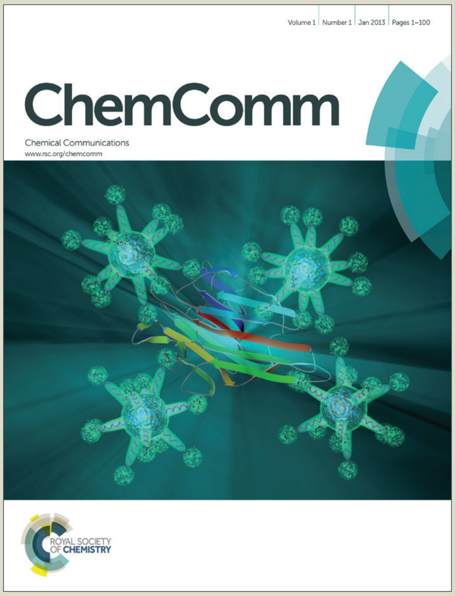
ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Can Silylenes Rival Transition Metal Systems in Bond-Strengthening π-Back Donation? A Computational Investigation.

Amrita Pal[a] and Kumar Vanka*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Full quantum chemical calculations with density functional theory (DFT) show that bond-strengthening back-donation to a π-diborene, recently discovered for transition metal systems (Braunschweig and co-workers, *Nat Chem.*, 2013, *5*, 115-121), would be just as favored for Main Group silylene complexes. This result not only shows the range and applicability of the bond-strengthening back-bonding interaction, but also showcases the potential of silylene complexes to do new chemistry, such as the cooperative activation of carbon monoxide and carbon dioxide.

The most distinctive feature of transition metal catalysis, indeed, the very basis of it, is the interaction between the metal and the ligand through the donation of electron density from a filled metal orbital to an empty, anti-bonding ligand orbital. This serves to weaken one of the bonds in the ligand, thus giving rise to most of the transition metal chemistry known today (see references 12 and 13 in the Supporting Information file). However, a radical new development by Braunschweig and co-workers shows that bond-weakening back-donation is not the sole possibility in metal-ligand interactions. They have found[1] that donation of electron density can take place from a filled metal orbital (of a palladium and a platinum based complex) to a singly occupied orbital (the SOMO) of the ligand (a π-diborene: PhB=BPh), an interaction that leads to the stabilization of the bond in the π-diborene ligand. This unprecedented finding is not only interesting conceptually, but is also likely to lead to important developments in transition metal catalysis. However, an important question that needs to be asked is: would such a bond-strengthening back-donating interaction also be possible for *non*-transition metal systems? It is known that Main Group systems such as carbenes[2-5] and silylenes[6-9] can activate small molecules (see references 14-16 in the Supporting Information file) by weakening ligand bonds, just like transition metal complexes. What we decided to investigate was whether Main Group complexes such as silylenes might also be able to demonstrate the unusual bond-strengthening back-donation interaction. Such an interaction, if also possible for silylene systems, would not only expand the scope of applicability of this newly discovered form of bonding, but would also showcase the potential of the Main Group complexes to do new chemistry. It is to be noted here that while several recent papers (see references 17-28 of the Supporting Information file) have discussed the implications of the work of Braunschweig and coworkers, our study is the first one that considers the possibility of bond strenghtening back-donation by a Main Group system.

The reason we have focused attention on silylenes is because they are likely to have HOMOs that would be closer in energy to the SOMOs of complexes such as π-diborene. For example, our calculations indicate that the gap between the HOMO of the silylene $(Si\{Si(SiMe_3)_3\}\{N(SiMe_3)Dipp\})$ (**I** in Fig. 2 below) and the SOMO of the π-diborene complex is only 2.4 kcal/mol. This would indicate that bond-strengthening back-donation interactions can happen between the silylene and the π-diborene complex, as illustrated in Fig. 1 below.

