



Cite this: *New J. Chem.*, 2024, **48**, 4675

Received 31st January 2024,
Accepted 14th February 2024

DOI: 10.1039/d4nj00523f

rsc.li/njc

1,3-Zwitterions consisting of a phosphonium cation linked to a silicate centre through a one-atom bridge, $X_3P-E-SiY_4$ (3), are computationally studied. Their phosphonium acidic group together with a Lewis base constitute a frustrated Lewis pair (FLP) in the activation of H_2 , with the silicate side-arm providing Coulombic stabilization to the positive charge at the Lewis base.

The development of FLPs (frustrated Lewis pairs)¹ has been a fundamental discovery in p-block chemistry. They are composed of Lewis acidic and basic centres that, generally, are not likely to form a binary adduct due to steric factors. This concept arose from the early finding that H_2 (and other small molecules) can be reversibly activated by combinations of Lewis acids and bases with high steric demand, demonstrating capabilities exclusively attributed to transition metals until then.² The acceptor-donor nature of the elements of groups 13 and 15 are classic examples of Lewis acids and bases, respectively. Therefore, it could be envisaged that such systems could activate small molecules³ through a synergistic action of both centres, provided that their direct interaction is sterically precluded.

It was not until 2006's discovery of p -(Mes₂PH)C₆F₄-BH(C₆F₅)₂⁴ that this chemical frustration could be used for synthetic purposes, being capable of activating the H_2 molecule under very mild conditions (25 °C, 1 atm). Thereafter, the scope of FLP activations was broadened including a variety of small molecules such as olefins,⁵ alkynes,⁶ and a number of element oxides, primarily carbon dioxide⁷ and nitrous oxide.⁸ Furthermore, FLP chemistry now includes unique stoichiometric

transformations such as metal-free catalytic hydroaminations,⁹ polymerizations¹⁰ and even recent applications in bio-inorganic and materials chemistry, as well as in heterogeneous catalysis.¹¹

Among the most commonly used Lewis bases are phosphines,¹² amines,¹³ thioethers¹⁴ and carbenes,¹⁵ while polyfluorinated boranes¹⁶ and aluminium-based centres¹⁷ have been used as Lewis acidic counterparts in FLPs. In addition, Lewis acids based on carbon or silicon have been reported, the latter being able to act as Lewis acid (silylium–phosphine adducts)¹⁸ or base (silylium–silylene) FLPs.¹⁹ The phosphonium cation²⁰ is a well-known Lewis acid in which the acidity is derived from a σ^* orbital.²¹ 1,3,5-Triphosphinine (1,3,5-triphosphabenzene) was reported to act as a kind of intramolecular FLP in the cleavage of the H_2 molecule through resonance structures in which a positive charge is located at the phosphorus and a negative charge at the carbon.²² These cationic Lewis acids are able to promote dehydro-fluorination reactions, isomerization, hydrosilylation and hydrogenation of olefins, as well as dehydrocoupling of silanes with alcohols, acids, amines and thiols.²³

1,3-Zwitterionic species²⁴ could be good candidates for behaving as FLPs provided that the cationic and anionic centres could exhibit Lewis acid and basic properties, respectively. A recent example of a crypto-FLP bearing a P–O–Si framework with a basic phosphide centre and (neutral) electrophilic Si atom was reported.²⁵ An interesting inverse combination of 1,3-zwitterionic species for the formation of an FLP, that has not yet been reported, is the use of a phosphonium cation as a Lewis acid, bearing a one-atom bridged negatively charged centre.

