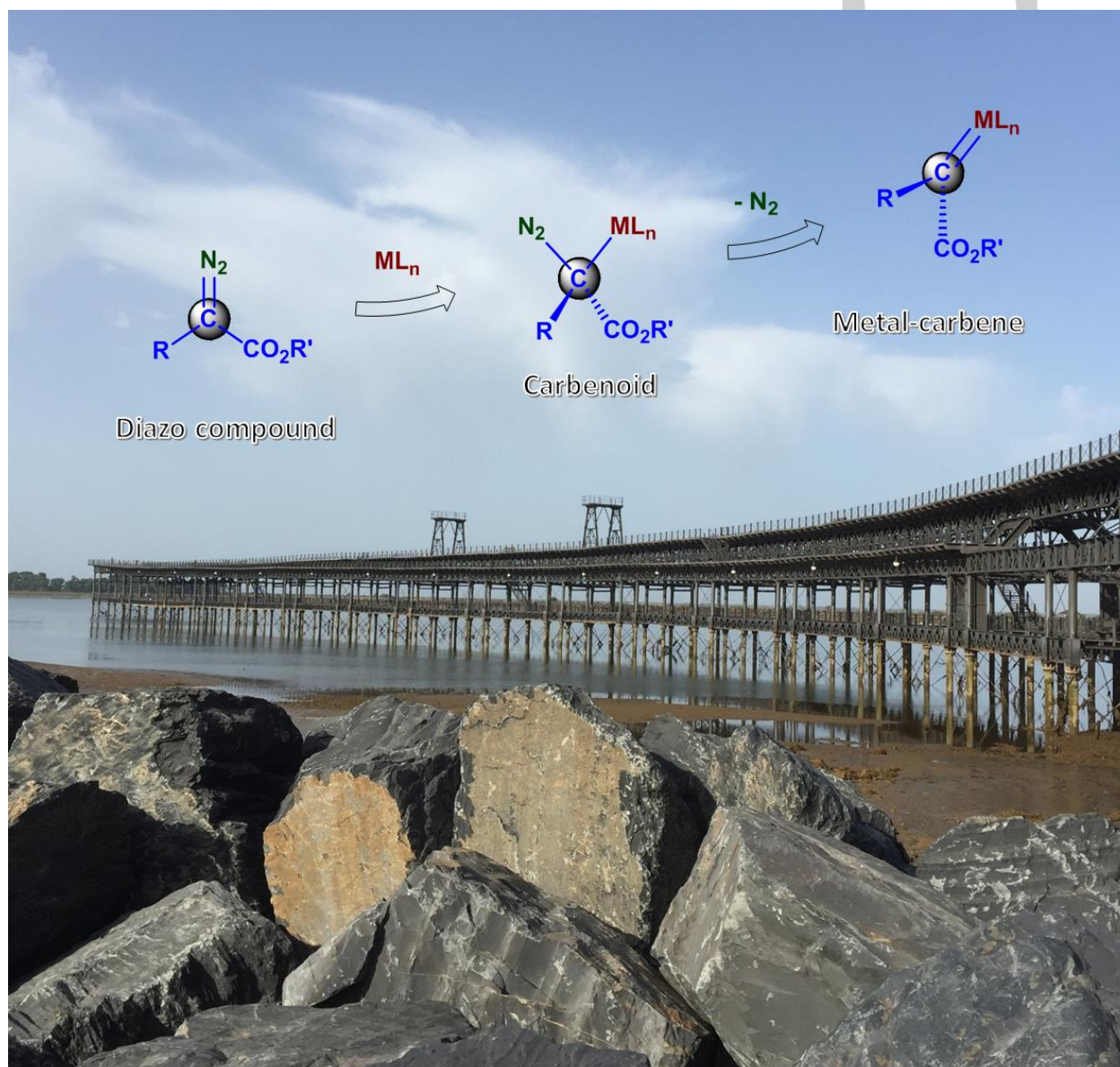


POST-PRINT VERSION

Carbenoids

Dimensioning the term carbenoid

Ana Caballero^{*[a]} and Pedro J. Pérez^{*[a]}*In Memory of Prof. Peter Hofmann ((optional))*

Dimensioning the term carbenoid

Ana Caballero*^[a] and Pedro J. Pérez*^[a]

Abstract: The current use of the term carbenoid is discussed, particularly in the context of carbene transfer reactions from diazo compounds, where intermediates of type $L_nM=CR^1R^2$, or one of its resonance forms, are tagged with such name. We herein discuss this issue, on the basis of the data evidencing the metal-carbene nature of those intermediates, as well as the existence of carbenoids of type $(N_2)(M)C R^1R^2$ *en route* to the formation to $L_nM=CR^1R^2$ from diazo reagents. We propose the exclusive use of the carbenoid term to species of type $(X)(M)C R^1R^2$ with a tetrasubstituted carbon center that upon loss of X afford an effective carbene transfer process.

