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Notes

Occurrence of Hydrogen Single Bridges in Main Group Chemistry

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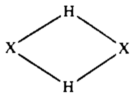
In main group chemistry, three-center–two-electron bonds generally occur in symmetrical double bridges, **1**, as in diborane ($X = BH_2$), the ethane dication ($X = CH_2^+$),[1] or the heavier analogues of ethylene (X = Si, Ge, Sn, Pb).[2] Electron-deficient single bridges are less frequent. They are encountered in three typical situations. First, as a unique link, such bonds mainly occur in charged species such as $B_2H_7^-$ (**2**),[3] its derivatives,[4] heavier analogues,[5] or isoelectronic species like $C_2H_7^+$,[1,6] or organic cations like **3**,[7] and occasionally in neutral systems which, however, are clearly zwitterionic in nature, like **4** or **5**.[8,9] The second class is represented by the nonclassical form of the ethyl cation, **6**. Lastly, unusual cyclic arrangements like **7** have been found in neutral Sn_2H_4 and Pb_2H_4.[10] We will show here how a simple scheme lies behind these structures and straightforwardly accounts for both their rarity and diversity.



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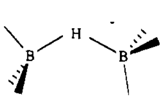

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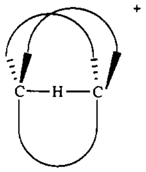

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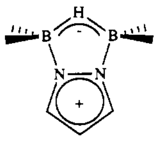

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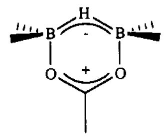

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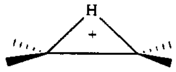

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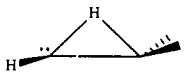

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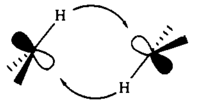
The building of an X–H–Y electron-deficient link from X–H + Y fragments (eq 1) necessarily implies a certain charge

$$X\text{–}H + Y \rightarrow X\text{–}H\text{–}Y \qquad (1)$$

displacement of the X–H bonding electron pair. In symmetrical systems like **1**, the two bridges permit such a binding *without* inducing any global charge dissymmetry, **8**.[11] Another way of preventing strong unilateral charge migration can be achieved by a regular dative counterpart. This is done in **7**, which can be viewed as two interacting methylene-type fragments, **9**.[10]



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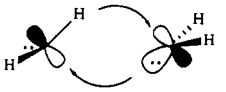

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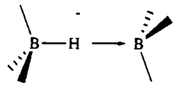
In ionic systems, the electron migration can obviously be a favorable process, *providing the transfer occurs in the right way.* In other words, the only allowed starting fragments in eq 1 must necessarily be either $X\text{–}H^-$ or Y^+: this is achieved in $B_2H_7^-$, **10**, or $Si_2H_5^+$, **11**, **12**.[12,13] The closure of the classical form of the ethyl cation, **13**, also proceeds from the same mechanism. On



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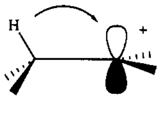

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(1) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*, John Wiley and Sons: New York, 1986.

(2) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130.

(3) (a) Greenwood, N. N.; Earnshow, A. *Chemistry of the Elements*, Pergamon Press: Oxford, England, 1984. (b) Shore, S. G.; Lawrence, S. H.; Watkins, M. I.; Bau, R. *J. Am. Chem. Soc.* **1982**, *104*, 7669. (c) Khan, S. I.; Chiang, M. Y.; Bau, R.; Koetzle, T. F.; Shore, S. G.; Lawrence, S. H. *J. Chem. Soc., Dalton Trans.* **1986**,

(4) (a) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063. (b) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420. (c) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027.

(5) (a) Atwood, J. L.; Hrncir, D. C.; Rogers, R. D.; Howard, J. A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6787. (b) Howell, J. L.; Sapse, A. M.; Singman, E.; Snyder, G. *J. Am. Chem. Soc.* **1982**, *104*, 4758.

