

# Borane–Lewis Base Complexes as Homolytic Hydrogen Atom Donors

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**Abstract:** Radical stabilization energies (RSE)s have been calculated for a variety of boryl radicals complexed to Lewis bases at the G3(MP2)-RAD level of theory. These are referenced to the B–H bond dissociation energy (BDE) in BH<sub>3</sub> determined at W4.3 level. High RSE values (and thus low

BDE(B–H) values) have been found for borane complexes of a variety of five- and six-membered ring heterocycles. Variations of RSE values have

**Keywords:** boranes • Lewis bases • radicals • stabilization energy

been correlated with the strength of Lewis acid–Lewis base complex formation at the boryl radical stage. The analysis of charge- and spin-density distributions shows that spin delocalization in the boryl radical complexes constitutes one of the mechanisms of radical stabilization.

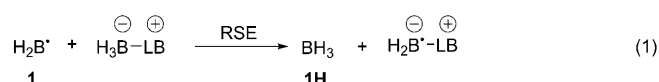
## Introduction

Complexes of boranes with neutral Lewis bases (LB) such as water, alcohols, amines, phosphanes and carbenes play a large role as hydrogen storage and release agents. Aside from applications in the area of molecular hydrogen (H<sub>2</sub>) storage,<sup>[18,19]</sup> recent developments concern the use of new hydrogen-atom donors in radical reactions.<sup>[1–4,26]</sup> Hydrogen-atom abstraction can, in principle, occur from the borane as well as the Lewis-base portion of these complexes, provided that hydrogen atoms are available at these positions. The fact that both components are better hydrogen atom donors in the complex as compared to the separate fragments offers the promise of a modular approach for the development of new tin-free hydrogen atom donors for organic synthesis.<sup>[1–3]</sup> Using quantum mechanical methods suitable for the reliable description of radical thermochemistry we are studying here the potential use of Lewis-base complexes with small heterocycles as hydrogen-atom donors in radical reactions.

## Results and Discussion

The stability of substituted boryl radicals can be quantitatively expressed using the isodesmic hydrogen-transfer reaction in Equation (1). The stability values obtained using this equation are identical to the difference in homolytic B–H bond dissociation energy (BDE) in BH<sub>3</sub> (**1H**) itself and in BH<sub>3</sub>–Lewis base complexes.

Negative values imply a stabilizing influence of the Lewis base on the boryl radical **1** and indicate weaker (and thus more reactive) B–H bonds in the Lewis-base complex than in the BH<sub>3</sub> parent system.



The homolytic B–H bond dissociation energy in BH<sub>3</sub> (**1H**) itself is, however, not well established. Using currently available heat of formation data from the NIST database yields BDE(B–H) in BH<sub>3</sub> (**1H**) of +312.1 kJ mol<sup>−1</sup> (Table 1).

Reviewing thermochemical data for boron hydrides in 1998, Yu and Bauer concluded that the large disparity between calculated and measured data is likely due to the inaccurate experimental data for 'BH<sub>2</sub> (**1**) and recommended a value of BDE(BH<sub>2</sub>–H) = +447 kJ mol<sup>−1</sup> (derived from various theoretical calculations).<sup>[21]</sup> Direct or indirect BDE computations using the G2 and G3 compound methods

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200903395>.

Table 1. Homolytic B–H bond dissociation energy (BDE(B–H)) in BH<sub>3</sub> (**1H**) in kJ mol<sup>-1</sup> derived from experimental and theoretical data.

