Multiple Bonding

DOI: 10.1002/anie.200702299

Structural Changes Accompanying the Stepwise Population of a B–C π Bond[**]

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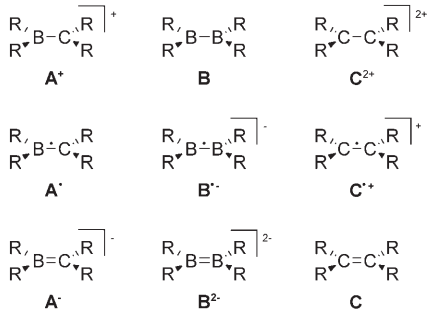
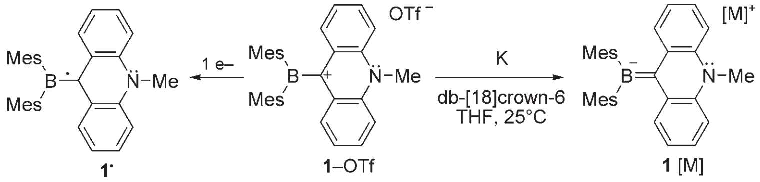
Owing to their negative charge and the large radius of boron, borataalkenes (type $\mathbf{A}^-$) are usually very reactive and have only been isolated on a few occasions.[1–3] The derivative $[\mathrm{Mes_2B{=}CH_2}]^-$ (Mes = 2,4,6-trimethylphenyl) is one of the simplest examples, and was isolated by deprotonation of the corresponding methyl compound.[1,4–6] While the chemistry of borataalkenes has not been widely investigated, studies have shown that they can act as nucleophilic reagents[4–6] or as ligands in transition-metal complexes.[7–9] Electrogenerated diborataalkenes, such as $[p\text{-}(\mathrm{Mes_2B})\mathrm{C_6H_4}(\mathrm{BMes_2})]^{2-}$, have also been detected using spectroelectrochemistry.[10–12] Interestingly, however, the structural changes accompanying the stepwise population/depopulation of a boron–carbon π bond have not been studied experimentally.



Examination of the literature indicates that such structural data is available for tetraaryldiboranes (type **B**) such as Mes$_2$BBMesPh which undergoes two one-electron reductions to afford the corresponding radical anion (type $\mathbf{B}^{\bullet -}$) and dianion (type $\mathbf{B}^{2-}$).[13–16] Structural studies carried out on $[\mathrm{Mes_2BBMesPh}]^{\bullet -}$ and $[\mathrm{Mes_2BBMesPh}]^{2-}$ confirm that reduction of the neutral diborane leads to population of the boron–boron π bond. Comparable studies have also been carried out on isoelectronic carbon derivatives.[17] For example, tetraarylalkenes (type **C**), such as tetraanisylethylene, can be oxidized to afford the corresponding radical cations (type $\mathbf{C}^{\bullet +}$) and dication (type $\mathbf{C}^{2+}$) whose structures have also been determined.[18] A common feature observed in the structure of these redox-active species is a lengthening of the boron–boron bond (type $\mathbf{B}^{2-}$) or ethylenic carbon–carbon bond (type **C**) upon oxidation, in agreement with the stepwise removal of the central π electrons.

We recently reported the synthesis of a 9-borylated acridininium ion $\mathbf{1}^+$ which could be reduced with magnesium to produce the corresponding 9-borylated acridinyl radical $\mathbf{1}^{\bullet}$ (Scheme 1).[19] The cyclic voltammogram of $\mathbf{1}^+$ also suggested the formation of $\mathbf{1}^-$ as another stable reduction species. Here, we now report that $\mathbf{1}^-$ is in fact a borataalkene which is generated by population of the central boron–carbon π bond of $\mathbf{1}^+$. We also report the structural characterization of crystalline salts of $\mathbf{1}^+$ and $\mathbf{1}^-$ which allows us to precisely track the structural changes accompanying the stepwise population of a B–C π bond.



Scheme 1. $[\mathrm{M}]^+ = [\mathrm{K(db\text{-}[18]crown\text{-}6)(thf)_2}]^+$, OTf = trifluoromethanesulfonate.

