

COMMUNICATION



Cite this: *Chem. Commun.*, 2018, **54**, 5716

Received 17th February 2018,
Accepted 10th May 2018

DOI: 10.1039/c8cc01391h

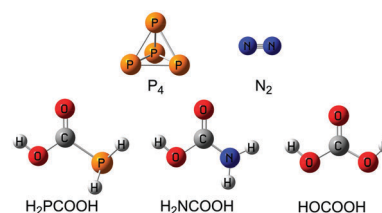
rsc.li/chemcomm

First identification of unstable phosphino formic acid (H_2PCOOH)[†]

Cheng Zhu,[†] Robert Frigge,^{ab} Andrew M. Turner,^{ab} Ralf I. Kaiser,[†] Bing-Jian Sun,[†] Si-Ying Chen^c and Agnes H. H. Chang^{*c}

The hitherto elusive phosphino formic acid molecule (H_2PCOOH) was detected for the first time in the gas phase. Theoretical calculations revealed an unexpected kinetic stability of H_2PCOOH compared to the isovalent carbamic acid (H_2NCOOH) although the replacement of a single nitrogen atom by phosphorus decreases the bond order from a partial double ($-\text{C}=\text{N}-$) to a single ($-\text{C}-\text{P}-$) bond. This work provides a fundamental framework to explore the synthesis and stability of derivatives of carbonic acid (H_2CO_3), in which one or both hydroxyl groups (OH) are replaced by hydride moieties involving third row atoms.

For the last century, Langmuir's concept of isovalency in which 'two molecular entities with the same number of valence electrons have similar chemistries'¹ has been instrumental in developing modern concepts of chemical bonding² and in understanding basic principles of molecular structure and reactivity of isovalent systems.^{2,3} Specific attention has been devoted to contrasting the nitrogen chemistry with the analogous chemistry of phosphorus.⁴ Located in main group 15, nitrogen and phosphorus have both five valence electrons and hence are isovalent. Nevertheless, their chemical bonding can be quite distinct as evident from the structures of the diatomic nitrogen molecule (N_2) compared to the tetra phosphorus molecule (P_4) carrying nitrogen–nitrogen triple and phosphorus–phosphorus single bonds, respectively (Scheme 1). Likewise, fully saturated hydrides of nitrogen are limited to hydrazine (N_2H_4) and triazene (N_3H_5),⁵ whereas phosphanes with up to eight phosphorus atoms (octaphosphane; P_8H_{10}) have been prepared recently.⁶ The divergent chemical stability of nitrogen *versus* phosphorus compounds is illustrated in particular when comparing carbamic acid (H_2NCOOH) with



Scheme 1 Structures of tetraphosphorus (P_4 , T_d), dinitrogen (N_2 , $D_{\infty h}$), phosphino formic acid (H_2PCOOH , C_1), carbamic acid (H_2NCOOH , C_1), and carbonic acid (HOCOOH , C_{2v}).

the isovalent phosphorus analogue phosphino formic acid (H_2PCOOH) (Scheme 1). Carbamic acid was successfully synthesized in low temperature matrices containing ammonia (NH_3) and carbon dioxide (CO_2) by annealing the ices from 10 K to 80 K. The overall pathway involved an initial formation of an ammonia–carbon dioxide van der Waals complex followed by the reaction of the Lewis base (NH_3) with the Lewis acid (CO_2) and a successive proton transfer from the nitrogen to the oxygen atom.⁷

