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Phosphorus stabilized carbenes: theoretical predictions

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Dedicated to Professor F. Mathey on the occasion of his 60th birthday

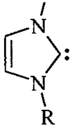
Abstract

B3LYP/6-311 + G** and B3LYP/3-21G(*) isodesmic stabilization energies of several five and six membered cyclic carbenes containing phosphorus were calculated to estimate their stability against dimerization. Bridgehead tricoordinate phosphorus in α-position from the carbene increases the stability. Tetracoordinate phosphorus, in β-position from the divalent carbon (forming a phosphorus ylide) has also a significant stabilizing effect. The combination of the above effects results in systems, which are likely to be synthesizable, their stabilization energy approaching that of the Arduengo carbene. © 2002 Published by Elsevier Science B.V.

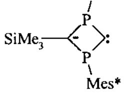
Keywords: Stable phosphinocarbenes; Phosphorus ylides; Ab initio calculations

1. Introduction

Since the successful isolation of imidazol-2-ylidene (**1** R: Ad) [1] by Arduengo et al. in 1991, the interest in these compounds is steadily increasing, and several other stable carbenes have been reported [2]. The common structural feature for most of these molecules is that the divalent carbon atom is substituted by π-donors [3]. Although the stabilizing effect arising this way is large, to make the carbenes bottleable further factors as aromaticity [4] or/and bulky protecting groups [5] are needed. While the most effective π-donor is the amino [6] group, aminooxy- [7] and aminothiocarbenes [7,8] were also synthesized.


1

$(iPr_2N)_2PCT\,SiMe_3$
2



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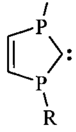

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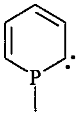

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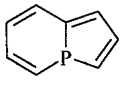

6

The effect of phosphorus containing substituents on the stability of carbenes is much less studied. The *planar* phosphino group as a substituent of carbocations [9] and silylenes [10] is known as a very effective π-donor (Scheme 1), and ought to stabilize carbenes as well. Also a pentavalent, doubly bonded phosphorus in β-position from the divalent carbon should serve as an excellent π-donor, as it is easily understandable by using the 'ylide' resonance form [11] (Scheme 1) of $>C{=}PR_3$. Thus, it can be expected that the above substituents attached to the divalent carbon result in nucleophilic carbenes.

Some phosphinocarbenes are known as stable compounds [12]. Compound **2** has been synthesized in 1988 by Bertrand et al. [2,12], A phosphino–phosphonio–carbene [13] and recently a phosphanyl–trifluoromethyl carbene [14] have also been reported and structurally characterized. Compound **2** has similar reactivity to carbenes in certain reactions [15]. However, it does not

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Scheme 1.

form complexes with transition metals [16]. Based on other reactions it has also been considered [17] to be a λ^5-phosphacetylene. Alternatively, to describe the electronic nature of **2** the push–pull carbene [2a,2b] term has also been used (note that the silyl group in **2**, as well as the phosphonio and the trifluoromethyl moieties are π-acceptors), to make a distinction from the nucleophilic Arduengo-type carbenes. According to model calculations for **2**, both bent [18] (similarly to the carbene structures) and linear (phosphaacetylene) [16,19] structures have been reported. Even for the bent structure the barrier to linearization is low [18]. It is clear that the Bertrand type system differs significantly from the stable nucleophilic carbenes in terms of electronic structure and reactivity.

Is there a possibility to obtain stable nucleophilic carbenes, substituted by phosphorus? An anion, with a diphosphinocarbene unit, 1,3-bis-(tritertiarybutylphenyl)-1,3-diphosphacyclobutan-2,4-diyl-2-id (**3**) has been reported by the Niecke group [20]. This compound has been shown to complex transition metals, like the Arduengo carbene [21]. To the stability of this four membered ring, however, the repulsion of the anions (that helps preventing dimerization) should also contribute to a certain extent. 1,3-Diphosphole-2-ylidene (**4**, the phosphorus analogue of the Arduengo-type carbene) has also been suggested computationally as a possibly stable species [22] as judged from its singlet–triplet energy gap. The six membered phosphinine-2-ylidene (**5**) was suggested as a possible synthetic target too on the basis of computational studies [23], and it has been considered as a reaction intermediate as well [24].