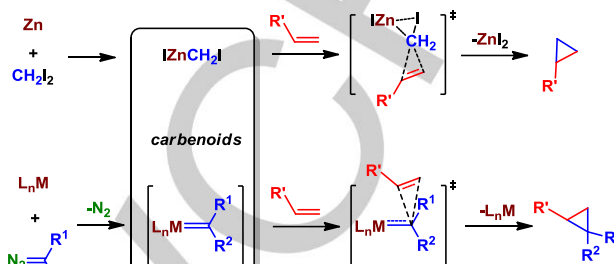
Introduction

The term carbenoid was first coined^[1] half a century ago by Closs and Moss referring to those compounds exhibiting reactions qualitatively similar to those of carbenes but not being necessarily free divalent CR_2 species. In 1995, a definition was provided by IUPAC in the following manner: "complexed carbene-like entity that displays the reactivity characteristics of carbenes, either directly or by acting as sources of carbenes".^[2] A literature survey for "carbenoid"^[3] reveals that the term is mainly applied to the two types of species shown in Scheme 1. On one hand, a compound containing a tetracoordinated carbon atom with one metal-carbon bond, from which a carbene group can be transferred,^[4] the most common example being the so-called Simmons-Smith reaction (Scheme 1a).^[5] In this transformation, diiodomethane reacts with Zn to give the I_2ZnCH_2 carbenoid species that reacts with an olefin affording the cyclopropane product. On the other, there are examples of all transition metals from groups 8 to 11 to decompose diazo reagents $N_2=CR^1R^2$ and subsequently transfer the carbene CR^1R^2 group to a number of different substrates (Scheme 1b).^[6] The reaction takes place through the intermediacy of $L_nM=CR^1R^2$ species that are also frequently tagged as carbenoids in the literature. The aforementioned survey^[3] has shown that from 2000 to date, ca. 70% of the nearly 1,000 references containing the term carbenoid are referred to in situ generated or isolable species $RR^1C(M)X$, whereas the remaining 30% are related $L_nM=CR^1R^2$ species from

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diazo compounds. In this contribution we wish to provide our view

on this definition, with a proposal of removing the use of this term to the latter class of compounds. It is noteworthy that Echavarren

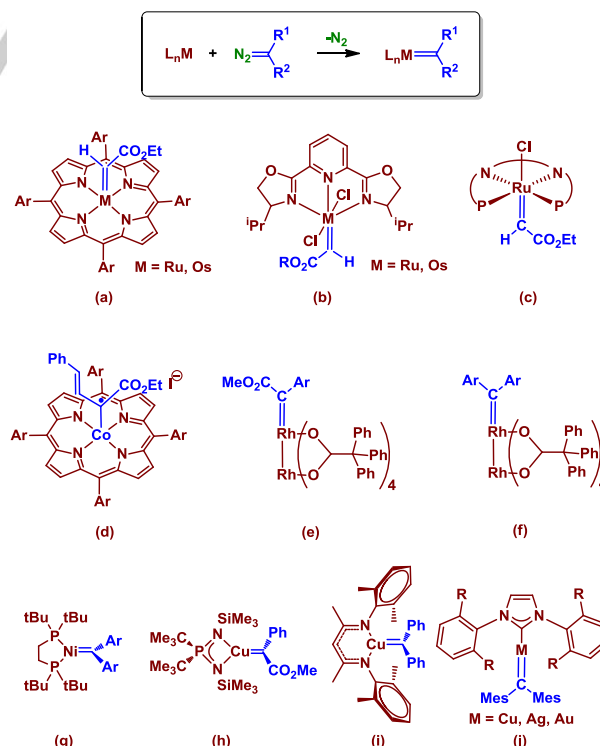


Scheme 1. Current uses of the term carbenoid. Top: The Simmons-Smith reaction, based on a zinc-carbenoid. Bottom: the metal-mediated carbene transfer from a diazo compound.