BDE(B–H) [kJ mol <sup>-1</sup> ]	Source	Ref.
+312	exptl. $\Delta H_f^0$ for BH <sub>3</sub> → ·BH <sub>2</sub> + H	[12,13][a]
+312	exptl. $\Delta H_f^0$ for BH <sub>3</sub> + ·CH <sub>3</sub> → ·BH <sub>2</sub> + CH <sub>4</sub> and exptl. BDE(CH <sub>3</sub> –H)	[13][a],[14][b],[15][c]
+447	review	[21][d]
+467	UB3LYP/LACVP*	[2]
+446	G2	[11]
+441	CBS-4	[11]
+443	G3	[22]
+442.76	G3(MP2)-RAD evaluation of BH <sub>3</sub> + ·CH <sub>3</sub> → ·BH <sub>2</sub> + CH <sub>4</sub> and exptl. BDE(CH <sub>3</sub> –H) <sup>[c]</sup>	this work
+441.53	W1 evaluation of BH <sub>3</sub> + ·CH <sub>3</sub> → ·BH <sub>2</sub> + CH <sub>4</sub> and exptl. BDE(CH <sub>3</sub> –H) <sup>[c]</sup>	this work
+441.15	W4 evaluation of BH <sub>3</sub> → ·BH <sub>2</sub> + H	this work
+441.14	W4.3 evaluation of BH <sub>3</sub> → ·BH <sub>2</sub> + H	this work

[a] Using  $\Delta H_f^0(\text{BH}_3) = +106.69 \text{ kJ mol}^{-1}$ ;  $\Delta H_f^0(\text{BH}_2) = +200.83 \text{ kJ mol}^{-1}$ ;  $\Delta H_f^0(\text{H}) = (217.998 \pm 0.006) \text{ kJ mol}^{-1}$ .<sup>13</sup> [b] Using  $\Delta H_f^0(\text{CH}_4) = (-74.60 \pm 0.30) \text{ kJ mol}^{-1}$ ;  $\Delta H_f^0(\text{CH}_3) = (+146.7 \pm 0.3) \text{ kJ mol}^{-1}$ .<sup>14</sup> [c] Using  $\text{BDE}(\text{CH}_3\text{--H}) = (+439.28 \pm 0.13) \text{ kJ mol}^{-1}$ . [d] Using  $\Delta H_f^0(\text{BH}_3) = +89.2 \text{ kJ mol}^{-1}$ ;  $\Delta H_f^0(\text{BH}_2) = +318.0 \text{ kJ mol}^{-1}$  from ref. [21] and  $\Delta H_f^0(\text{H}) = (217.998 \pm 0.006) \text{ kJ mol}^{-1}$  from ref. [12].

arrive at slightly lower values in the range of 446–443 kJ mol<sup>-1</sup>, closely matched by the result obtained at W1 level at +441.5 kJ mol<sup>-1</sup>. Thermochemical calculations based on hybrid DFT methods such as the B3LYP scheme<sup>[1,2,26]</sup> predict a notably higher BDE value at around 447 kJ mol<sup>-1</sup>. The W4.3 compound scheme represents the most sophisticated theoretical approach employed here and predicts a value of  $\text{BDE}(\text{BH}_2\text{--H}) = +441.1 \text{ kJ mol}^{-1}$ .<sup>[24,25]</sup> The W4 family of methods is currently considered to deliver sub-kJ accuracy for systems composed of first-row elements only and we will therefore assume a  $\text{BDE}(\text{BH}_2\text{--H})$  reference value of +441.1 kJ mol<sup>-1</sup> for the subsequent discussion. Results for a number of complexes at G3MP2-RAD level have been compiled in Table 2 and are shown graphically in Figure 1 together with the BDE values for the corresponding B–H bonds. In order to provide a quantitative comparison to popular hydrogen-atom donors used in organic synthesis the BDE scale also includes horizontal lines for thio-phenol (HSPh) with  $\text{BDE}(\text{S--H}) = (349.4 \pm 4.5) \text{ kJ mol}^{-1}$ ,<sup>[12]</sup> tris(trimethylsilyl)silane (TTMSS, HSi(SiMe<sub>3</sub>)<sub>3</sub>) with  $\text{BDE}(\text{Si--H}) = 351.5 \text{ kJ mol}^{-1}$ ,<sup>[12,17,20]</sup> and tri-*n*-butyltinhydride (HSnBu<sub>3</sub>) with  $\text{BDE}(\text{Sn--H}) = 328.9 \text{ kJ mol}^{-1}$ .<sup>[12,17,20]</sup> In line with earlier studies by Rablen<sup>[11]</sup> we find here that borane complexes with aliphatic amines have rather similar BDE(B–H) values as BH<sub>3</sub> itself. Borane complexes with phosphanes, in contrast, are much better hydrogen-atom donors with RSE values of the resulting boryl radicals of around 50 kJ mol<sup>-1</sup>. Even more stabilized boryl radicals are obtained through complexation with carbenes, in line with recent results by Curran et al.<sup>[2]</sup> This is not only true for imidazolyl carbene complexes such as **15**, but also the dihydro analogues such as **19**, thiazolyl complex **18**, and triazolyl complex **22**. These systems cover a range of BDE(H–B) values from 330–302 kJ mol<sup>-1</sup> and thus fall into the region of HSnBu<sub>3</sub>. Visual inspection of Scheme 1 shows that this range of BDE values can also be covered with borane complexes of five- and six-membered ring heterocycles, all of which include N(sp<sup>2</sup>) centers as complexation partner for borane.