The aim of the present work is to investigate the stability of carbenes, substituted by phosphorus containing moieties, such as $>C{=}PRR'R''$ and $-PRR'$ groups, by using quantum chemical calculations. We will show, that both groups are effective, resulting in nucleophilic carbenes, provided that the tricoordinate phosphorus attached to the carbene is forced to be planar by other effects than the electron acceptor property of the carbene. Phosphorus in phosphinocarbene (H_2P–CH) itself is planar [19,20,22], since such an arrangement is favorable for an effective overlap between the carbene empty orbital and the phosphorus lone pair. Apparently, the energy gained by this π-interaction is larger than the pyramidalization energy of the phosphino group (35 kcal mol^{-1} in phosphine, PH_3 [25]). However, H_2P–CH is unstable against dimerization [26], since in the double bonded dimer (H_2P–CH=CH–PH_2) the tricoordinate phosphorus is repyramidalized (regaining the corresponding energy), reaching a favorable conformation for the tricoordinate phosphorus. By other words, the stabilization resulting from the π-interaction between the tricoordinate phosphorus and the carbene is partly consumed for the planarization of the phosphorus. Thus, to stabilize a phosphinocarbene, the $>$P– group should be *planarized* by other effects than the electron acceptor property of the carbene. To flatten the pyramid of the tricoordinate phosphorus a substantial energy is needed (see above). This planarization can be achieved by several ways as discussed recently in a comprehensive manner [27]. Apart from the planarizing effect of π-electron acceptors (as carbenes themselves [18,19]), anellation of aromatic rings helps to flatten tricoordinate phosphorus, as has been demonstrated in case of phosphindolizines (**6**) [28].

Recently we have shown a simple and economic method, which can be used to predict the stability of a carbene against dimerization [26]. The energy of the isodesmic reaction 1

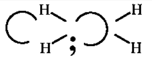
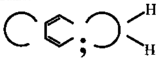
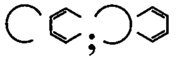
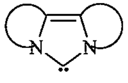
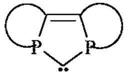
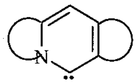
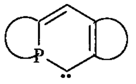
$$R_1R_2C{:} + CH_4 = R_1R_2CH_2 + H_2C{:} \qquad (1)$$

E1 was shown to correlate with a correlation coefficient of 0.994 with the dimerization Gibbs free energy of the carbenes. Thus, to estimate the thermodynamic stability of a carbene against dimerization, there is no need to carry out exceedingly expensive calculations on the carbene dimers, instead ***E1***, the energy of the economic isodesmic reaction, should be computed. Those carbenes synthesized before (with reasonable large protecting groups such as mesityl or di-isopropylphenyl) had the highest ***E1*** energies, and accordingly the smallest dimerization Gibbs free energies [26]. For these systems the stabilization energy in the isodesmic reaction (***E1***) is about 90 kcal mol^{-1} or larger [26]. Thus, ***E1*** values close to 90 kcal mol^{-1} indicates that the carbene under consideration is a reasonable synthetic target. In the present work we use stabilization energies from the above isodesmic reactions (***E1***), to characterize the stability of new carbenes as synthetic targets.

2. Results and discussion

First we consider **4**, the phosphorus analogue of the Arduengo carbene, which was suggested to be a potentially stable carbene by Schoeller [21]. Compound **4** (R–H) is not planar, however, the barrier to planarization is 9.8 kcal mol^{-1} at the B3LYP/6-311 + G** level. The stabilization energy in reaction 1 (***E1***) is 46.3 kcal mol^{-1}, a rather low value, and accordingly the Gibbs free energy for the dimerization is -100.8 kcal mol^{-1},

Table 1
B3LYP/6-311+G** ***E1*** stabilization energies in kcal mol^{-1} for five and six membered aminocarbene and phosphinocarne rings with different substituent patterns

			
	109.3 (115.0)	107.0 (114.7)	111.2 (117.2)
	46.3 (45.5)	55.4 (56.8)	62.3 (66.2)
	85.7 (89.0)	86.8 (90.7)	-
	64.6 (62.6)	76.9 (80.7)	-

B3LYP/3-21G(*) data are in parenthesis.