The current computational study explores this possibility for three different silylene complexes (**I**, **II** and **III** in Fig. 2), representing both cyclic and acyclic silylenes. The full quantum chemical calculations in this study have been done with density functional theory (DFT). The Turbomole 6.0 suite of programs[10] (with PBE/TZVP) has been employed. Calculations have also been done with Gaussian 09 in order to obtain and visualize the HOMOs and SOMOs for the different silylene-π-diborene and the metal-π-diborene complexes. For more details, please see the Computational Details Section of the Supporting Information file.

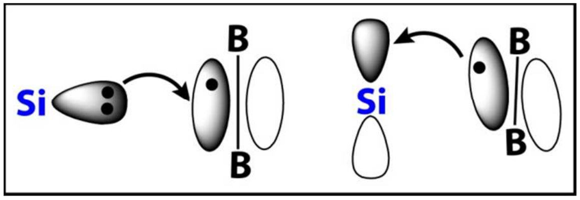


Fig. 1 The schematic representation of bond-strengthening back-donation interactions between a silylene complex and a π-diborene.

As shown in Table S2 of the Supporting Information file, the HOMO-SOMO gap between the silylene and the π-diborene is small for all the three cases considered. Encouraged by this result, we proceeded to optimize the geometries of the π-diborene complexed to the cyclic and acyclic silylenes, and compared them to the metal-π-diborene complexes, which were also optimized.

Fig. 2 The three silylene complexes considered in the current work.

In the free diphenyl diborene, the B-B bond distance is 1.526 Å (since diphenyl diborene does not exist in isolation, this can be considered a reference calculation). As discussed by Braunschweig *et al.*[1], the experimentally observed interaction of this molecule with the zero valence platinum complex[1] exhibits considerable lowering of the B-B bond distance (to 1.510 Å) from its free form. Our calculation optimizing the reported model Pd based diborene complex, **Pd-Me-bb** (see Fig. 3), confirms the strengthening of the B-B bond. The C-B bond distances in **Pd-Me-bb** are seen to have increased from 1.510 Å to 1.528 Å and 1.530

ChemComm Accepted Manuscript

Å, which indicates that the strengthening of the B-B bond comes at a cost to the C-B bonds. **Pd-Me-bb** is seen to show almost equal Pd-B bond distances of 2.102 Å and 2.107 Å, which signifies the bonding contribution involving both the boron atoms. The C-B-B bond angles are 169.2° and 174° respectively, which indicate an almost planar structure, which is also in accordance with the proposed model by Braunschweig and co-workers. The other two metal complexes, (**Pd-et-bb**) and (**Pt-et-bb**) exhibit similar structural characteristics, which have been shown in Fig. S1 and Fig. S2 of the Supporting Information file. The corresponding values are shown in Table S1. Furthermore, as also discussed by Braunschweig and co-workers[1], the HOMO and HOMO-I of **Pd-Me-bb**, shown in Fig. 4 below, indicate the bonding and back-bonding interactions between the metal center and the π-diborene ligand.

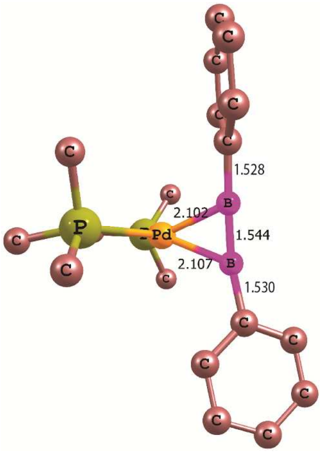


Fig. 3 The optimized structure for Pd(PMe$_3$)$_2$ complexed to the π-diborene; hydrogen atoms have not been shown for the purpose of clarity.