Reaction of **1**-OTf with potassium and dibenzo-[18]crown-6 (db-[18]crown-6) in THF leads to formation of the borataalkene salt **1**-[K(db-[18]crown-6)(thf)$_2$] (Scheme 1). This salt is extremely air-sensitive and has been isolated in a crystalline form by diffusion of hexane into a THF solution. In the ^{11}B NMR spectrum, the resonance which appears at $\delta = 40$ ppm is close to those reported for $[\mathrm{Mes_2BCH_2}]^-$ ($\delta = 35$ ppm)[1] and 8,10,11a-trimethyl-7-mesityl-11a*H*-7-boratabenzo[de]anthracene ($\delta = 45.5$ ppm),[2] thus reinforcing a borataalkene formulation for $\mathbf{1}^-$. The ^{1}H resonance of the *N*-methyl group of $\mathbf{1}^-$ at $\delta = 3.09$ ppm is shifted upfield by 1.9 ppm when compared to that of $\mathbf{1}^+$. This shift is consistent with the loss of aromaticity of the central ring in the acridinyl moiety, once again in agreement with the formulation of $\mathbf{1}^-$ as a borataalkene.

We have previously reported the structure of the neutral radical $\mathbf{1}^{\bullet}$ and speculated that the length of the central B–C

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[**] This work was supported by the National Science Foundation (CHE-0646916), the Welch Foundation (A-1423), and the Petroleum Research Funds administered by the American Chemical Society (44832-AC4).

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bond of this derivative may lie between a B–C single bond and a B–C double bond.[19] To confirm this hypothesis, it was necessary to compare the structure of $\mathbf{1}^{\bullet}$ to that of $\mathbf{1}^{+}$ and $\mathbf{1}^{-}$. Single crystals of **1**-OTf were obtained by vapor diffusion of diethyl ether into a dichloromethane solution of the salt.[20] These crystals belong to the monoclinic space group $P2_1/n$ (Figure 1 a). Examination of the cell packing diagram indicates that there is no short contact between $\mathbf{1}^{+}$ and the triflate anion. The sum of the angles around boron atom B1 (359.9°) and the methylium carbon atom C9 (360.0°) show that both are trigonal planar. The central ring of the acridinium moiety remains strictly planar and features short intracyclic C9–C and N1–C bonds, indicating substantial aromaticity. Finally, the bond B1–C9 (1.627(5) Å) is distinctly longer than the B1–C15 and B1–C25 bonds (av. 1.586 Å). Moreover, B1–C9 is twisted by 62.4°, suggesting that there is no π conjugation between the boron center and the acrydinyl ring.