Herein, the formation of these types of zwitterions $X_3P-E-SiY_4$ (3) from stable $\sigma^4\lambda^5$ -phosphorus derivatives $X_3P=E$ (1) and saturated SiY₄ compounds (2) is explored (Scheme 1). Species 1 already have resonant structures with 1,2-dipolar structure. Nevertheless, this dipole is unable to activate small molecules. Species 3 could also enable a P-to-Si E-group transfer, giving rise to X_3P (4) and $E:-SiY_4$ (5). This scheme has been studied

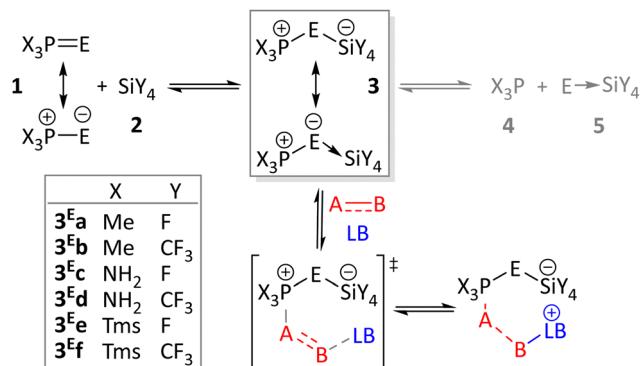
^a Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Spain. E-mail: artuesp@um.es

^b Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität, Bonn, Germany. E-mail: r.streubel@uni-bonn.de

^c Departament de Química, Universitat de les Illes Balears, Palma de Mallorca 07122, Spain

† Electronic supplementary information (ESI) available: Computational details, other theoretical results and computed structures. See DOI: <https://doi.org/10.1039/d4nj00523f>





Scheme 1 Studied potential interconversions ($E = \text{CH}_2, \text{SiH}_2, \text{NH}, \text{PH}, \text{O}$ or S) and possible vicarious Coulombic stabilization of the silicate moiety upon small molecule FLP activation.

for different families varying the E bridge that contains group 14 ($\text{CH}_2, \text{SiH}_2$), 15 (NH, PH) or 16 (O or S) central atoms. Interestingly, 3 could provide the phosphonium acidic centre engaged in an intermolecular FLP with an external Lewis base (LB), the silicate side arm allowing vicarious stabilization *via* additional Coulombic interaction with the newly originated cationic centre resulting upon small molecule AB activation (Scheme 1).

The choice of substituents was first investigated, as they might play a key role in finding stable 1,3-zwitterionic dipoles 3 (Scheme 1). Electron donating substituents X at P (PX_3^{Do}) and electron acceptors Y at Si ($\text{SiY}_4^{\text{Acc}}$) are expected to favour the formation of zwitterionic structures 3 by stabilizing the separated electric charges. With this aim, simple model donor substituents Me, NH_2 and SiMe_3 (Tms), together with F and CF_3 as acceptor substituents, were studied. As expected, the above-mentioned combination of substituents does indeed stabilize 1,3-dipolar species 3. Most of the energies for the dipole 3 formation process are highly exergonic (Table S1, ESI[†]), especially for CH_2 - and NH -bridged dipoles and most O-bridged ones with the highest exergonicity found for $\text{Tms}_3\text{P}-\text{CH}_2-\text{Si}(\text{CF}_3)_4$ (3^{C}f). As a general trend, the dipole formation is more exergonic as a function of the bridge “E” element group in the order tetrel \geq pnictogen $>$ chalcogen and decreasing for third (Si, P and S) compared to second-row elements (C, N and O). Indeed, S-bridged zwitterionic structures 3^{S}a-f are not formed as such, but van der Waals complexes 1-2 with only peripheral interactions (no direct $\text{S}\cdots\text{Si}$ bond) were found instead (Fig. S2, ESI[†]). Other exceptions are 3^{Si}a,c and 3^{P}a whose formation is moderately endergonic. On the contrary, the opposite combinations of accepting substituents on P (PX_3^{Acc}) and donor substituents on Si (SiY_4^{Do}) destabilize the molecular 1,3-zwitterionic species 3, which were never located as minima.

The E-group transfer reaction from 1 to 2 by means of the alternative cleavage of the E-Si bond in 3 (Scheme 1) leads to a hypothetical species $\text{E:}\rightarrow\text{SiY}_4$ (5) which was never located as a minimum, as it rearranges furnishing a [1,2]Y-migration product Y-E-SiY_3 (5'). Nevertheless, this E-Si bond-cleavage with

rearrangement is generally endergonic (Table S1, ESI[†]) and leads to products ($4+5'$) that are much less stable than the starting materials (1+2), except for all SiH_2 -bridged zwitterions. In only a few exceptional cases ($3^{\text{Si}}\text{a,c,e}$ and 3^{O}e) such a cleavage is exergonic (Table S1, ESI[†]).