The least stabilized boryl radical of this series **10** with  $\text{RSE}(\mathbf{10}) = 77.3 \text{ kJ mol}^{-1}$  includes 1,3-imidazole as the com-

Table 2. Radical stabilization energies (RSE) for a variety of boryl radicals together with the BDE(B–H) values of the corresponding boranes, the complexation energies of borane–Lewis base complexes ( $E_c(\text{H}_3\text{BLB})$ ), and complexation energies of boryl radical–Lewis base complexes ( $E_c(\text{H}_2\text{B}^*\text{LB})$ ). All energies have been obtained at G3(MP2)-RAD level and are given in kJ mol<sup>-1</sup>.

System	RSE(H <sub>2</sub> B <sup>*</sup> –LB)	BDE(H–BH <sub>2</sub> –LB)	$E_c(\text{H}_3\text{BLB})$	$E_c(\text{H}_2\text{B}^*\text{LB})$
<b>1</b>	0.0	441.1	–	–
<b>2</b>	–12.6	428.7	–158.3	–170.9
<b>3</b>	–12.8	428.3	–280.8	–139.7
<b>4</b>	–13.7	427.4	–114.1	–127.8
<b>5</b>	–14.0	427.1	–170.6	–184.6
<b>6</b>	–16.7	424.4	–99.9	–116.7
<b>7</b>	–24.6	416.5	–158.3	–113.8
<b>8</b>	–52.1	389.0	–159.9	–212.0
<b>9</b>	–54.3	386.8	–91.4	–145.6
<b>10</b>	–77.3	363.8	–136.7	–213.9
<b>11</b>	–79.4	361.7	–142.8	–222.2
<b>12</b>	–95.2	345.9	–129.0	–224.2
<b>13</b>	–97.9	343.2	–119.7	–217.6
<b>14</b>	–109.2	331.9	–84.1	–193.3
<b>15</b>	–110.7	330.4	–220.6	–331.3
<b>16</b>	–112.5	328.6	–228.0	–340.5
<b>17</b>	–116.3	324.8	–147.5	–263.8
<b>18</b>	–116.6	324.5	–211.2	–327.7
<b>19</b>	–116.9	324.2	–228.1	–345.0
<b>20</b>	–117.7	323.4	–124.4	–242.0
<b>21</b>	–137.2	303.9	–107.3	–244.5
<b>22</b>	–138.7	302.4	–216.0	–354.7
<b>23</b>	–144.3	296.8	–132.0	–276.3
<b>24</b>	–146.6	294.5	–109.2	–255.8
<b>25</b>	–152.5	288.6	–126.1	–278.6
<b>26</b>	–163.6	277.5	–73.6	–237.2
<b>27</b>	–165.8	275.3	–126.5	–292.2
<b>28</b>	–184.0	257.1	–66.1	–250.1