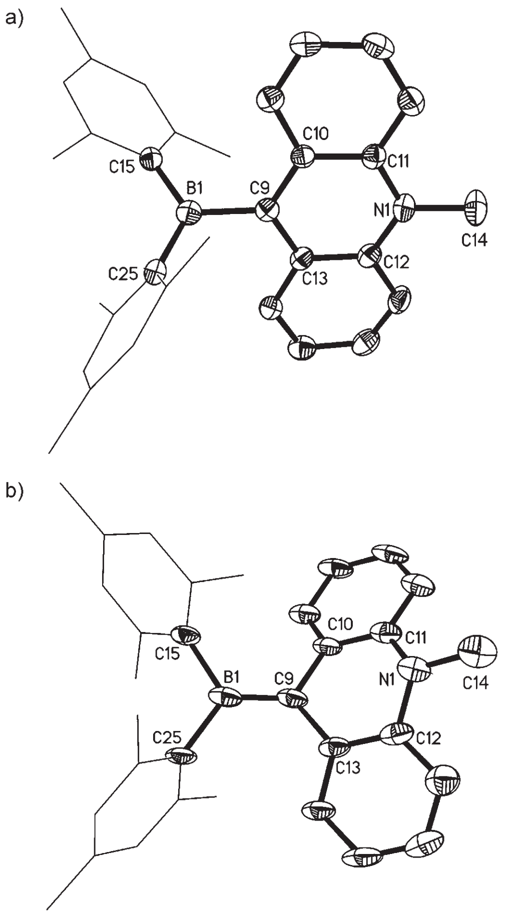


Figure 1. Crystal structures of the $\mathbf{1}^{+}$ ion in **1**-OTf (a) and the $\mathbf{1}^{-}$ ion in **1**-[K(db-[18]crown-6)(thf)$_2$]·THF·0.5 hexane (b). Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: $\mathbf{1}^{+}$: B1-C9 1.627(5), B1-C15 1.584(5), B1-C25 1.589(5), C9-C10 1.425(4), C9-C13 1.426(4), N1-C11 1.388(4), N1-C12 1.386(4), N1-C14 1.498(4). $\mathbf{1}^{-}$: B1-C9 1.462(8), B1-C15 1.626(8), B1-C25 1.628(8), C9-C10 1.502(7), C9-C13 1.475(7), N1-C11 1.419(7), N1-C12 1.435(6), N1-C14 1.448(7).

The borataalkene salt **1**-[K(db-[18]crown-6)(thf)$_2$] crystallizes in the triclinic space group $P\bar{1}$ as a THF/hexane solvate (Figure 1 b).[20] These crystals are dark red and extremely sensitive. Examination of the cell packing diagram indicates that there is no short contact between the borataalkene $\mathbf{1}^{-}$ and [K(db-[18]crown-6)(thf)$_2$]$^{+}$ ion. The boron atom B1 and the carbon atom C9 adopt a trigonal-planar geometry (sum of angles at B1: 359.8°; at C9: 360.0°). The B1–C(9) bond (1.462(8) Å) is short and lies within the range observed for other borataalkenes such as [Mes$_2$BCH$_2$]$^{-}$ (1.444(8) Å)[1] and 8,10,11a-trimethyl-7-mesityl-11a-*H*-7-boratabenzo[de]-anthracene (1.48 Å).[2] It also features only slight twisting (15.3°) as expected for a doubly bonded species. The central C$_5$N ring of the acridine moiety displays a marked puckering (see below) and the nitrogen atom is also slightly pyramidal (sum of angles at N1: 353.4°). These structural features, as well as the relatively long intracyclic C9–C and N1–C bonds, indicate a loss of aromaticity of the central C$_5$N ring of the acridine moiety, once again in accordance with the formation of a B–C double bond between B1 and C9.

Since the structure of $\mathbf{1}^{\bullet}$ has been previously determined,[19] the present structural analysis of **1**-OTf and **1**-[K(db-[18]crown-6)(thf)$_2$] allows us to analyze the structural changes induced by reduction of $\mathbf{1}^{+}$ into $\mathbf{1}^{\bullet}$ and $\mathbf{1}^{-}$ (Figure 2). In all three structures, the boron atom B1 and the carbon atom C9 adopt a trigonal-planar geometry. The B1–C9 bond undergoes a noticeable shortening on going from $\mathbf{1}^{+}$ to $\mathbf{1}^{\bullet}$ to $\mathbf{1}^{-}$. Similar trends have been predicted theoretically for [*p*-(Mes$_2$B)C$_6$H$_4$(BMes$_2$)] and its corresponding radical anion and dianion.[12] More importantly, the B1–C9 bond determined for $\mathbf{1}^{\bullet}$ (1.559(5) Å) lies almost exactly between the B–C single bond measured in $\mathbf{1}^{+}$ (1.627(5) Å) and the B–C double bond observed in $\mathbf{1}^{-}$ (1.462(8) Å); Figure 2). In accordance with the above, we note that the dihedral angles formed by the trigonal planes containing B1 and C9 decrease steadily on going from $\mathbf{1}^{+}$ to $\mathbf{1}^{-}$ (62.4° in $\mathbf{1}^{+}$, 44.8° in $\mathbf{1}^{\bullet}$, 15.3° in $\mathbf{1}^{-}$; Figure 2). Conversion of $\mathbf{1}^{+}$ into $\mathbf{1}^{\bullet}$ and $\mathbf{1}^{-}$ is also accompanied by an increase in the puckering of the central C$_5$N ring of the acridine moiety. This puckering is reflected by the displacement of C9 and N1 atoms above the plane containing the C10-C11-C12-C13 atoms (displacements in Å for C9: 0.04 in $\mathbf{1}^{+}$, 0.12 in $\mathbf{1}^{\bullet}$, 0.33 in $\mathbf{1}^{-}$; and for N1: 0.04 in $\mathbf{1}^{+}$, 0.16 in $\mathbf{1}^{\bullet}$, 0.42 in $\mathbf{1}^{-}$). Together, these results suggest that the reduction of $\mathbf{1}^{+}$ leads to the sequential population of the B–C π bond which is