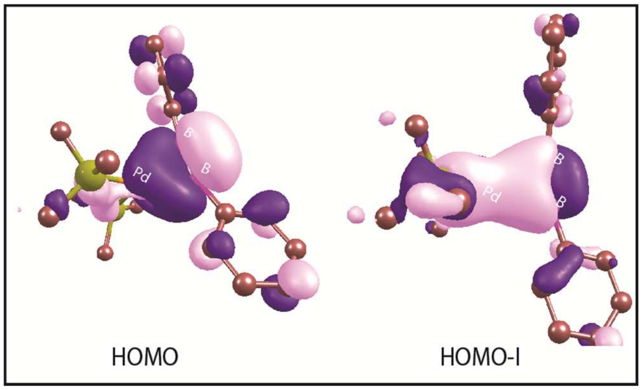


Fig. 4 The HOMO (-0.11 Ha) and the HOMO-I (-0.17 Ha) for the complex shown in Fig. 3 above.

Now, moving on to the silylenes **I-III**, the optimized structure of π-diborene coordinated to **I** (**I-bb**) is shown in Fig. 5 below. It is seen that **I-bb** not only has the same bonding features as **Pd-et-bb**, but also shows evidence of greater interaction between the silicon and the π-diborene. The B-B bond distance is 1.544 Å in **Pd-et-bb**, but it is only 1.516 Å in **I-bb**. Moreover, the Si-B bond lengths (2.047 Å and 2.116 Å) are also comparable to the Pd-B bond lengths. The C-B-B bond angles are 156.3° and 166.2°, which again indicate the slight distortion from planarity, as in the case of **Pd-et-bb**. Also, like in **Pd-et-bb**, there is an increase in the C-B bond distances (1.546 Å and 1.531 Å respectively), which suggests that the B-B strengthening in the presence of the silylene leads to a concomitant reduction in the bond strength of the C-B bonds. Furthermore, as shown in Fig. 6 below, the HOMO and the HOMO-I of **I-bb** also reveal the same bonding and back-bonding interactions as observed in **Pd-et-bb**, though, interestingly, the HOMO of **I-bb** resembles the HOMO-I of **Pd-et-bb**, and the HOMO-I of **I-bb** resembles the HOMO of **Pd-et-bb**. The reason for this is that the shapes of the HOMO and the LUMO are switched for the bare **Pd(PMe$_3$)$_2$** and silylene **I** complexes. (The HOMO and LUMO for both the cases are shown in Fig. S16 and Fig. S17 of the Supporting Information file.) Finally, the ΔG of the formation of the π-diborene with **I** (ΔG = -39.8 kcal/mol) is in the same range as the corresponding **Pd-et-bb** formation (ΔG = -39.2 kcal/mol). All of these structural, electronic and energetic features therefore strongly indicate that silylene **I** would be either as effective, or more effective at bond-strengthening back-donation with π-diborene than the palladium complex.

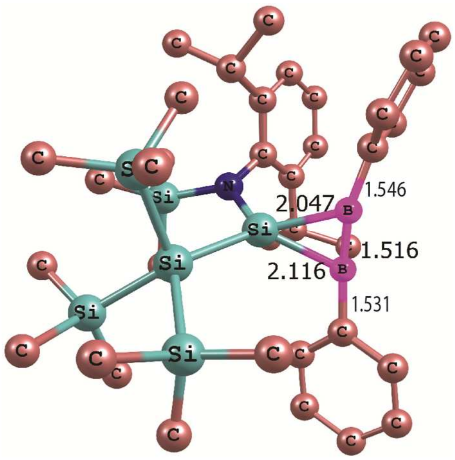


Fig. 5 The optimized structure for silylene **I** complexed to the π-diborene; hydrogen atoms have not been shown for the purpose of clarity.

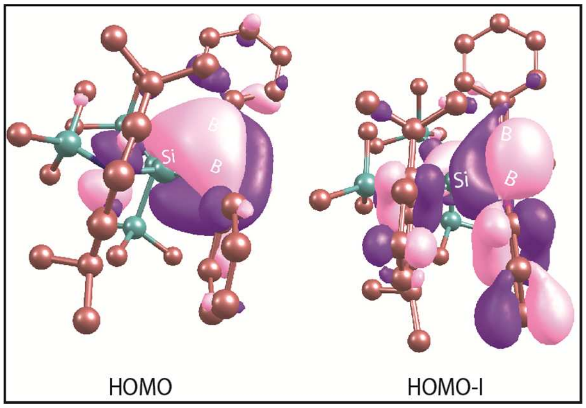


Fig. 6 The HOMO (-0.15 Ha) and the HOMO-I (-0.17 Ha) for the complex shown in Fig. 5 above.