and co-workers have recently published a Concept article about this issue focused on gold compounds.^[7]

Metal-carbene complexes from diazo compounds are Fischer-type carbene complexes

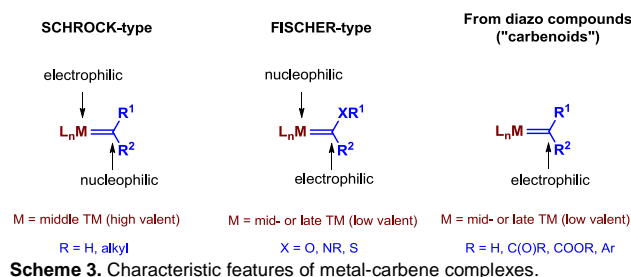
The transfer of a carbene group from a diazo compound was reported more than a century ago by Silberrad and Roy.^[8] Fifty years later, Yates proposed^[9] for the first time that the metal could be participating in the process upon forming a metal-carbene



Scheme 2. Representative examples of isolated metal-carbene complexes from the reaction of a diazo compound and a transition metal complex.

entity from which the carbene group is further transferred. Extensively employed for decades in organic synthesis,^[10] it has been only since the 90s that the first examples of the isolation and characterization of metal-carbene complexes derived from the interaction of a metal source and a diazo compound were reported.^[11] Scheme 2 displays some representative examples, which unambiguously demonstrate that such metal-carbene complexes exist as intermediates in carbene transfer reactions.

Metal-carbenes constitute a class of well-known organometallic complexes.^[12] Historically, their classification was divided in separate groups as Fischer and Schrock carbene complexes (Scheme 3). The former usually display a heteroatom directly bonded to the carbene carbon atom, which shows electrophilic character, whereas the latter display nucleophilic character at that carbon. The metals typically forming these complexes are middle or late transition metals, in low oxidation state, for Fischer type- and middle, high valent transition metals, for Schrock type-carbene complexes. In the case of the metal-carbene complexes originated upon the action of a diazo compound, for which the term carbenoid is yet commonly applied,^[12] most of them contain a carbonyl group vicinal to the carbenic carbon atom, the other group being H or aryl. In some cases two aryl substituents have also been employed. The nature of the carbene ligand in those complexes is mainly electrophilic, since their reaction with nucleophiles such as olefins promotes the formation of cyclopropane rings. Because of this, it seems reasonable to classify the complexes shown in Scheme 2 as *Fischer carbene complexes and not carbenoids*: they show similar electrophilic behavior at the carbene carbon atom, similar reactivity toward nucleophiles, and they are coincidental in the transition metals leading to their formation.

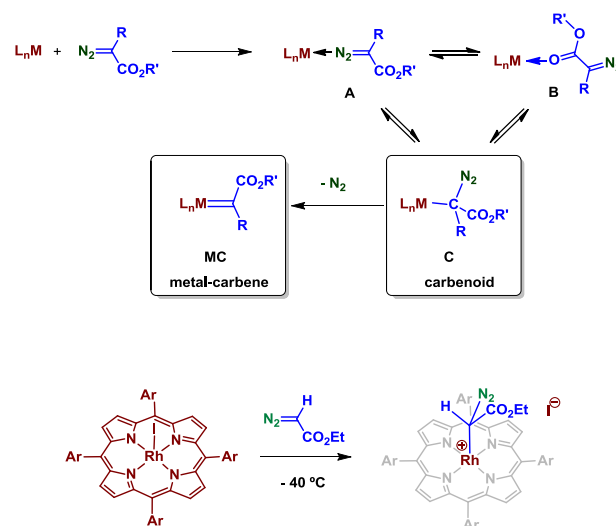


Scheme 3. Characteristic features of metal-carbene complexes.