The intramolecular single electron transfer (SET) from the potentially reducing $\sigma^3\lambda^3\text{-P}(\text{III})$ -compound (4) to the P-E bond cleavage species $\text{E:}\rightarrow\text{SiY}_4$ (5) was also explored. However, although all species 5^- were found to be stable (*i.e.* no rearrangement observed), the hypothetical (separated) ion pair $4^{\bullet+} + 5^-$ turned out to be highly unstable (see Table S1, ESI[†]). Most likely, this is because the electronic effects of the substituents that favour formation of the zwitterion 3 are destabilizing the intramolecular SET from 4 to 5.

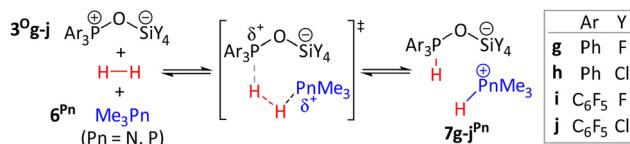
Once the appropriately substituted dipolar species 3 were shown to be stable compounds, the Coulombic interactions between the P and Si ionic centres were studied. As expected, the P-Si distances of dipolar species 3 with a third-row atom at the bridging E position are larger than those having second row atoms, due to their larger atomic size. (Table S2, ESI[†]). The Wiberg bond indices (WBI) for the P-Si (electrostatic) interaction are generally quite low, with only three non-linear molecules displaying values above 0.015 (3^{Si}c , 3^{P}c and 3^{P}d), thus accounting for very weak interactions. Moreover, the atoms-in-molecules²⁶ (AIM) methodology reveals the existence of bond critical points (BCP) corresponding to non-covalent interactions (NCI) between the X and Y substituents on P and Si, respectively (Fig. S1, ESI[†]), which satisfactorily explains the observed shortening of the P-Si distance in some cases.

In zwitterionic species 3 it is worth inspecting the nature of the E-Si bond formally arising from the interaction between the stable species $\text{X}_3\text{P}=\text{E}$ (1) and SiY_4 (2). To highlight the effect of the bridging unit “E”, a small subset of compounds 3 with the simplest substituents, namely $\text{Me}_3\text{P}-\text{E}-\text{SiF}_4$, was selected for this study. According to IUPAC, a dative bond is formed between two entities, one of them acting as a donor and the other as an acceptor of the pair of electrons to be shared in the complex formed. Compared to covalent bonds it presents “significant polarity, less resistance and greater length” and its signature is “that its minimum energy breakdown in the gas phase or in inert solvents follows the heterolytic bond cleavage path”. When compared to the covalent E-Si bond in analogous dipolar structures HE-SiF_4 , lacking the PX_3 fragment, a clear elongation of the E-Si bond in 3 is observed (Table S3, ESI[†]), which may be indicative of a dative linkage. The elongation varies in the order $\text{SiH}_2 < \text{PH} < \text{CH}_2 < \text{NH} < \text{O} \ll \text{S}$, the latter agreeing with their van der Waals complex (1-2) nature.

The computed bond dissociation energies (BDE) show a clear preference for the heterolytic over the homolytic cleavage, and summation of the (Mulliken) electric charges over the atoms belonging to the SiY_4 group ($q_{\text{SiY}_4}^{\text{M}}$) shows a remarkable charge transfer and hence unveils its acceptor character (Table S3, ESI[†]), both facts pointing to a E: \rightarrow Si dative bond nature.