plexation partner. At the high-stabilization end of this group we find pyrazine complex **27** with  $\text{RSE}(\mathbf{27}) = 165.8 \text{ kJ mol}^{-1}$ . This implies a  $\text{BDE}(\text{B--H}) = 275.3 \text{ kJ mol}^{-1}$ , which is significantly lower than the  $\text{BDE}(\text{Sn--H})$  in HSnBu<sub>3</sub>. Finally, complexation with simple carbonyl compounds can also lead to exceedingly stable boryl radical complexes such as **26** and **28**. The RSE values obtained for complexation with ketones and aldehydes go beyond –160 kJ mol<sup>-1</sup>, but are strongly re-

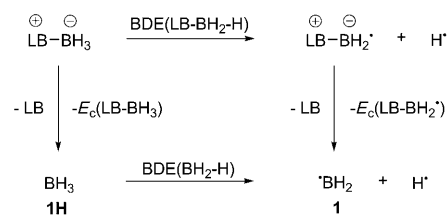
duced on introduction of electron donors as in amide complex **14**.

In how far the boryl radical RSE values (and thus also the B–H BDE of the corresponding boranes) depend on the strength of complexation between borane and Lewis base has been discussed already by Rablen. It is easily demonstrated with the thermochemical cycle shown in Scheme 1 that a quantitative relation exists between the BDE(B–H) values and the complexation energies of the respective borane–Lewis base complexes.

According to Scheme 1 the four energies in this cycle are related to each other as given in Equation (2). With respect to the definition of RSE values given in Equation (1) this can be rearranged to Equation (3) indicating that the RSE values listed in Table 1 are identical to the difference between the two complexation energies described in Scheme 1.

$$\text{BDE}(\text{LB} - \text{BH}_2 - \text{H}) = -E_c(\text{LB} - \text{BH}_3) + \text{BDE}(\text{BH}_2 - \text{H}) + E_c(\text{LB} - \text{BH}_2^{\bullet}) \quad (2)$$

$$\text{RSE}(\text{LB} - \text{BH}_2^{\bullet}) = E_c(\text{LB} - \text{BH}_2^{\bullet}) - E_c(\text{LB} - \text{BH}_3) \quad (3)$$



Scheme 1. Thermochemical cycle relating B–H bond dissociation processes to complexation energies for borane–Lewis base complexes.

Earlier studies by Rablen on small model systems have shown that correlation of BDE(LB–BH<sub>2</sub>–H) with the closed-shell complexation energy  $E_c(\text{LB} - \text{BH}_3)$  alone gives a very poor correlation. Analysis of the larger dataset compiled here confirms this finding (Figure 2a) in that a very low correlation coefficient of  $R^2 = 0.06$  is found for the correlation between RSE values and  $E_c(\text{LB} - \text{BH}_3)$ . Moreover, the correlation line is of negative slope ( $-0.24$ ), implying more stable boryl radicals for systems with smaller  $E_c(\text{LB} - \text{BH}_3)$  complexation energies. In contrast, a significantly better correlation with  $R^2 = 0.55$  and a positive slope of  $0.56$  is found between RSE values and the complexation energies between Lewis bases and the BH<sub>2</sub><sup>•</sup> radical  $E_c(\text{LB} - \text{BH}_2^{\bullet})$  (Figure 2b). This indicates that the RSE values are more strongly influenced by the bonding situation at the radical stage and is fully in line with the electron-deficient nature of the BH<sub>2</sub><sup>•</sup> radical.