The same structural, energetic and electronic features are also observed in the cases of the silylenes **II** and **III**. The optimized structures of **II-bb** and **III-bb** are shown in the Fig. S4 and Fig. S6 of the Supporting Information file. Also, the relevant bond lengths and bond angles for **II-bb** and **III-bb** have been compiled in Table S1. The HOMO and HOMO-II of **II-bb** and **III-bb** are shown in Fig. S5 and Fig. S7 (see the Supporting Information file). Since **I** is an acyclic silylene and **II** is a cyclic silylene (both have been synthesized[11, 12]), the results suggest that the bond-strengthening back-donation interaction with π-diborene would be present in a range of silylenes. Silylene **III** is a proposed cyclic silylene structure, where isopropyl groups have been suggested for the cyclic backbone (see Fig. 2 above). The calculations indicate that this

ChemComm Accepted Manuscript

proposed silylene complex would show the best bond-strengthening back-bonding interaction, reducing the B-B bond distance to 1.496 Å. This result suggests that new silylenes can be designed, with greater electron donation to the silylene center, which would lead to the further stabilization of the π-diborene. Indeed, the pronounced B-B bond shortening observed in all the optimized silylene-bb cases suggests that the strengthening will be measurable and observable as shortened bonds, should the compounds be synthesized. This is in constrast to the calculations done by Braunschweig *et al.*[1], where the calculated B-B bond length in the palladium-bb complex was found to be longer than the experimental value. It is to be noted here that the B-B bond-shortening has also been observed for **III-bb** optimized with the B3LYP hybrid functional: the B-B bond is seen to shorten (value: 1.496 Å) in the silylene complexed case (**III-bb**) in comparison to the free diborene (value: 1.512 Å).

A final point in this regard is about the calculation of the Wiberg Bond Indices (WBI), which was also done for the three silylene-diborene complexes. The values obtained further indicate the strengthening of the B-B bond. As shown in Table S4 of the Supporting Information file, the WBI for the B-B bond is found to be 1.43 and 1.50 for the **Pd-me-bb** and **Pd-et-bb** case, while it is 1.63 for **I-bb**, 1.70 for **II-bb**, and 1.78 for **III-bb**. The value of the WBI in the free diborene was found to be 1.44, thereby indicating the significant bond strengthening in all the silylene cases considered.

NBO analysis done for the **Pd-Me-bb** complex shows that the occupancies for the bonds between the two borons are 1.91 and 1.52. The data also indicates that both the borons contribute almost equally to the bonds (see Section NBO analysis of the Supporting Information file). The analysis for the **I-bb** complex indicates that the bonds between the borons have characteristics identical to the **Pd-Me-bb** case: the occupancies for the B-B bonds are 1.9 and 1.6, and the other parameters are almost the same as for the **Pd-Me-bb** complex (see Section NBO analysis). Hence this again indicates the similarity in bonding between the silylene-bb and palladium-bb complexes.