(6) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(7) McMurry, J. E.; Lectka, T. *Acc. Chem. Res.* **1992**, *25*, 47.

(8) (a) Idelmann, P.; Müller, G.; Scheidt, W. R.; Schüssler, W.; Köster, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 153. (b) Müller, G.; Krüger, C. *Acta Crystallogr., C* **1986**, *42*, 1856.

(9) Yalpani, M.; Boese, R.; Köster, R. *Chem. Ber.* **1990**, *123*, 1285.

(10) Trinquier, G. *J. Am. Chem. Soc.* **1991**, *113*, 144.

(11) Larger neutral boron hydrides basically enter such a scheme.

(12) (a) Raghavachari, K. *J. Chem. Phys.* **1991**, *95*, 7373. (b) Trinquier, G. *Chem. Phys. Lett.* **1992**, *188*, 572. (c) Trinquier, G. *J. Am. Chem. Soc.* **1992**, *114*, 6807.

(13) Structures similar to **11** and **12** are also found for the $SiH_4 + Si^+$ adduct: Raghavachari, K. *J. Chem. Phys.* **1988**, *88*, 1688.

(14) In an SCF description of $Si_2H_5^+$, when starting from an arrangement like **14**, the two fragments SiH_3^+ and SiH_2 repel each other and the system evolves toward one of the four possible $Si_2H_5^+$ minima.

(15) In an SCF description of $C_2H_3^-$, when starting from a bridging position in **15**, the hydrogen atom rocks to the left, leading to an $H_3C\text{-}C^-$ arrangement (Kabbaj, O. K. Private communication).

(16) Structure **16** is found to be a real minimum, at the SCF level, on the Pb_2H_6 potential surface. The corresponding binding energy with respect to $PbH_4 + PbH_2$ is calculated at 5.0 kcal/mol (SCF) and 9.2 kcal/mol (MP4). This is much smaller than that of $Pb_2H_5^+$ (in an arrangement $H_3Pb\text{–}H\text{–}PbH^+$ like **11**) with respect to $PbH_4 + PbH^+$ (20 kcal/mol at SCF level; 24.6 kcal/mol at MP4 level). The $Pb\text{–}H_b$ distances in the $Pb\text{–}H_b\text{–}Pb$ bridges are calculated at 1.90 and 2.01 Å in the "allowed" bridge in $Pb_2H_5^+$ but 1.78 and 2.34 Å in the unfavored bridge in Pb_2H_6. The global electron transfer from the PbH_4 fragment is 4 times weaker in Pb_2H_6 than in $Pb_2H_5^+$. All these indicators therefore underline the intermolecular character of complex **16**. A similar complex has recently been reported for Si_2H_6: Becerra, R.; Frey, H. M.; Mason, B. P.; Walsh, R.; Gordon, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 2751.

(17) We thank A. Gourdon and J. Aussoleil, from the CEMES-LOE Laboratory, for the permission to use their computing facilities to consult the Cambridge Structural Database.

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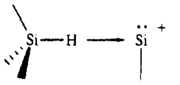

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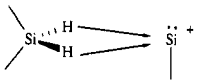

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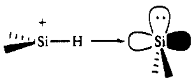

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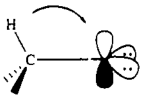

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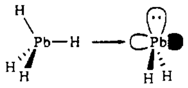

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the other hand, arrangements like **14** or closures like **15** are clearly forbidden.[14,15] A neutral entity such as **16**, where neither back-transfer nor charge sharing can occur, is not expected to be stabilized. However, since there is, in this case, no conspicuous polarity violation, a weakly bound intermolecular complex will be possible.[16]

Such naïve arguments appear to account for existent as well as nonexistent structures. We believe the present model could be added to the handful of simple rules that enable the chemist to understand or anticipate unusual structures.[17]

Registry No. Hydrogen, 12385-13-6.