Another approach to analyse dative bonding arises from the representation of the Laplacian of the electron density along the bond path.²⁷ The $\nabla^2\rho$ function shows a pronounced sharp





Scheme 2 Activation reaction of the H_2 molecule by the dipole structures 3°g-j and Lewis bases 6°p .

minimum, which is a valence shell charge concentration (VSCC) band corresponding to the electron donor atom of the ligand, VSCC_{C} for 3°a as a case in point (Fig. S3, ESI[†]), and another shoulder attributable to the associated acceptor Si atom (VSCC_{Si}). Both lie within the basin of the donor atom, which constitutes a signature for dative bonds together with a small positive value of $\nabla^2\rho$ at the BCP ($2.88 \text{ e } \text{\AA}^{-5}$). For the rest of the E bridges, the two VSCC minima fall within the same basin (see ESI[†]) except for the bridge with S (3°a), which constitutes a van der Waals complex, as already indicated.

Since the main interest of FLPs is their potential use in the activation of small molecules, the efficacy of the zwitterionic molecules 3 was checked for this purpose. As aforementioned, 3 can provide the phosphonium acidic centre acting as an intermolecular FLP with an external base, for which the two lighter trimethyl-pnictogens Me_3Pn ($\text{Pn} = \text{N, P}$) 6°p were used as models. As cases in point, two oxygen atom-bridged triphenyl-phosphonium silicates $\text{Ph}_3\text{P}-\text{O}-\text{SiY}_4$ ($\text{Y} = \text{F}$ (3°g), Cl (3°h)) were employed as zwitterionic species and their FLP behaviour checked for the activation of H_2 (Scheme 2).

The quantum chemical calculations provide evidence that the H_2 molecule is activated by these complexes $3^{\circ}\text{g,h}/6^{\circ}\text{p}$, endergonically producing the corresponding ion pairs $7\text{g,h}^{\circ\text{p}}$ by cleavage of the H-H bond with a moderate energy barrier (Fig. 1). The lowest barriers correspond to the FLPs engaging the amine 6°N as a base (*ca.* 25 kcal mol⁻¹) and the most stable final adducts are those having Cl as a substituent at silicon, $7\text{h}^{\circ\text{N}}$ and $7\text{h}^{\circ\text{P}}$ (Fig. 1). Altogether, $3^{\circ}\text{h}/6^{\circ}\text{N}$ resulted in the most favourable FLP combination for the activation of H_2 .

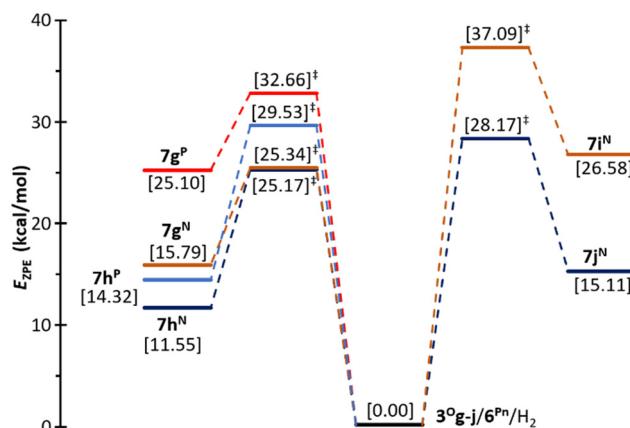


Fig. 1 Computed (CCSD(T)/def2-TZVPP//PBEh-3c) zero-point corrected energy profile for the activation reaction of the H_2 molecule by 6°N,P and 3°g,h (left) and by 6°N and 3°i,j (right) according to Scheme 2.

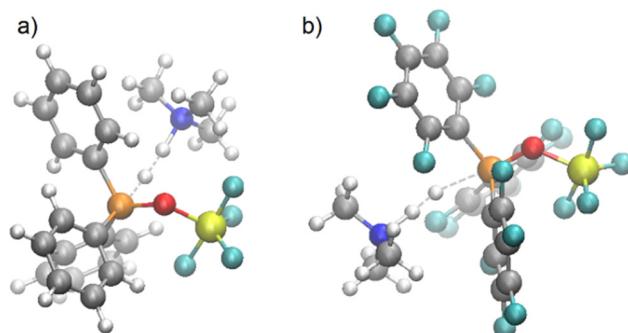


Fig. 2 Computed (PBEh-3c) TS for the formation of $7\text{g}^{\circ\text{N}}$ (left) and $7\text{i}^{\circ\text{N}}$ (right).

