

Fullerenes as Neutral Carbon-Based Lewis Acids**

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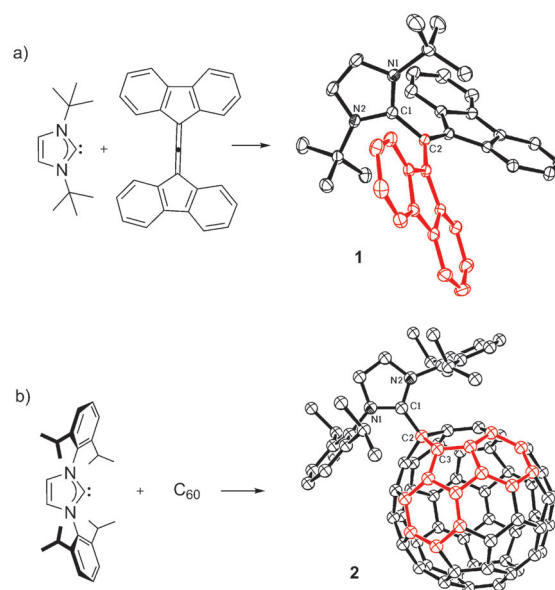
carbenes · density functional calculations ·
frustrated Lewis pairs · fullerenes ·
small-molecule activation

Since G. N. Lewis classified molecules into those that can donate an electron pair (bases) and those able to accept it (acids),^[1] this formally simple description has been an extremely useful tool to rationalize and also predict the reactivity of both main-group and transition-metal complexes. Thus, when a Lewis acid is combined with a base, a neutralization reaction takes place with the concomitant formation of a Lewis adduct.

If we focus our attention on carbon-based Lewis bases, we find that they are very diverse in nature; typical examples are ylides, isonitriles, N-heterocyclic carbenes (NHCs), and enamines. In contrast, this notable variety is not found for carbon-based Lewis acids, which remain restricted mainly to trityl cations and some electron-poor allenes.^[2]

In this regard, the recent paper by Bazan and co-workers is remarkable.^[3] Inspired by earlier experimental work with a bisfluorenyl-substituted allene, in which a related structural motif can be detected (Scheme 1a),^[4] these authors report that the archetypal fullerene molecules, C₆₀ and C₇₀, can behave as all-carbon Lewis acids that form the corresponding Lewis adducts by reaction with highly basic N-heterocyclic carbenes (Scheme 1b). In a typical experiment, equimolar amounts of C₆₀ and 1,3-bis(diisopropylphenyl)imidazol-2-ylidene were allowed to react at room temperature over 24 h in *o*-dichlorobenzene (*o*-DCB). After removal of the solvent under vacuum, the crude product was washed with toluene and THF. Single crystals suitable for X-ray diffraction analysis were obtained from *o*-DCB at −35 °C.

Interestingly, the cyclopropanation reaction that often takes place when carbenes or carbene surrogates are allowed to react with fullerenes was not evident: the obtained product displayed a single junction connecting the carbene and fullerene fragments with a C1–C2 bond 1.502(16) Å long. To gain insight into the nature of the bonding in **2**, the authors performed density functional calculations at the B3LYP/6-31G** level. In agreement with the experimental data, natural bond order analysis indicated that the C–C bond between the carbene and the fullerene is a single bond



Scheme 1. a) Carbene–allene adduct **1** formed by reaction between *It*Bu and bisfluorenyl allene. b) Reaction of C₆₀ with IDipp to afford the IDipp–C₆₀ adduct **2**.

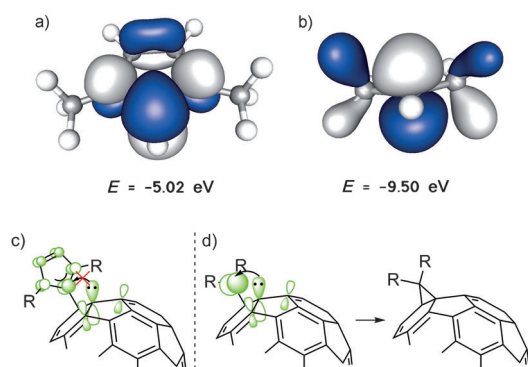
(Wiberg bond index of 0.97) with an electron occupancy of 1.97 e. Moreover, according to natural population analysis, total charges of +0.84 e and −0.84 e reside in the imidazole and the fullerene moieties, respectively. This overall picture of the charge distribution corresponds to a neat transfer of electron density from the carbene to the fullerene as typically occurs in Lewis acid/base adducts.

