Towards a Classification of Singlet Carbenes

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According to one-electron perturbation theory singlet carbenes can be classified as (a) electrophilic, (b) nucleophilic or (c) ambiphilic in their addition properties towards olefines. The nucleophilicity of the σ-orbital in :CX_2X_2 should increase with decreasing electronegativity of X_1 (X_2).

The addition of a singlet ground state carbene to olefines can be viewed in terms of one-electron perturbation theory by two types of interactions of the participating orbitals [1]. For the simplest case, σ2-methylene plus ethylene, this is illustrated in Figure 1.

![Figure 1. Orbital interaction diagram for the formation of a π-complex between σ2-methylene and ethylene.](image)

Transfer of electron density can occur from (a) the HOMO π of the olefin to the empty p-AO of the methylene (type I interaction) and (b) the σ-orbital (of the methylene) into the LUMO π* (type II interaction) [2]. In this respect the singlet carbene can act as an electrophilic (n→p) and/or nucleophilic (σ→π*) species.

The energy profit due to interaction of type I and type II is given by one-electron perturbation theory (with neglect of overlap) [3] to

\[ \Delta E = \delta E_I + \delta E_{II} \]

\[ \delta E_I = \left( \frac{\epsilon_{\sigma} - \epsilon_{\pi^*}}{\epsilon_{\pi}} \right) \]

\[ \delta E_{II} = \left( \frac{\epsilon_{\pi^*} - \epsilon_{\sigma}}{\epsilon_{\sigma}} \right) \]

The increase of energy is a sum of two hyperbolic functions, I as the electrophilic and II as the nucleophilic branch [3].

The following cases can be differentiated:

(a) \[ |\delta E_I| \gg |\delta E_{II}| \], electrophilic carbene

Raising the energy of the π-bonding level in olefines by introduction of electron donating substituents (e.g. methoxy groups, etc.) enhances the addition reaction. Its experimental verification has been well established [4].

(b) \[ |\delta E_I| \ll |\delta E_{II}| \], nucleophilic carbene

This requires (b1) the elevation of the σ-orbital and/or (b2) the empty p-AO (MO) of the carbene. Only the latter case (b2) has been verified in nucleophilic carbenes, such as cycloheptatrienylidene or cyclopropenylidene in which the nonbonding p-AO (of methylene) is replaced by an antibonding MO of the cyclic π-conjugated system.

The former case (b1), the lifting of the doubly occupied σ-orbital is met in carbenes of the type

\[ \sigma_{X_1} \]

where \( X_1 \) (\( X_2 \)) are electron donating or accepting groups or atoms, and represent a combination of inductive and mesomeric effects.

According to the Walsh rules [5] the p-character of the σ-orbital (and hence its energy) raises with decreasing electronegativity of \( X_1 \), \( X_2 \) resp. In other words it will increase in the order of \( X_1 \) (\( X_2 \)) = F < OCH_3 < N(CH_3)_2 etc., and as supported by \textit{ab initio} calculations (here not included). To our knowledge a systematic investigation of this effect...
on the nucleophilicity of carbenes (orbital energy of \( \sigma \)) has not been reported so far [6].

(c) \( |\delta E_1| \sim |\delta E_{11}| \), *electrophilic + nucleophilic* (*"ambiphilic"*) [7] carbene

Its reactivity is increased by introduction of electron donating or electron releasing substituents into the olefin.

The present approach towards carbene reactivity has a clear advantage over the characterization with Hammett parameters [7a]: (1) It accounts for the substrate dependence of the carbene reactivity. (2) The electrophilic and nucleophilic properties of singlet carbenes can be recast in terms of the Pauling electronegativity of \( X_1, X_2 \) resp., whereby (3) the orbitals required for the computations of \( \delta E_1 \) and \( \delta E_{11} \) can be easily evaluated by simple Hückel theory [3a]. A more detailed analysis of these considerations will be presented in a forthcoming report [8].

*Note added to proof*

While this manuscript has been submitted for publication a study has appeared (R. A. Moss, M. Fedorynski and W.-C. Shieh, J. Amer. Chem. Soc. 101, 4736 (1979)) and which is in conformity with our conclusions.


[2] Overlap repulsion (type III interaction) between the doubly occupied orbitals \( \alpha \) and \( \sigma \) is responsible for the discrimination of the \( \sigma \)-approach in the concerted 1,4-addition of \( \sigma^2 \)-methylene to cis-butadiene [1a, 2a]. a) H. Fujimoto and R. Hoffmann, J. Phys. Chem. 78, 1167 (1974).


[6] Quantum mechanical calculations at different levels of sophistication reveal that the conformational stability of singlet difluorocarbene is stronger than that of singlet methylene.
a) R. Hoffmann, G. D. Zeiss, and G. V. Van Dine, J. Am. Chem. Soc. 90, 1485 (1968); b) V. Staemmler, Theor. Chim. Acta, 1974, 309. This is another consequence of the Walsh rules. However, the different electronegativity of \( X \) only slightly affects the equilibrium geometries of these species [6a, b].