In these processes the approximation of H_2 (and the Lewis base 6) occurred exclusively *syn* with respect to the silicate side-arm (Fig. 2), thus making profit of the vicarious Coulombic stabilization with the newly generated pnictogenium centre (Pn^+). The beneficial effect of this Coulombic interaction is demonstrated by the fact that the analogous control reaction between triphenylphosphine oxide and trimethylamine did not produce the desired activation of the dihydrogen molecule, but 1,2-addition along the $\text{P}=\text{O}$ bond ($\text{Ph}_3\text{P}(\text{H})-\text{OH}$).

In order to make the phosphonium centre more electrophilic, pentafluorophenyl (instead of phenyl) substituents were placed at P in zwitterions 3°i,j (Scheme 2). As expected, the effect of increased electrophilicity causes the LUMO energy to decrease from $-0.657/-0.834 \text{ eV}$ in 3°g,h to $-1.661/-1.894 \text{ eV}$ in 3°i,j , respectively, favouring the approximation of the hydridic H atom to the sigma hole of the phosphonium cation, which corresponds to the LUMO of mainly $\sigma^*(\text{P}-\text{O})$ character

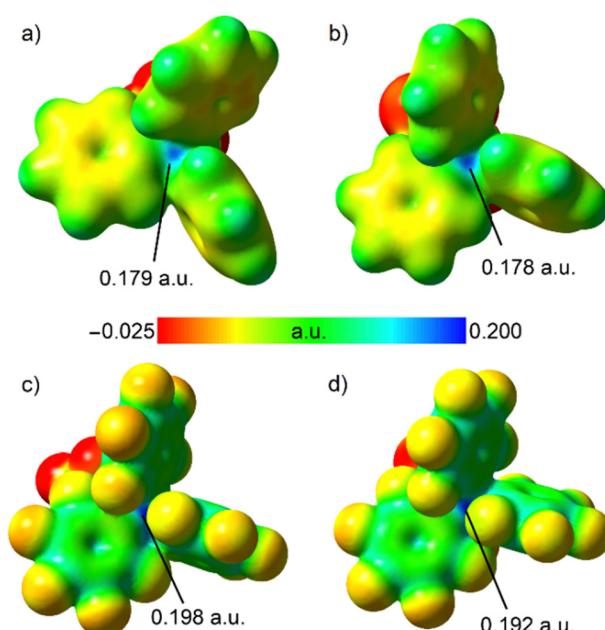


Fig. 3 Computed (B3LYP-D4/def2-TZVP//PBEh-3c) electrostatic potential plot mapped onto an electron density isosurface (0.01 a.u.) for (a) 3°g , (b) 3°h , (c) 3°i and (d) 3°j .

(Fig. S8, ESI†). This is also reflected in the higher magnitude of the sigma-hole in $3^0_{i,j}$ compared to $3^0_{g,h}$ (Fig. 3). However, this does not entail a decrease in the energy of the transition state with respect to the *P*-phenyl substituted homologues (Fig. 1), most likely because the sigma hole (*anti*) approximation (Fig. 3b) precludes the vicarious stabilization by Coulombic interaction between the silicate side arm and the newly originated cationic centre at the pnictogen atom of the Lewis base. This demonstrates that the stabilization caused by the Coulombic interaction of the silicate side-arm in the *syn* approximation to $3^0_{g,h}$ (Fig. 3a) is more effective than a Lewis acidic centre with a considerably lower LUMO in $3^0_{i,j}$. For the latter, no *syn* approximation pathway was found. Localization of the transition state for the formation of $7i,j^P$ was not possible probably due to the larger size of the P atom in the Lewis base **6** and the scarce space left by the F-substituents to access the phosphonium acidic centre.