showing that **4** (R–H) is highly unstable against dimerization. For the nitrogen analogue (**1**) ***E1*** is 109.3 kcal mol^{-1}, and the dimerization Gibbs free energy was calculated +0.9 kcal mol^{-1} [29], showing the markedly different stability of the two compounds. Comparing the ***E1*** values for H_2NCH (59.9 kcal mol^{-1} [26]), H_2NCNH_2 (86.5 kcal mol^{-1} [26]) and **1** (with R–H 109.3 kcal mol^{-1} [26]) a steady increase can be seen resulting in the bottleable **1**. For the phosphorus analogues, however, the ***E1*** values are rather small (H_2PCH 33.3 kcal mol^{-1} [25], H_2PCPH_2 48.5 kcal mol^{-1} and **4** (R–H) 46.3 kcal mol^{-1}), and they do not increase as much as in case of the nitrogen analogue in the investigated series. This behavior is apparently a consequence of the different planarization barriers of the tricoordinate nitrogen and phosphorus. Since neither H_2PCPH_2, [30] nor **4** is planar [20], it is reasonable to consider that the pyramidalization of two tricoordinate phosphorus atoms (ca. 70 kcal mol^{-1}) cannot be compensated by the energy gain obtainable by the stabilization of a carbene (and in case of a planar **4** by the aromatic stabilization energy). ***E1*** is rather small (64.6 kcal mol^{-1}) for **5**, the six membered phosphinocarbene ring as well, and accordingly the dimerization Gibbs free energy is −82.4 kcal mol^{-1} [25]. (Note, that in this case only one phosphorus should have been planarized by the π-acceptor carbene, accordingly ***E1*** is larger, than for **4**.)

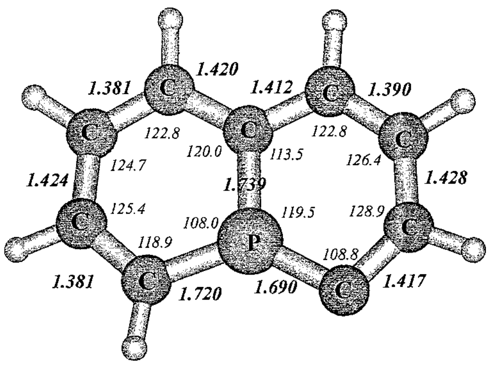
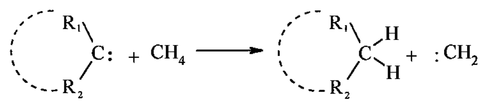
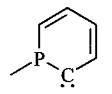
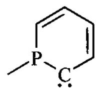
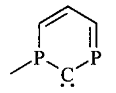
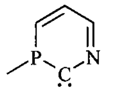
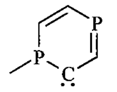
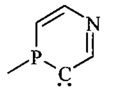
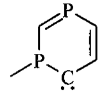
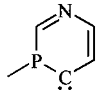


Fig. 1. B3LYP/6-311+G** optimized structural parameters (in Å and °) of **7**.

Our expectation was, that by ring annellation at the tricoordinate phosphorus ***E1*** will increase, as it is indeed demonstrated by the values in Table 1. The B3LYP/3-21G(*) values are somewhat higher then those obtained by the larger basis set, but they follow the same trend. While for the nitrogen containing compounds the effect of the ring annellation is small [31], much larger effect can be seen in case of the phosphorus derivatives, where the ring annellation results in about 10 kcal mol^{-1} increase of ***E1*** at each phosphorus atoms both in the five and six membered rings. Nevertheless, the stabilization energy in most of these cyclic phosphinocarbenes remains considerably lower than the desired 90 kcal mol^{-1} value. In case of **7**, however, ***E1*** is approaching 80 kcal mol^{-1}, thus it is worth to investigate possible additional stabilizing effects of substituents on this ring system (see below). The most important B3LYP/6-311+G** structural data of **7** are shown in Fig. 1. The bond lengths of the two rings show little alternation, indicating that the ring system

Table 2
B3LYP/6-311+G** ***E1*** energies in kcal mol^{-1} for the six membered ring phosphinocarbene **5** with additional P and N heteroatoms



Compound	*E1*	Compound	*E1*
	**64.6** (62.6)		**64.6** (62.6)
	**61.1** (64.7)		(the ring has opened up upon optimization)
	**61.1** (62.9)		**56.4** (57.3)
	**60.9** (62.9)		**57.7** (58.8)