There is one typical feature of Fischer metal-carbene complexes that is the observance of rotation around the metal-carbon bond. It is well known that such rotation implies the weakening of such double bond, i. e., a decrease of the π -backbonding contribution (see Scheme 5). Examples in the literature are numerous, even the seminal chromium complex $(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Me}$ showing such behavior.^[13] Dynamic studies led to determination of the rotation barrier of $12.4 \text{ kcal mol}^{-1}$. This rotation becomes crucial in some reactions, as is the case of the Ru(Grubbs)-catalyzed olefin metathesis, where a 90° rotation of the $\text{Ru}=\text{CHR}$ moiety is required to achieve the geometry needed to interact with the olefin.^[14] In support of metal-carbene complexes generated from diazo compounds being Fischer-type metalcarbenes, such rotation has also been observed. The first example of a copper-carbene of this class was described by Straub and Hofmann (Scheme 2g).^[19] The rotation barrier found of ca. 36 kcal mol^{-1} was due to a rotation around the Cu-C bond, and it is worth mentioning that the authors classified this compound as a Fischer-type carbene.

The diazocompound-carbenoid-metalcarbene sequence

The interaction of a diazo compound with a metal center may occur through the different donor atoms of the diazo reagents.^[10b] These are the diazo functionality (that may coordinate in several



Scheme 4. Top: Intermediates relevant for metal-diazo interaction, and subsequent formation of carbenoid and metal-carbene species. Bottom: detection of a rhodium-carbenoid by Kodadek and co-workers prior to the carbene transfer step.

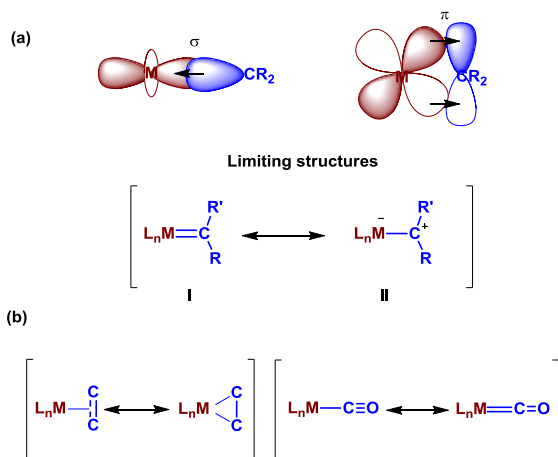
fashions, **A** in Scheme 4), the donor atoms of the substituents (oxygen atoms in carbonyl or carboxylate groups, **B** in Scheme 4) and the carbon atom supporting the diazo group (**C** in Scheme 4). In some cases, intermediates **A** and **B** are usually stable enough to be detected and/or isolated, and they are commonly located outside of the catalytic cycle, either as catalyst resting states^[15] or dead-ends.^[16] However, it is intermediate **C** the only productive species toward the direct formation of the metal-carbene complex. This is in fact a *carbenoid* species since removal of a leaving group (N_2 in this case),^[3a] originates the metal-carbene complex **MC**. In the seminal work of these investigations, Kodadek and co-workers described^[17] the detection by NMR spectroscopy of such rhodium-carbenoid when reacting a rhodium-porphyrin complex with ethyl diazoacetate at -40°C (Scheme 4). Addition of styrene led to carbene transfer and further cyclopropane formation, albeit the rhodium-carbene intermediate was too reactive to be detected. Thus, the use of the carbenoid term referred to these transformations is appropriated when referring to species such as **C**, but not to the metal-carbene intermediate **MC**.

Limiting structures in metal-carbene species are not carbenoids

Another feature frequently associated with the use of the carbenoid term in carbene transfer reactions from diazo compounds is the nature of the carbon atom bonded to the metal.

More precisely, the question refers to whether its reactivity approaches to that expected for a carbenic carbon or a carbocation. When available, structural data has been employed to support one or the other. The aforementioned Concept article from Echavarren's group^[7] contains a complete discussion on this structural feature in gold-based carbene complexes. Key point is that both situations are limiting cases of the same class of metal-carbene compounds. In Fischer carbene complexes the M-CR¹R² bond is explained in terms of two contributions: the σ donation from the carbene group to the metal and the π back donation from the metal center to the carbene group (Scheme 5). Electrophilicity at the carbene carbon atom is enhanced upon decreasing the latter contribution, a strategy employed to promote its reaction with poor nucleophiles such as the C-H bond of alkanes.^[6] Thus, two limiting structures I and II can be proposed for this class of compounds (formed from extrusion of nitrogen from the carbenoids (L_nM)C(N₂)R¹R², **C** in Scheme 4) in which the limits for M-C bond order are 1 (lack of π back donation) or 2 (complete π back donation, Scheme 5). This simple explanation for the M-L double bond is based in the Dewar-Chatt-Duncanson model,¹⁸ and is also applied to several classes of compounds, such as olefin or carbonyl complexes, among others. Pure examples of the limiting cases are rare, and a range of bond situations occurs for each case.