Analysis of the spin-density distribution indicates that, in particular for the borane complexes with five- and six-membered ring heterocycles, spin delocalization into the ring system is one of the key factors responsible for large RSE values. This also raises the question whether the term “boryl radical” is still appropriate for the most stable systems shown in Figure 1. For a more detailed discussion we select here the NHC complex **16**, the pyridine complex **23** and the aldehyde complex **28**, together with their respective closed-shell parent systems. The BH<sub>3</sub> fragments in closed-shell complexes **16H**, **23H**, and **28H** are all characterized by a small negative partial charge, the actual values decreasing with

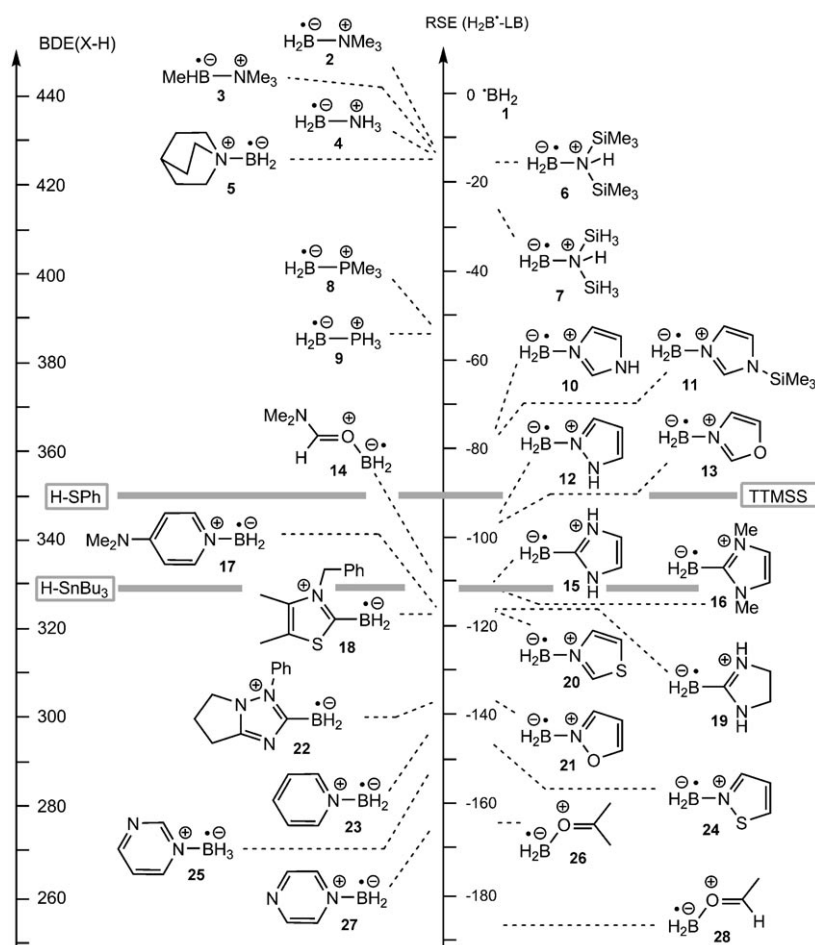


Figure 1. Radical stabilization energies (RSE, in  $\text{kJ mol}^{-1}$ ) for a variety of boryl radicals as obtained at G3-(MP2)-RAD level of theory together with the BDE(B–H) values of the corresponding boranes.