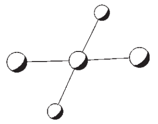
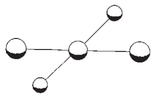
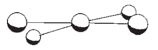
$\mathbf{1}^{+}$	$\mathbf{1}^{\bullet}$	$\mathbf{1}^{-}$
		
$d = 1.627(5)$ Å $\alpha = 62.4°$	$d = 1.559(5)$ Å $\alpha = 44.8°$	$d = 1.462(8)$ Å $\alpha = 15.3°$

Figure 2. View of the central core of $\mathbf{1}^{+}$, $\mathbf{1}^{\bullet}$, and $\mathbf{1}^{-}$ along the B1–C9 vector with the B1–C9 distance d and the dihedral angle α formed by the trigonal planes containing B1 and C9.

accompanied by a loss of aromaticity in the central ring of the acridine moiety.

To better appreciate the origin of the structural changes induced by reduction of $\mathbf{1}^{+}$, the structures of $\mathbf{1}^{+}$, $\mathbf{1}^{\bullet}$, and $\mathbf{1}^{-}$ have been optimized at the B3LYP/6-31 g(d) level of theory and subjected to a natural bond orbital (NBO) analysis at the same level of theory.[21,22] In the case of $\mathbf{1}^{+}$, one σ-bonding orbital occupied by 1.95 electrons connects the B1 and C9 atoms in agreement with existence of a B−C single bond (Figure 3). NBO analysis of $\mathbf{1}^{-}$ affords one σ- and one π-bonding orbital spanning the B1 and C9 atoms (Figure 3). These orbitals are occupied by 1.95 and 1.67 electrons respectively. It is interesting to note that the contour plot of the π bond shows a polarization toward the carbon atom of the B=C linkage (72 % on C and 28 % on B). Because of its open-shell electronic configuration, NBO analysis of radical $\mathbf{1}^{\bullet}$ affords orbitals in both the α and β spin manifolds. The B1 and C9 atoms are connected by two σ-bonding orbitals, one being the α and one the β spin manifold, and are each occupied by 0.98 electrons. In addition to these two σ interactions, the NBO analysis indicates that there is a π-bonding interaction between B1 and C9 in the α spin manifold. This orbital is occupied by 0.81 electrons and features a strong polarization toward the C9 atom (83 % on C and 17 % on B). The presence of this π-bonding orbital confirms that the B1−C9 bond of $\mathbf{1}^{\bullet}$ has multiple-bond character. The combined occupancies of the orbitals connecting B1 and C9 in $\mathbf{1}^{+}$, $\mathbf{1}^{\bullet}$, and $\mathbf{1}^{-}$ are equal to 1.95, 2.77, and 3.62, respectively, which suggests an increase of the bond order upon reduction. However, because some of these interactions are strongly polarized, the bond orders are likely to be less than 1, 1.5, and 2. More realistic numbers may in fact be provided by the Wiberg bond indices which are equal to 0.83 for $\mathbf{1}^{+}$, 0.96 for $\mathbf{1}^{\bullet}$, and 1.34 for $\mathbf{1}^{-}$.