The above information, albeit general and well-known, seems crucial at this point since there are examples in the literature in which a higher contribution of the carbocationic resonance has been assigned with a carbenoid character.¹⁹ This is, in our opinion, a wrong use of such term. First, the differences between a carbenoid and a metal-carbene have been clarified above, being two distinct species even within the same chemical reaction. Second, the existence of two (or more) resonance forms of the same chemical entity cannot lead to different names. For instance, it is common referring to a metal-olefin complex with a high contribution of the metallacyclopropane limiting structure (or resonance form), or to a metal-carbonyl complex with a high

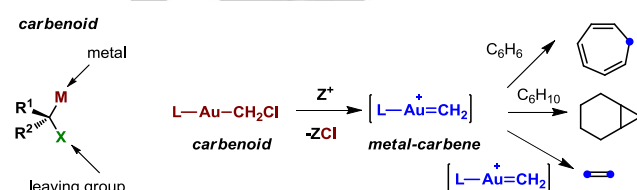


Scheme 5. (a) Simple view of the metal-carbene bond and limiting structures of metal-carbene complexes. (b) The resonance forms of metal-olefin and metal-carbonyl complexes.

contribution of the M=C=O form, but they are unambiguously olefin- and carbonyl-complexes. Analogously, the metal-carbene complexes may display a certain character close to structures I or II but that should not affect neither its classification nor its name.

True carbenoids

In the previous paragraphs, we aimed to demonstrate the misuse of the term carbenoid when applied to a metal-carbene entity originated from a diazo reagent. Thus, it seems appropriate to refer also to the species that are *true* carbenoids.^[3] These are compounds bearing a tetrasubstituted carbon atom, with one metal-carbon bond, and a leaving group X (Scheme 6) from which a carbene group or an alkyl moiety can be transferred onto a substrate. Most developed carbenoid reagents are based on Li, Mg and Zn, and their reactivity is no longer restricted to homologation or cyclopropanation reactions, but also to a number of other transformations.^[3]



Scheme 6. A gold(I) isolable carbenoid compound as a gold-carbene precursor for methylene transfer reactions.

In addition to the large number of examples with main group or post-transition metals, a very recent report from Echavarren's group has shown that gold(I) carbenoids are excellent precursors for gold carbene complexes.^[20] Compounds LAuCH₂Cl (L = phosphine, phosphine or NHC ligands) undergo halide extrusion (Scheme 6) to promote the transfer of the methylene unit to organic substrates, through the LAu=CH₂⁺ intermediate. This is the ultimate example for our aim of differentiating carbenoids and metal-carbene complexes, whether or not diazo reagents are employed as the carbene source.

Conclusions

The examples of isolated metal-carbene complexes from the direct interaction of a transition metal complex and a diazo compound as well as the detection or isolation of carbenoid species that are precursors of metal-carbene complexes should serve as the bases for the elimination of the use of the term carbenoid for the complexes of general formula L_nM=CR¹R² in the context of diazo compounds as carbene source. Moreover, we believe this term should be exclusively employed to define compounds or formula R¹R²C(M)X with a central, tetrasubstituted carbon atom bearing a leaving group X and a metal-carbon bond, from which extrusion of X triggers the elimination of the CR¹R² unit, that can be eventually transferred to another substrate. The reaction pathway for the latter transfer may involve or not the presence of a metal-carbene complex.

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Keywords: carbenoids • metal-carbene complexes • carbene transfer • diazo reagents • nomenclature

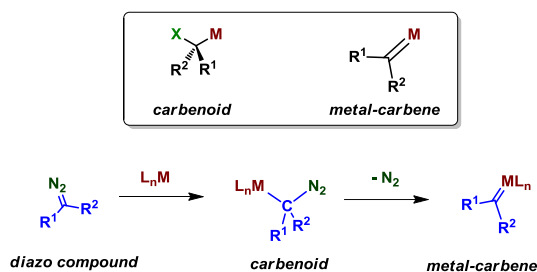
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CONCEPT



The term carbenoid is employed in the current literature to define either species bearing a tetrasubstituted carbon from which a metal-carbene species can be formed or to the latter complex itself, particularly in the context of carbene transfer reaction from diazo compounds. The exclusive use of this term to the former species is proposed.

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