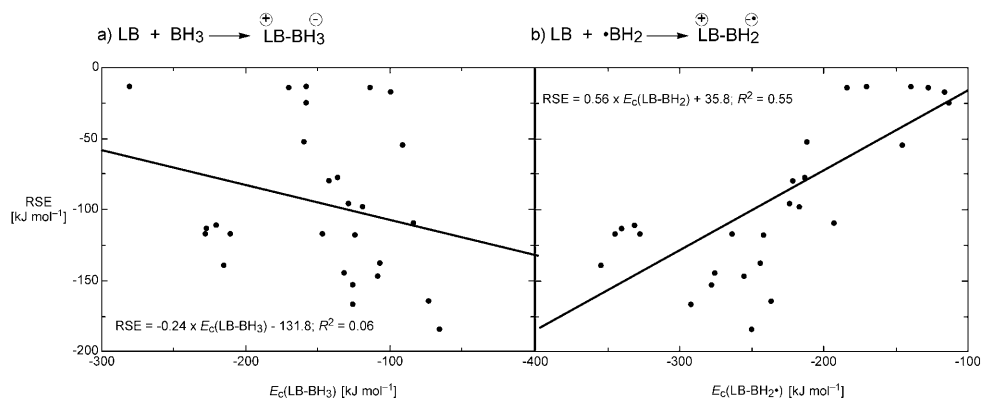


Figure 2. Correlation of RSE values for boryl radical–Lewis base complexes with a) borane–Lewis base complexation energy  $E_c(\text{LB}-\text{BH}_3)$ ; and b) boryl radical–Lewis base complexation energy  $E_c(\text{LB}-\text{BH}_2^+)$ .

the electronegativity of the complexation partner (Figure 3). The most negative overall charge is found for carbene complex **16H** with  $q(\text{BH}_3) = -0.51e$ . This is at variance with the Lewis structures shown in Equation (1), but in line with earlier results obtained in EDA analyses.<sup>[23]</sup> According to these latter studies the Lewis bases bind to  $\text{BH}_3$  through a combination of s-donor, p-acceptor and (in some cases) also p-donor interactions, leading to an only moderate buildup of negative charge on the  $\text{BH}_3$  fragment. Hydrogen abstraction from the  $\text{BH}_3$  unit generally leads to a significant depletion of charge density from the borane fragment. Taking again carbene complex **16** as an example, the  $\text{BH}_2$  fragment carries a residual negative charge of only  $q(\text{BH}_2) = -0.17e$ . In boryl radical complexes **23** and **28** the boryl radical is bound to more electronegative elements than in carbene complex **16**, leading to positive partial charges of the  $\text{BH}_2$  group of  $q(\text{BH}_2, \mathbf{23}) = +0.25e$  and  $q(\text{BH}_2, \mathbf{28}) = +0.40e$ . Along with these changes in the overall charge distribution one can also note a gradual migration of the unpaired spin from the  $\text{BH}_2$  fragment to the Lewis base complexation partner. Thus, while in boryl radical complex **16** most of the unpaired spin density is located on the boron atom, this is not so in pyridine complex **23** and acetaldehyde complex **28**. In **23** only 24% of the spin density reside on the boron atom, while most of the spin density is delocalized over the pyridine ring system. Both the charge as well as the spin density distribution can for this system most readily be described with the Lewis structures **23b** and **23c** (Scheme 2), leaving little weight for Lewis structure **23a**.

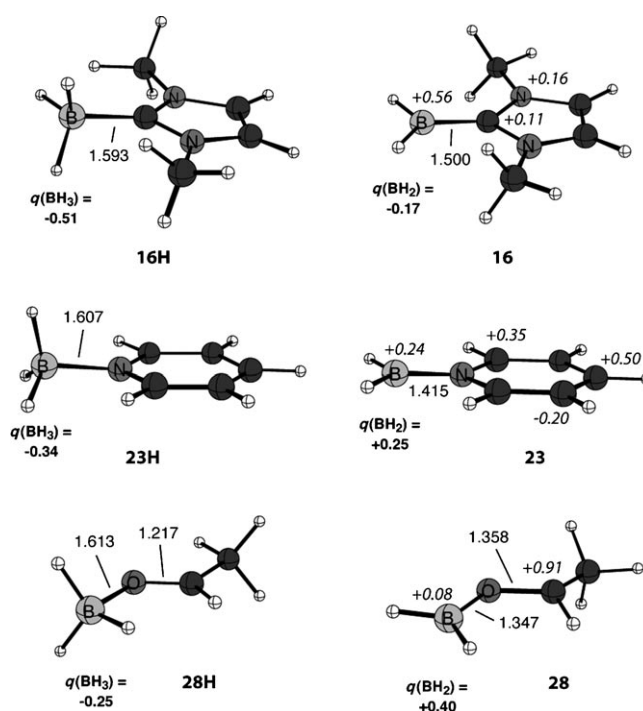
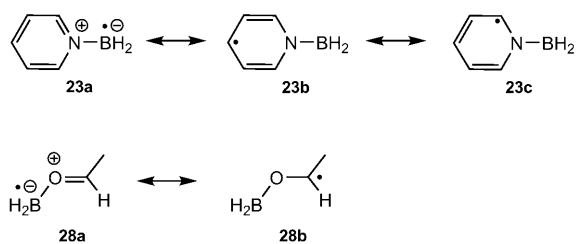


