



Preface

Carbenes are electron-deficient two-coordinate carbon compounds that have two non-bonding electrons at one carbon. In the ground state, the two unshared electrons may be either in the same orbital and have antiparallel spins (singlet state), or in two different orbitals with parallel spins (triplet state).

As early as the 1850s, attempts to prepare the parent carbene (CH_2) by dehydration of methanol had been reported. It is interesting to note that at that time the tetravalency of carbon was not established and, therefore, the existence of stable carbenes was considered to be quite reasonable. At the very beginning of the XXth century, Staudinger and Curtius demonstrated that carbenes, generated from diazo compounds or ketenes, were highly reactive species. It quickly became clear that their six valence-electron shell, which defied the octet rule, was responsible for their fugacity. As a consequence, the quest for stable carbenes became an unreasonable target, and indeed remained so for quite some time! In the 1950s, Breslow and Wanzlick, realized that the stability of a carbene could be dramatically enhanced by the presence of amino substituents, but were not able to isolate a “monomeric” carbene.

In 1964, Fischer and Maasböl reported the first stable transition metal complexes featuring carbenes as ligands. The reactivity of the so-called Fischer-carbene complexes led to the characterization of these species as “electrophilic carbene” complexes in which the carbene carbon is positively charged. Almost 10 years later, Schrock isolated an entirely new type of carbene complex, sometimes called an alkylidene complex or Schrock carbene, in which the polarization of the metal-carbon bond is inverted: the carbene carbon is negatively charged.

Both Schrock and Fischer carbenes were prepared by a method that did not involve trapping of the carbene. In

1988, my group reported the synthesis of the first stable carbene, namely a (phosphino)(silyl)carbene, but unfortunately this compound appeared to be very reluctant to act as a ligand for transition metals. In marked contrast, the seminal discovery by Arduengo in 1991 of stable cyclic diamino carbenes, the so-called NHCs, open the way for the synthesis of numerous transition metal complexes by simple complexation of a carbene.

Currently, all these different types of carbene complexes are no longer considered to be curiosities, instead they are powerful tools, which have found numerous applications in many different fields. A quick search on SCOPUS for articles containing “carbene complexes” yields 819 hits for the period of 1996–2000, and 1280 from 2001 to the present: more than a 50% increase! Interestingly, among these papers, not less than 116 and 147, respectively, have been published in the Journal of Organometallic Chemistry.

This Special Issue gives a flavor of the wide scope of carbene transition metal complex chemistry in 2005. It is a collection of 91 papers, which includes review articles, full papers and communications. I hope the readers will enjoy this Issue as much as I enjoyed handling the manuscripts.

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