B3LYP/3-21G* values in parenthesis.

has a significant aromatic character. To investigate the aromatic character of **7**, different aromaticity measures were used. For that ring of **7** containing the carbene the Bird index (BI) [32], the NICS aromaticity measure [33] and the bond shortening index (BDSHRT) [34] are 78, − 10.4 and 63, respectively. For the other ring of **7** BI, NICS and BDSHRT are 85, − 10.9 and 64, respectively. BI is on a 0–100 scale [32] (benzene has a BI of 100 [32], phosphinine 96 [28]), the NICS and BDSHRT values can be compared to those of phosphinine (− 8.4 and 62, respectively) [28], or to those of the six membered ring of (the planar) phosphindolizine (− 11.4 and 61, respectively), (all calculated at the same level of the theory as in the present work) [28].

In order to search for further stabilizing effects, the CH units in **7** were replaced by nitrogen and by σ^2,λ^3-phosphorus. The replacement of CH by N was shown to decrease somewhat the aromaticity in phosphinines [35], and increase slightly the aromatic stabilization in azoles [36]. The conjugative ability of the CH units was shown to be similar to that of phosphorus (σ^2,λ^3-P) [37]. The results are given in Tables 2 and 3, for **5** and **7**, respectively. From the data it is clear that substitution of the CH units by N or σ^2,λ^3-P does not result in any significant change of the stabilization of the carbene.

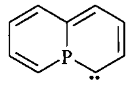
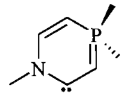
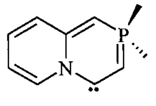
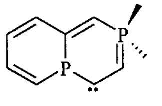
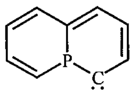
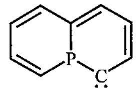
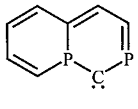
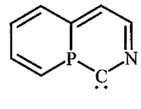
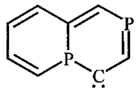
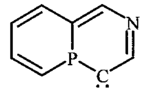
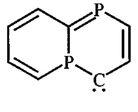
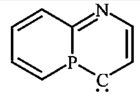
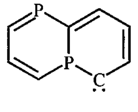
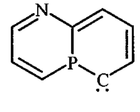
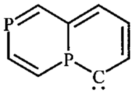
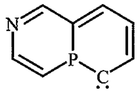
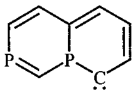
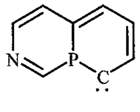
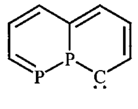
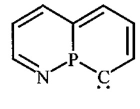
			
7	**8**	**9**	**10**

Table 3
B3LYP/6-311+G** ***E1*** energies in kcal mol^{-1} for the fused six membered ring phosphinocarbene **7** with additional P and N heteroatoms

Compound	*E1*	Compound	*E1*
	**76.9** (80.7)		**76.9** (80.7)
	**75.8** (82.0)		(the ring has opened up upon optimization)
	**77.1** (81.4)		**73.5** (77.6)
	**75.7** (80.1)		**76.4** (76.2)
	**75.8** (79.8)		**73.2** (77.1)
	74.8 (78.9)		**75.2** (78.6)
	**76.3** (80.5)		**72.8** (76.9)
	**75.0** (78.5)		**71.0** (75.0)

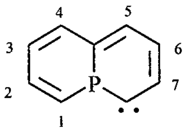
B3LYP/3-21G* values in parenthesis.

Table 4
B3LYP/6-311+G** isodesmic stabilization energies (***E1***) of phosphinine-2-ylidenes and pyridine-2-ylidenes substituted by $\sigma^4\lambda^5$-P in β-position from the carbene center in kcal mol^{-1}

E1: 93.3 (97.5)	*E1*: 91.2 (96.1)	*E1*: 88.5 (92.2)
8	**9**	**10**

B3LYP/3-21G(*) data are in parenthesis.