Conclusions

A series of zwitterionic species $X_3P-E-SiY_4$ (**3**) with group 14 (CH_2 , SiH_2), 15 (NH , PH) or 16 (O or S) E-bridges were computationally studied. Only those having donor substituents at P and acceptor substituents at Si turned out to be stable. The E-Si linkage in **3** could be better described as a dative bond ($E:\rightarrow Si$) on the basis of either the observed elongated bonds, significant charge transfer, predominant heterolytic over homolytic bond cleavage, or AIM-related criteria. In the presence of an external Lewis base Me_3Pn ($Pn = N, P$), 1,3-dipolar compounds **3** display FLP reactivity in the activation of H_2 which is facilitated by vicarious stabilization in the transition state due to the Coulombic interaction of the pendant silicate side-arm with the newly generated pnictogenium centre (Pn^+) in the resulting ion pair **7**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors acknowledge Servicio de Cálculo Científico (SCC – University of Murcia) for the computational resources used. A. R. P. is indebted to an Erasmus Placement opportunity (3 months) and the University of Bonn Fellowship Programme (3 months) for financing short stays in Bonn. A. F. thanks MICIU/AEI of Spain (PID2020-115637GB-I00, FEDER funds) for financial support and the Alexander von Humboldt foundation for the J. C. Mutis award.

Notes and references

1 (a) G. Linti and H. Schnöckel, *Coord. Chem. Rev.*, 2000, **206**, 207, 285; (b) B. D. Ellis and C. L. B. Macdonald, *Coord. Chem. Rev.*, 2007, **251**, 936; (c) Y. Xiong, S. Yao and M. Driess, *Angew. Chem., Int. Ed.*, 2013, **52**, 4302.

- 2 S. Schulz, *Coord. Chem. Rev.*, 2015, **297–298**, 49.
- 3 D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018.
- 4 G. C. Welch, R. R. San Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124.
- 5 (a) G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880; (b) P. Spies, G. Erker, K. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072.
- 6 (a) L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan and J. Paradies, *Angew. Chem., Int. Ed.*, 2012, **51**, 10164; (b) L. Greb, C. G. Daniliuc, K. Bergander and J. Paradies, *Angew. Chem., Int. Ed.*, 2013, **52**, 5876; (c) J. Paradies, *Synlett*, 2013, 777; (d) J. Paradies, *Angew. Chem., Int. Ed.*, 2014, **53**, 3552; (e) J. S. J. McCahill, G. C. Welch and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 4968.
- 7 (a) K. Chernichenko, A. Madarasz, I. Papai, M. Nieger, M. Leskela and T. Repo, *Nat. Chem.*, 2013, **5**, 718; (b) M. A. Dureen and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 8396; (c) C. Jiang, O. Blacque and H. Berke, *Organometallics*, 2010, **29**, 125; (d) M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 659.
- 8 (a) C. M. Mamming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2009, **48**, 6643; (b) A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660; (c) A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem., Int. Ed.*, 2009, **48**, 9839.
- 9 (a) E. Otten, R. C. Neu and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 9918; (b) R. C. Neu, E. Otten and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2009, **48**, 9709.
- 10 (a) T. Mahdi and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2013, **52**, 12418; (b) Y. Wang, Z. Liu, W. Guo, C. Zhang and X. Zhang, *Macromolecules*, 2023, **56**, 4901.
- 11 D. W. Stephan, *Science*, 2016, **354**, aaf7229.
- 12 (a) Y. Guo and S. Li, *Inorg. Chem.*, 2008, **47**, 6212; (b) M. Shi, L. H. Chen and C. Q. Li, *J. Am. Chem. Soc.*, 2005, **127**, 3790.
- 13 (a) T. A. Rokob, A. Hamza and I. Pápai, *J. Am. Chem. Soc.*, 2009, **131**(30), 10701; (b) M. G. Gardiner and C. L. Raston, *Coord. Chem. Rev.*, 1997, **166**, 1; (c) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46; (d) S. J. Geier, M. A. Dureen, E. Y. Ouyang and D. W. Stephan, *Chem. – Eur. J.*, 2010, **16**, 988.
- 14 (a) V. Sumerin, F. Schulz, M. Nieger, M. Leskel, T. Repo and B. Rieger, *Angew. Chem., Int. Ed.*, 2008, **47**, 6001; (b) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskel, T. Repo, P. Pykk and B. Rieger, *J. Am. Chem. Soc.*, 2008, **130**, 14117; (c) S. J. Geier, A. L. Gille, T. M. Gilbert and D. W. Stephan, *Inorg. Chem.*, 2009, **48**, 10466; (d) G. Ers, H. Mehdi, I. Papai, T. A. Rokob, P. Kiraly, G. Tarkanyi and T. Soos, *Angew. Chem., Int. Ed.*, 2010, **49**, 6559. For imines, see: (e) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050. For aromatic N-heterocycles, see: (f) S. J. Geier and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 3476; (g) S. J. Geier, A. L. Gille, T. M. Gilbert and D. W. Stephan, *Inorg. Chem.*, 2009, **48**, 10466; (h) S. J. Geier, P. A. Chase and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 4884.