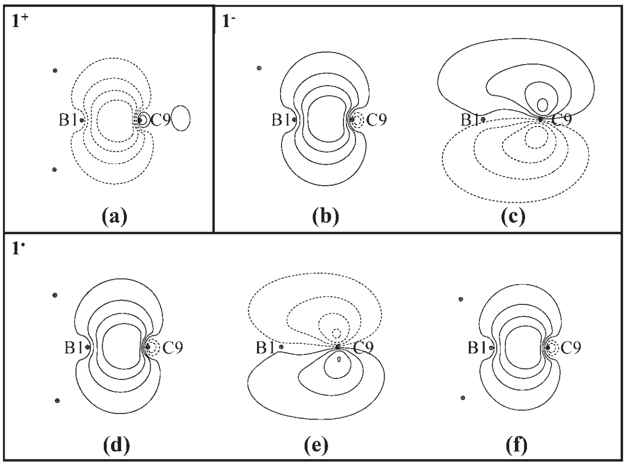


Figure 3. Selected natural bond orbital contours. $\mathbf{1}^{+}$: $\sigma_{\text{B1-C9}}$ (a). $\mathbf{1}^{-}$: $\sigma_{\text{B1-C9}}$ (b) and $\pi_{\text{B1-C9}}$ (c). $\mathbf{1}^{\bullet}$: $\sigma_{\text{B1-C9}}$ ((d), α spin), $\pi_{\text{B1-C9}}$ ((e), α spin) and $\sigma_{\text{B1-C9}}$ ((f), β spin). Small round dots represent atom centers.

In conclusion, the results reported herein indicate that reduction of $\mathbf{1}^{+}$ results in the sequential population of the central boron–carbon π bond of this derivative. Population of this orbital is substantiated by a clear shortening of the boron–carbon bond as well as a decrease of its twist angle. The computational results are in agreement with these experimental findings and confirm an increase of the order of the B−C bond upon reduction. Another important outcome of this work is the discovery that borataalkenes are amenable to reversible redox chemistry and can in fact be considered as the reduced form of α-borylated carbocations.

Experimental Section

1-[K(db-[18]crown-6)(thf)$_2$]: The triflate salt **1**-OTf (50 mg, 0.08 mmol) was treated with excess potassium at room temperature in THF (2 mL) in the presence of db-[18]crown-6 (40 mg, 0.11 mmol). The color of the solution changed from yellow to blue, and then to red after about 30 minutes. **1**-[K(db-[18]crown-6)(thf)$_2$] was obtained as a THF/0.5 hexane solvate in the form of dark red crystals. These crystals are very sensitive and decompose at room temperature in an inert atmosphere. ^{1}H NMR ([D$_5$]pyridine, 499.95 MHz, 233 K): $\delta = 2.20$ (s, 6H, Mes-*p*-CH$_3$), 2.86 (s, 12H, Mes-*o*-CH$_3$), 3.09 (s, 3H, NMe), 3.64 (bs, 16H, db-[18]crown-6), 6.46 (d, 2H, $^3J_{\text{H-H}} = 7.5$ Hz), 6.51 (t, 2H, $^3J_{\text{H-H}} = 7.5$ Hz), 6.62 (t, 3H, $^3J_{\text{H-H}} = 7.5$ Hz), 6.83 (s, 4H, Mes-CH), 6.93(bs, 8H, db-[18]crown-6), 7.49 ppm (d, 2H, $^3J_{\text{H-H}} = 7.5$ Hz). ^{13}C NMR ([D$_5$]pyridine, 125.7 MHz, 233 K): $\delta = 20.2$ (Mes-*p*-CH$_3$), 23.2 (Mes-*o*-CH$_3$), 32.4 (NMe), 66.3 (crown), 68.1 (crown), 108.9, 110.5 (crown), 117.9, 119.5, 120.7 (crown), 123.4, 126.5, 130.8, 140.8, 143.4 (crown), 143.7, 146.0, 151.7 ppm. Despite extended acquisition time, the resonance of the B=C carbon atom was not detected. ^{11}B NMR ([D$_5$]pyridine, 160.4 MHz, 233 K): $\delta = 40$ ppm. An elemental analysis could not be obtained because of the sensitivity of the compound.

