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## Carbenic philicity and the “intrinsic reactivity index”

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### ABSTRACT

The reactivity of electrophilic, ambiphilic, and nucleophilic singlet carbenes is considered in terms of a recently proposed “intrinsic reactivity index” (IRI). Comparisons of IRI are made with previously described analyses, and it is concluded that IRI is not as useful for the determination or analysis of carbene philicity as FMO-based or empirical treatments.

*Keywords: Frontier molecular orbital energies, reactivity indices, singlet carbenes*

As one of the classic reactive intermediates of organic chemistry, carbenes have been the subject of many reactivity studies; empirical and theoretical analyses of their selectivity and philicity have been performed as well.<sup>1</sup> From the empirical perspective, the “carbene selectivity index,”  $m_{\text{CXY}}$ , represents the kinetic selectivity of carbene CXY toward a standard set of alkenes, relative to the selectivity of  $\text{CCl}_2$ .<sup>2</sup> Not only does  $m_{\text{CXY}}$  correlate the selectivity and reactivity of a number of singlet carbenes, but it rationalizes the expressed electrophilicity, ambiphilicity, or nucleophilicity of these species.<sup>2b,3</sup>

From the theoretical vantage point, frontier molecular orbital (FMO) theory has proven both popular and effective for analysis of carbenic reactivity and philicity. Houk et al. found that carbenic philicity could be rationalized by examination of the energies associated with the HOMOs and LUMOs of carbenes and their alkene reaction partners.<sup>2b,4,5</sup>

Mendez and Garcia-Garibay computed charge transfer ( $\Delta N$ ) between alkenes and carbenes in terms of the chemical potential ( $\mu$ ) and absolute hardness ( $\eta$ ) of the reactants.<sup>6</sup> Differences in chemical potential drive charge transfer, with electron density migrating from regions of high chemical potential to low chemical potential; *i.e.*, from regions of low electronegativity to high electronegativity.<sup>6</sup> Mendez and Garcia-Garibay

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