In a first approximation, the stability of **2** can be attributed to the confluence of two main factors, namely: 1) the strength of the newly formed C–C bond makes the adduct formation process irreversible; and 2) the LUMO of the partially formed imidazolium fragment is much higher in energy than the LUMO of less stabilized carbenium ions. This precludes formation of the cyclopropane derivative from the the primary adduct (Scheme 2a–d).^[5]

The generality of the adduct formation between NHCs and fullerenes has also been confirmed by extension of this reaction to C₇₀. Again a single-bonded adduct was obtained and interestingly, its formation occurs with complete regioselectivity. Of the five plausible regioisomeric products only the one with the carbene moiety bonded to one of the ten apical carbons of C₇₀ is observed.

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Scheme 2. Distinct reactions between carbenes and fullerenes: a) LUMO of 1,3-dimethylimidazolium cation; b) LUMO of dimethyl carbocation, both calculated at the B3LYP/6-31G* level. c) Adduct formation with NHCs. d) Cyclopropanation with nonstabilized carbenes.

At least two different routes leading to the formation of **2** can be proposed: 1) direct formation of the Lewis adduct by donation of the carbene electron pair to the fullerene and 2) a stepwise process involving an initial single-electron transfer from the carbene to the fullerene followed by recombination of the two generated radicals. Evaluation of the redox potentials of NHCs and fullerene suggests, however, that the second route might not be relevant at least for this particular transformation.^[6] Nevertheless, a careful mechanistic study is desirable. Assuming that **2** is formed by a classic Lewis neutralization, it can be deduced from the paper of Bazan and co-workers that the use of fullerenes as Lewis acids is feasible and therefore, a few new applications of these carbon allotropes can be envisaged.

Especially attractive will be their use as carbogenic Lewis acid partners in “frustrated Lewis pair (FLP) chemistry”.^[7] While the continuous expansion of the Lewis bases employed in this area has led, to a certain extent, to the discovery of new FLP-induced transformations, the Lewis acid partners have remained mainly restricted to $B(C_6F_5)_3$ and related polyfluorinated boranes.^[8] After this work of Bazan et al., the use of fullerenes in this context as borane surrogates should be relatively straightforward. It is only necessary to avoid the formation of adducts, something that a priori is possible just by employing more sterically demanding NHCs.^[9]

More intriguing is the still-open question of whether these plausible frustrated Lewis pairs might be able to activate small molecules such as H_2 . Avoiding adduct formation by steric protection is a necessary requirement but not at all sufficient. Moreover, a certain degree of unquenched acidity and basicity has to be fulfilled by both Lewis partners in order to ensure an appropriate cooperation towards the activation of the substrate.^[10] The fact that very few classical Lewis adducts between fullerenes and typical bases (such as phosphines and pyridines) have been previously reported may indicate that C_{60} is not a particularly strong Lewis acid and, as consequence, its reactivity in this particular field might be only moderate, at best.^[11]

Nevertheless, even in this worst-case scenario, fullerene chemistry is already rich enough to offer solutions. For example, the innate acidity of C_{60} or any other fullerene structure could be increased to the necessary level by a number

of already available transformations such as polyhalogenation, the introduction of electron-withdrawing groups in the original core, or the use of endohedral fullerenes.^[12]

In conclusion, this article from Bazan et al., the extensive work of Stephan, Erker, and others on the activation of inert molecules by applying the concept of frustrated Lewis pairs, and the activation of H–H bonds using single carbene centers recently reported by Bertrand further advance our perception of the structure and reactivity of carbon-based compounds. Hopefully, this seminal research will be the starting point of new chemistry and applications for carbon and the beginning of a trend in catalysis defined by the development of new carbon-based catalytic systems.^[13]

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