Table 5
B3LYP/3-21G(*) stabilization energies (***E1***) of the amino derivatives of **7** in kcal mol^{-1}



position of the amino group	*E1*	position of the amino group	*E1*
1	80.7	1 2	84.3
2	80.9	1 6	83.5
3	82.8	2 6	84.6
4	79.5	2 7	86.8
5	79.0	6 7	87.2
6	84.2		
7	84.3	2 6 7	87.4

A much larger effect has been observed in case of **7**, however, when the CH unit in β-position from the carbene is replaced by a σ^4,λ^5-P, as expected by considering the electron donor properties of the carbon atom of a phosphorus ylide (see above). (The analogous structure derivable from **5** opens up during the geometry optimization.) The nitrogen analogues of **5** and **7** are also considerably stabilized by the phosphorus ylide. The stabilization energies for **8**, **9** and **10**—each containing one σ^4,λ^5-P—are collected in Table 4. These values are close to 90 kcal mol^{-1}, thus **8**, **9** and **10** are reasonable synthetic targets (additional steric stabilization in α-position from the carbene might also be needed). Again the stabilization energies obtained by the smaller 3-21G(*) basis set are somewhat higher than the B3LYP/6-311 + G** values, the trends, however, are similar.

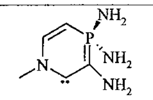
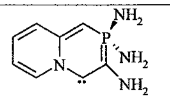
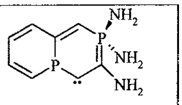
To investigate the possibility of further electronic stabilization by substituents attached to the ring, the effect of the amino group has been considered, because of its good π-electron donor property. This influence on the ***E1*** stabilization energies was first investigated on **7**, as it is shown in Table 5. For economic reasons, these calculations were carried out at the B3LYP/3-21G(*) level only, since we have noticed above that the trends are the same when using the two basis sets. The ***E1*** values obtained by the smaller basis set are somewhat (by 2–4 kcal mol^{-1}) higher than those obtained by the 6-311 + G** basis. The amino group is stabilizing **7**, in accordance with our expectations, the most pronounced is the effect, when the amino group is in the 6 and 7 positions (i.e. α- and β-position from the carbene center). The maximum stabilization with respect to **7** amounts ca. 7 kcal mol^{-1}.

The amino substituent is considered to stabilize **8**, **9** and **10** as well. Also the σ^4,λ^5-phosphorus is usually stabilized by amino substituents, thus, we have investigated the ***E1*** energies for **11**, **12** and **13**. As it is shown by the B3LYP/3-21G(*) stabilization energies collected in Table 6, the ***E1*** values of **11**, **12** and **13** are indeed the largest among the investigated compounds, approaching the Arduengo-carbene values (Table 1). This increase of the stabilization energy shows that the different stabilization effects act independently. The structural data of **11** and **13** are shown in Fig. 2. These compounds are not entirely planar, but the deviation from planarity is small. Their bond lengths are equalized, indicating that delocalization plays also some role in their stability.

3. Conclusions

Nucleophilic carbenes can effectively be stabilized against dimerization, when substituted by *planarized*

Table 6
B3LYP/3-21G(*) isodesmic stabilization energies (***E1***) of **11**, **12** and **13** in kcal mol^{-1}

		
(104.5)	(106.0)	(99.2)
11	**12**	**13**

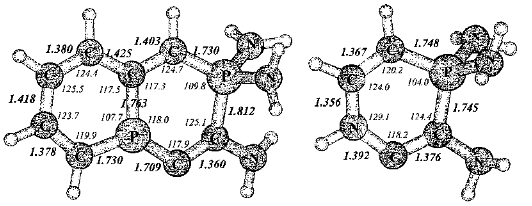


Fig. 2. B3LYP/6-311 + G** optimized structural parameters (in Å and °) of **11** and **13**.