Figure 3. Structures of radicals **16**, **23**, and **28**, together with those of the respective closed-shell parent systems (as obtained at UMPW1K/6-31+G(d) level). Distances are given in pm (regular type). Charges of the  $\text{BH}_3$  and  $\text{BH}_2$  fragments (in bold) and atomic spin density values (in italics) have been obtained at UMPW1K/6-31+G(d) level using the NPA scheme.



Scheme 2. Formal Lewis structures for boryl radical complexes **23** and **28**.

In boryl radical complex **28** most of the unpaired spin density is located at the carbonyl carbon atom, as readily described with Lewis structure **28b** (Scheme 2). Thus, while Lewis structure **28a** is useful for the purpose of describing a formal hydrogen atom abstraction process from the  $\text{BH}_3$  complex of acetaldehyde, the actual product of this process is best understood as a borylketyl radical with the spin density distribution described by **28b**. This interpretation is also in line with the significantly larger C–O bond length in radical **28** as compared to that in the closed-shell parent com-

pound **28H**. The reactivity of boryl radical adducts **23** and **28** in radical chain reactions<sup>[1,2]</sup> may thus be quite different from that of “true” boryl radicals such as **16**.

## Conclusion

In conclusion we have shown that BDE(B–H) values closely similar to those of frequently used hydrogen-atom donors can be obtained through complexation of borane with a large number of small-ring heterocycles. This includes, but is not limited to, complexes with N-heterocyclic carbenes, whose proficiency as hydrogen atom donors in radical-chain reactions has recently been demonstrated.

## Computational Details

Geometry optimization of all systems has been performed at the (U)MPW1K/6-31+G(d) level of theory. Thermochemical corrections to 298.15 K have been calculated without scaling at the same level of theory using the rigid rotor/harmonic oscillator model. Relative enthalpies are obtained using the G3(MP2)-RAD Scheme proposed by Radom et al.<sup>[5]</sup> This level of theory has recently been used to assess the stability of a wide variety of radicals.<sup>[6–8]</sup> Given the fact that the B3LYP/6-31G(d) functional used for geometry optimizations in the original procedure does not give satisfactory results for systems of zwitterionic character, we use the MPW1K/6-31+G(d) functional here instead.<sup>[16]</sup> All enthalpies cited in the text have been obtained using this modified G3(MP2)-RAD procedure, if not mentioned otherwise. The URCCSD(T)/6-31G(d)//MPW1K/6-31+G(d) single point calculations required for this latter method have been performed with MOLPRO,<sup>[9]</sup> all other calculations have been performed with Gaussian 03.<sup>[10]</sup> A detailed description and rationalization of the *Wn* protocols is given elsewhere,<sup>[25]</sup> a concise summary of the various steps in W4 and W4.3 theories is given in the computational details section of ref. [27]. A component breakdown of the final W4.3 data is given in the Supporting Information.

## Acknowledgements

We thank Professor Martin Newcomb (University of Illinois, Chicago) and Professor C. Chatgililoglu (ISOF Bologna) for insightful comments on experimental BDE values.

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Received: December 10, 2009

Published online: May 6, 2010