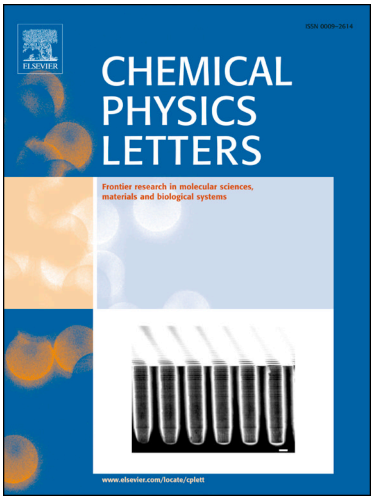

The first theoretical proof of the existence of a hydride-carbene bond

Mirosław Jabłoński

PII: S0009-2614(18)30680-8
DOI: https://doi.org/10.1016/j.cplett.2018.08.053
Reference: CPLETT 35883

To appear in: *Chemical Physics Letters*

Received Date: 9 July 2018
Accepted Date: 20 August 2018

Please cite this article as: M. Jabłoński, The first theoretical proof of the existence of a hydride-carbene bond, *Chemical Physics Letters* (2018), doi: https://doi.org/10.1016/j.cplett.2018.08.053

The first theoretical proof of the existence of a hydride-carbene bond

Mirosław Jabłoński[a,*]

[a] *Department of Quantum Chemistry, Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, PL-87 100 Toruń, Poland*

Abstract

We report the first theoretical proof of existance of dimers featuring hydride-carbene bond ($X^{\delta+}$–$H^{\delta-}\cdots\supset C$), i.e. an interaction between partially negatively-charged hydrogen atom (i.e. a hydride hydrogen) and the unoccupied orbital *p* on the carbenic carbon ($\supset$C) atom in singlet carbenes. These interactions are special case of charge-inverted hydrogen bonds and are rather weak with binding and dissociation energies amounting to ca. 7.2–7.7 kJ/mol (1.7–1.8 kcal/mol) and 3.1–5.3 kJ/mol (0.7–1.3 kcal/mol), respectively.

Keywords: charge-inverted hydrogen bond, CIHB, hydride, carbene, singlet, triplet, QTAIM, NBO, orbitals, electrostatic potential

---

1. Introduction

Carbenes are very important group of compounds in organic chemistry[1–5] owing to their high reactivity, which in turn results from peculiar electronic structure. Namely, first of all, they have a two-valent carbon atom, which can therefore only link two (CR_1R_2) or one (C=R) substituent. In addition, what is particularly important in carbene chemistry, they also have two unshared electrons, which in turn leads to the fact that carbenes can have either single or triplet electronic ground state[4]. In the triplet state, which, according to Hund's rule, is most often the ground state, the carbene carbon atom has two unpaired same-spin electrons occupying two perpendicular *p* orbitals. Whereas in the single state, the carbene carbon atom has one unshared pair of spin-paired electrons (i.e. a lone electron pair) and, what is the most important in this article, an empty, i.e. unoccupied, orbital *p* being perpendicular to the molecular plane (see Figure 1). Although the triplet state is most often the ground state of carbenes, the single state can also become the ground state if appropriate geometric conditions are met[6–8] or when either one or both the substituents R_1 and R_2 are strongly electronegative atoms (e.g. F, Cl, O, N) which stabilize the single state by partial donation of their electrons to the empty orbital *p*[8–12].

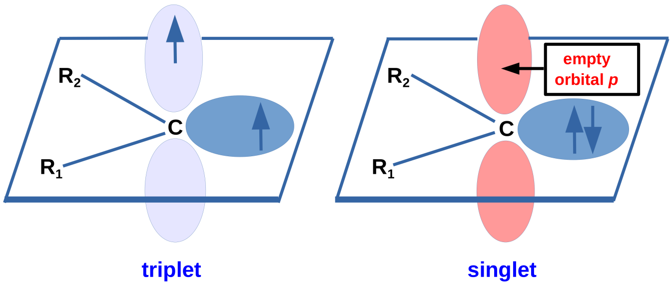

Figure 1: Triplet and singlet states of carbene.

It is clear (Figure 1) that owing to the presence of the lone electron pair on the carbene carbon atom, carbenes in their singlet electronic states should behave as good electron density donors, i.e. they should be nucleophiles or Lewis bases. Indeed, it has been shown[13–15] that they can act as proton acceptors in hydrogen bonding. On the contrary, it appears that the electrophilic properties of carbenes are not so often studied. In particular, we do not know any literature instances of dimers in which the empty orbital *p* on the carbene carbon atom would be an acceptor of negative charge, i.e. it would be a Lewis acid.

In this article, we report for the first time the possibility of dimers having a hydride-carbene interaction ($X^{\delta+}$–$H^{\delta-}\cdots\supset C$), i.e. an interaction between partially negatively-charged hydrogen atom (i.e. a hydride hydrogen) and the carbene carbon atom. Moreover, taking into account that this hydride hydrogen donates its electron charge to the empty (unoccupied) orbital *p* on the carbene carbon ($\supset$C), this type of bonding may also be considered as a peculiar type of charge-inverted hydrogen bond (CIHB)[16–21], where the carbene carbon atom is the carrier of an electron gap.

It has been shown that CIHB can be strong enough to become an important binding motif, both inter-[16–21] and intramolecular[22–25] one. In addition to CIHB, the hydride hydrogen atom may also participate in, e.g., hydride hydrogen bonds[26–28], dihydrogen bonds[29–32], hydride-halogen bonds [33–39] and σ interactions[40]. That is why it would seem that hydride-carbene bonds should form quite easily and therefore they should be relatively common. On the other hand, however, both the nucleophilic and electrophilic properties of carbenes as well as the strongly electrophilic area on the donor atom X suggest that it does not have to be this way and that formation of the hydride-carbene bond will significantly inter-

---

[*] Tel.: +48 56 61 14 695
Email address: `teojab@chem.uni.torun.pl` (Mirosław Jabłoński)
URL: `http://www.chem.uni.torun.pl/zchk/jab/jab.html` (Mirosław Jabłoński)