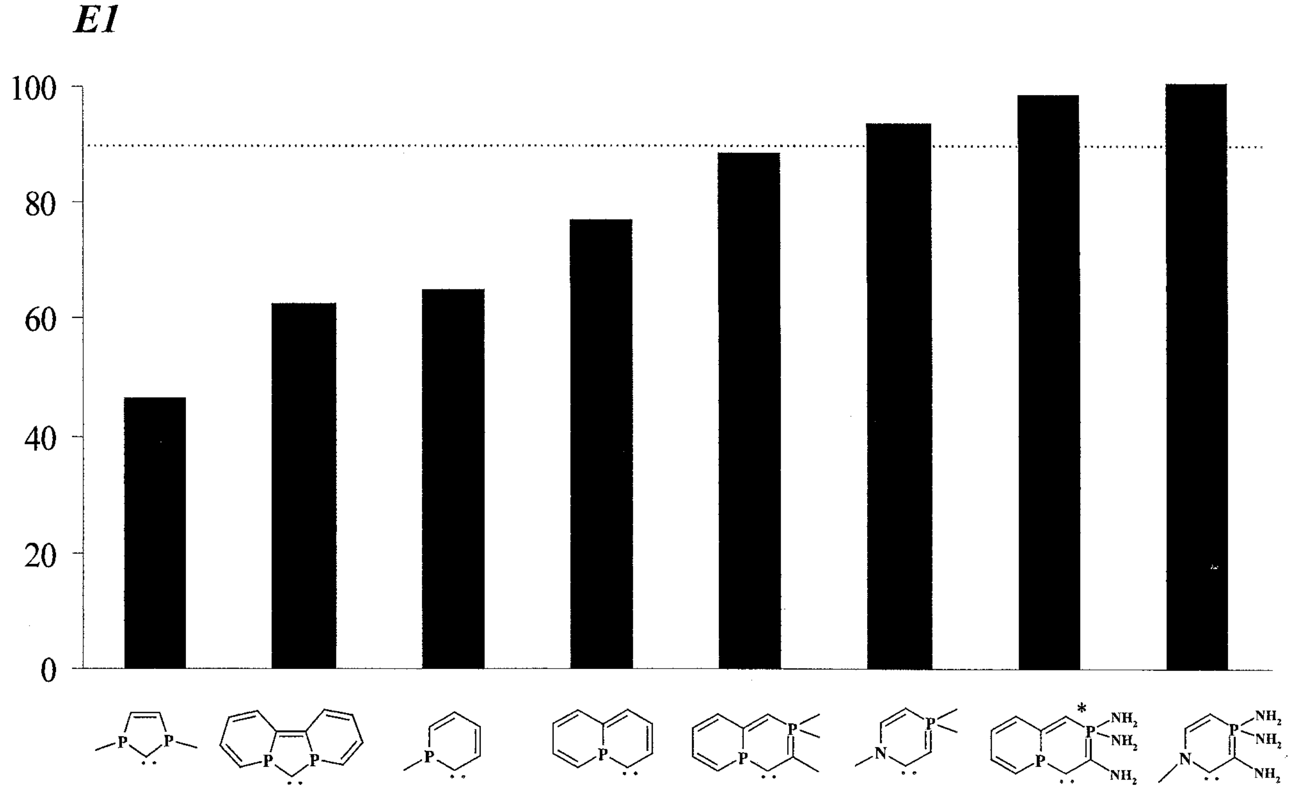


Fig. 3. B3LYP/6-311 + G** stabilization energies (***E1***) of some phosphinocarbenes and their most promising derivatives. * denotes B3LYP/3-21G(*) ***E1*** value, which is by about 2–4 kcal mol^{-1} higher than the B3LYP/6-311 + G** value (see text).

tricoordinate phosphorus, or by the carbon atom of a phosphorus ylide. By using isodesmic stabilization energies some cyclic carbenes exhibit high (***E1***) values, comparable to that of the Arduengo-carbene. The tricoordinate phosphorus planarized by ring annellation increases the stability of cabenes. Phosphorus ylides attached with their carbon atom to the carbene were also shown to stabilize the divalent state of carbon. The combination of the above effects results in systems, which are likely to be synthesizeable, having larger than 90 kcal mol^{-1} stabilization energy (***E1***). The ***E1*** stabilization energies of some cyclic phosphinocarbenes, and their most promising derivatives are shown in Fig. 3.

4. Calculations

Calculations were carried out with the GAUSSIAN 98 package [38] at the B3LYP/3-21G(*) and at the B3LYP/6-311 + G** levels of the theory. It has been shown before, that density functional calculations with the B3LYP functional provide good results in the isodesmic reactions used to estimate the stability of carbenes [26]. All geometries were fully optimized and the resulting structures were confirmed as minima on the potential energy hypersurface by second derivative calculations. Magnetic shieldings are calculated by the GIAO method at the HF/6-311 + G**//B3LYP/6-311 + G** level in order to have comparable NICS values to the previously published data. To produce Figs. 1 and 2, the MOLDEN program [39] was used.

Acknowledgements

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