15 M. A. Dureen, C. C. Brown and D. W. Stephan, *Organometallics*, 2010, **29**, 6594.

16 (a) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem., Int. Ed.*, 2008, **47**, 7428; (b) P. A. Chase and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2008, **47**, 7433; M. Alcarazo, C. Gomez, S. Holle and R. Goddard, *Angew. Chem., Int. Ed.*, 2010, **49**, 5788.

17 W. Uhl, P. Wegener, M. Layh, A. Hepp and E. Würthwein, *Z. Naturforsch. B*, 2016, **71**, 1043.

18 T. J. Herrington, B. J. Ward, L. R. Doyle, J. McDermott, A. J. P. White, P. A. Hunt and A. E. Ashley, *Chem. Commun.*, 2014, **50**, 12753.

19 A. Schafer, M. Reissmann, A. Schafer, M. Schmidtmann and T. Müller, *Chem. – Eur. J.*, 2014, **20**, 9381.

20 N. Burford and P. J. Ragogna, *J. Chem. Soc., Dalton Trans.*, 2002, 4307.

21 C. B. Caputo, L. J. Hounjet, R. Dobrovetsky and D. W. Stephan, *Science*, 2013, **341**, 1374.

22 L. E. Longobardi, C. A. Russell, M. Green, N. S. Townsend, K. Wang, A. J. Holmes, S. B. Duckett, J. E. McGrady and D. W. Stephan, *J. Am. Chem. Soc.*, 2014, **136**, 13453.

23 A. Bismuto, G. S. Nichol, F. Duarte, M. J. Cowley and S. P. Thomas, *Angew. Chem., Int. Ed.*, 2020, **59**, 12731.

24 R. Kunzmann, Y. Omatsu, G. Schnakenburg, A. Espinosa Ferao, T. Yanagisawa, N. Tokitoh and R. Streubel, *Chem. Commun.*, 2020, **56**, 3899.

25 K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083.

26 (a) R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, Oxford, 1990; (b) R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893; (c) C. F. Matta and R. J. Boyd, in *The Quantum Theory of Atoms in Molecules*, ed. C. F. Matta and R. J. Boyd, Wiley-VCH, New York, 2007, p. 1.

27 (a) M. W. Stanford, J. I. Schweizer, M. Menche, G. S. Nichol, M. C. Holthausen and M. J. Cowley, *Angew. Chem., Int. Ed.*, 2019, **58**, 1329; (b) V. Nesterov, R. Baierl, F. Hanusch, A. Espinosa Ferao and S. Inoue, *J. Am. Chem. Soc.*, 2019, **141**, 14576; (c) A. Espinosa Ferao, A. García Alcaraz, S. Zaragoza Noguera and R. Streubel, *Inorg. Chem.*, 2020, **59**, 12829; (d) D. Biskup, G. Schnakenburg, R. T. Boeré, A. Espinosa Ferao and R. K. Streubel, *Nat. Commun.*, 2023, **14**, 6456; (e) D. Biskup, G. Schnakenburg, A. Espinosa Ferao and R. Streubel, *Dalton Trans.*, 2024, **53**, 2517.