The current calculations show the potential of silylenes to rival transition metal complexes in doing the newly discovered bond-strengthening back-bonding interaction. This indicates that the scope of the Main Group silylenes can be considerably expanded outside the range of dihydrogen activation[13]. For instance, silylenes can activate the π-diborene, leading to the bonding and activation of molecules such as CO and CO_2. As seen from Fig. S9 in the Supporting Information file, showing CO coordination to **I-bb**, the carbon oxygen bond length in the coordinated CO is 1.16 Å, which is much higher than the bond length (1.138 Å) in the free form of CO. As a result, the boron-boron bond length is also seen to increase to 1.6 Å. Further indication of the favorable binding of CO to the silyene complexed π-diborene is seen from the fact that CO coordination to **I-bb** is exergonic by 29.7 kcal/mol. The calculations also indicate that this would a barrierless process: a linear transit approach where the distance between the carbon of CO and the boron was decreased from 2.0 Å to 1.4 Å showed a steady decrease in energy till the product was formed. The analogous calculation of CO_2 binding to **I-bb** also indicates high favorability, being exergonic by 25.9 kcal/mol. The transition state for this binding reaction was obtained, and the barrier was calculated to be 13.8 kcal/mol, which indicates that the process would be very feasible at ambient temperatures. It is to be noted that the binding of the free silylene **I** to CO_2 is only exergonic by 6.0 kcal/mol, and that **I** does not bind CO at all. Also, the free π-diborene does not exist, and can only be formed when stabilized, as experimentally done[1] with the platinum complex, and computationally shown to be possible here. In other words, the chemistry that can be done with the silylene-π-diborene complex would not be possible by either isolated component. This indicates the importance of the bond-strengthening back-bonding interaction for the Main Group silylene complexes.

To summarize, the current computational investigations reveal that bond-strengthening π-back donation, which has been recently discovered for transition metal systems[1], can be done just as effectively by Main Group silylene complexes. This finding has significant implications with regard to the scope and range of the reactivity of silylenes. Moreover, since it is known that Main Group complexes are cheaper and greener than their transition metal counterparts, the current work has both conceptual and practical significance.

Funding from the FP7-NMP-EU-India-2 collaborative project HYPOMAP is gratefully acknowledged. KV is grateful to the Department of Science and Technology (DST). The authors also acknowledge the Multi-Scale Simulation and Modeling project - MSM (CSC0129)- for providing financial assistance

Notes and references

[a] Physical Chemistry Divison, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune – 411008, Maharashtra, India.

Electronic supplementary information available. See DOI: 10.1039/b000000x/

1. H. Braunschweig, A. Damme, R. D. Dewhurst and A. Vargas, *Nat Chem*, 2013, **5**, 115-121.
2. E. Despagnet-Ayoub, K. Miqueu, J.-M. Sotiropoulos, L. M. Henling, M. W. Day, J. A. Labinger and J. E. Bercaw, *Chem. Sci.,*2013, **4**, 2117-2121.
3. C. D. Martin, M. Soleilhavoup and G. Bertrand, *Chem. Sci.,*2013, **4**, 3020-3030.
4. G. D. Frey, V. Lavallo, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Science*, 2007, **316**, 439-441.
5. A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.,* 1991, **113**, 361-363.
6. B. Gehrhus, M. F. Lappert, J. Heinicke, R. Boese and D. Blaser, *J. Chem. Soc., Chem. Commun.,* 1995, 1931-1932.
7. M. Denk, R. Lennon, R. Hayashi, R. West, A. V. Belyakov, H. P. Verne, A. Haaland, M. Wagner and N. Metzler, *J. Am. Chem. Soc.,* 1994, **116**, 2691-2692.
8. M. Haaf, T. A. Schmedake and R. West, *Acc. Chem. Res.,* 2000, **33**, 704-714.
9. G. Bender, T. Wiegand, H. Eckert, R. Fröhlich, C. G. Daniliuc, C. Mück-Lichtenfeld, S. Ndambuki, T. Ziegler, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.,* 2012, **51**, 8846-8849.
10. TURBOMOLE V6.0 2009, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
11. R. Rodriguez, T. Troadec, T. Kato, N. Saffon-Merceron, J.-M. Sotiropoulos and A. Baceiredo, *Angew. Chem.,* 2012, **124**, 7270-7273.
12. A. V. Protchenko, A. D. Schwarz, M. P. Blake, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *Angew. Chem. Int. Ed.,* 2013, **52**, 568-571.
13. A. V. Protchenko, K. H. Birjkumar, D. Dange, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.,* 2012, **134**, 6500-6503.

ChemComm Accepted Manuscript