Received: May 24, 2007

Keywords: boron · multiple bonds · NBO analysis · reduction

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[1] M. M. Olmstead, P. P. Power, K. J. Weese, R. J. Doedens, *J. Am. Chem. Soc.* **1987**, *109*, 2541 – 2542.
[2] J. D. Hoefelmeyer, S. Solé, F. P. Gabbaï, *Dalton Trans.* **2004**, 1254 – 1258.
[3] R. A. Bartlett, P. P. Power, *Organometallics* **1986**, *5*, 1916 – 1917.
[4] A. Pelter, L. Williams, J. W. Wilson, *Tetrahedron Lett.* **1983**, *24*, 627 – 630.
[5] A. Pelter, B. Singaram, L. Warren, J. W. Wilson, *Tetrahedron* **1993**, *49*, 2965 – 2978.
[6] A. Pelter, K. Smith, S. M. A. Elgendy, M. Rowlands, *Tetrahedron* **1993**, *49*, 7104 – 7118.
[7] K. S. Cook, W. E. Piers, T. K. Woo, R. McDonald, *Organometallics* **2001**, *20*, 3927 – 3937.
[8] K. S. Cook, W. E. Piers, P. G. Hayes, M. Parvez, *Organometallics* **2002**, *21*, 2422 – 2425.
[9] K. S. Cook, W. E. Piers, R. McDonald, *J. Am. Chem. Soc.* **2002**, *124*, 5411 – 5418.
[10] W. Kaim, A. Schulz, *Angew. Chem.* **1984**, *96*, 611 – 612; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 615 – 616.
[11] A. K. Schulz, W. Kaim, *Chem. Ber.* **1989**, *122*, 1863 – 1868.
[12] J. Fiedler, S. Zališ, A. Klein, F. M. Hornung, W. Kaim, *Inorg. Chem.* **1996**, *35*, 3039 – 3043.
[13] A. Moezzi, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **1992**, *114*, 2715 – 2717.

[14] P. P. Power, *Inorg. Chim. Acta* **1992**, *198–200*, 443 – 447.

[15] W. J. Grigsby, P. P. Power, *Chem. Commun.* **1996**, 2235 – 2236.

[16] W. J. Grigsby, P. Power, *Chem. Eur. J.* **1997**, *3*, 368 – 375.

[17] W. W. Porter III, T. P. Vaid, *J. Org. Chem.* **2005**, *70*, 5028 – 5035.

[18] R. Rathore, S. V. Lindeman, A. S. Kumar, J. K. Kochi, *J. Am. Chem. Soc.* **1998**, *120*, 6931 – 6939.

[19] C.-W. Chiu, F. P. Gabbaï, *Angew. Chem.* **2007**, *119*, 1753 – 1755; *Angew. Chem. Int. Ed.* **2007**, *46*, 1723 – 1725.

[20] Crystal data: **1**-[OTf]: $0.17 \times 0.05 \times 0.02$ mm^3, $C_{33}H_{33}BF_3NO_3S$, $M_r = 591.47$, monoclinic, space group $P2_1/n$, $a = 14.163(3)$, $b = 8.2625(17)$, $c = 26.232(5)$ Å, $\beta = 97.51(3)°$, $V = 3043.3(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.291$ Mg m^{-3}, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $T = 110(2)$ K, 19205 measured reflections, 4711 unique, $R_{int} = 0.0557$, $R_1 = 0.0886$, $wR_2 = 0.1474$ (all data). [**1**][K(db-[18]crown-6)-(thf)$_2$]·THF·0.5 hexane: $0.27 \times 0.21 \times 0.01$ mm^3, $C_{67}H_{88}BKNO_9$, $M_r = 1101.29$, triclinic, space group $P\bar{1}$, $a = 13.544(3)$, $b = 14.278(3)$, $c = 18.858(4)$ Å, $\alpha = 91.46(3)$, $\beta = 110.26(3)$, $\gamma = 114.29(3)°$, $V = 3057.4(11)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.196$ Mg m^{-3}, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 150(2)$ K, 25198 measured reflections, 6741 unique, $R_{int} = 0.0699$, $R_1 = 0.1043$, $wR_2 = 0.1870$ (all data). Specimens of suitable size and quality were selected and mounted onto a 0.7-mm nylon loop with Apiezon grease. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. CCDC 648336 and CCDC 648337 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[21] A. E. Reed, F. Weinhold, L. A. Curtiss, D. J. Pochatko, *J. Chem. Phys.* **1986**, *84*, 5687 – 5705.

[22] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899 – 926.