Despite extensive interest in the isovalent phosphino formic acid (H_2PCOOH) from the preparative inorganic and also physical chemical viewpoint as isovalent systems of the nitrogen analogous carbamic acid (H_2NCOOH) molecule, free phosphino formic acid (H_2PCOOH) has not been isolated yet although an inherent barrier of 292 kJ mol^{-1} should inhibit the decomposition to carbon dioxide (CO_2) and phosphine (PH_3).^{8,9} Diemert *et al.* stabilized phosphino formic acid (H_2PCOOH) within the coordination sphere of transition metal complexes: $(\text{CO})_5\text{M}(\text{H}_2\text{PCOOH})$ and $[(\text{CO})_5\text{M}(\text{H}_2\text{PCOOH})]_2$ ($\text{M} = \text{Cr}, \text{W}$).¹⁰ Derivatives, in which the hydrogen atoms of the phosphino moiety were replaced by organic groups such as phenyl (C_6H_5), could be stabilized in chromium and tungsten based transition metal complexes as well.¹¹ The stability of free derivatives of phosphino formic acid–carbonic ester phosphides ($\text{RHPCOOR}'$) with R and R' being alkyl or aromatic groups¹² and sodium diphenylphosphinoformate ($(\text{C}_6\text{H}_5)_2\text{PCOONa}$)¹³ – was attributed to the lack of acetic hydrogen atoms at the carboxyl moiety, which likely hydrolyze the phosphino formic acid and their derivatives in solution.

^a Department of Chemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA

^b W.M. Keck Laboratory in Astrochemistry, University of Hawaii at Mānoa, Honolulu, HI 96822, USA. E-mail: ralfk@hawaii.edu

^c Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan. E-mail: hhchang@gms.ndhu.edu.tw

[†] Electronic supplementary information (ESI) available: Experimental and theoretical details, Fig. S1 and Tables S1–S5. See DOI: 10.1039/c8cc01391h

[‡] These authors contributed equally.

Here, we report on the very first experimental detection of the hitherto elusive phosphino formic acid (H_2PCOOH) molecule in the gas phase. Our experiments are merged with *ab initio* electronic structure calculations to verify the stability of gas phase phosphino formic acid (H_2PCOOH). The experiments were conducted in an ultrahigh vacuum (UHV) surface science machine operated at a base pressure of a few 10^{-11} Torr.^{6,14–18} Binary ice mixtures of phosphine (PH_3) and carbon dioxide (CO_2), phosphine (PH_3) and [^{13}C]-carbon dioxide ($^{13}\text{CO}_2$), as well as phosphine (PH_3) and [^{18}O]-carbon dioxide (C^{18}O_2) were prepared in separate experiments with thicknesses of 830 ± 50 nm at 5.5 ± 0.2 K. The non-equilibrium chemistry and bond-cleavage processes were stimulated by exposing these ices to energetic electrons for one hour at an average dose of 2.8 ± 0.6 eV per molecule. After the irradiation, the ices were heated at a rate of 1 K min^{-1} to 320 K (temperature programmed desorption; TPD). During the TPD phase, the subliming neutral molecules were first ionized *via* tunable vacuum ultraviolet (VUV) photoionization (PI), mass resolved in a reflectron time-of-flight mass spectrometer (PI-ReTOF-MS), and eventually identified by their arrival times through a multichannel plate *via* their mass-to-charge ratios. By systematically tuning the photoionization energies from 10.86 eV to 9.60 eV, we selectively ionize specific structural isomers based on their ionization energies (IE) as obtained from the electronic structure calculations and determine which isomer(s) is(are) produced thus ultimately identifying phosphino formic acid (H_2PCOOH).

The mass spectra of the subliming molecules released from the irradiated phosphine (PH_3)-carbon dioxide (CO_2) ices are revealed in Fig. 1 as a function of temperature recorded at photon energies of 10.86 and 9.60 eV. In addition to the precursor phosphine (PH_3) ($m/z = 34$; IE = 9.87 eV), phosphanes like diphosphine (P_2H_4) ($m/z = 66$; IE = 8.8 eV), and hydroxyphosphine (H_2POH) ($m/z = 50$; IE = 9.22–9.23 eV), ion signal was also observed at $m/z = 78$.^{19,20} Considering the molecular weight of phosphine (34 amu) and carbon dioxide (44 amu), the molecular weight of 78 amu is consistent with the formation of a molecule of the formula PH_3CO_2 . The corresponding TPD profile at $m/z = 78$ exhibits an onset of close to 180 K and a maximum of the ion counts at 192 K (Fig. 2(a)).

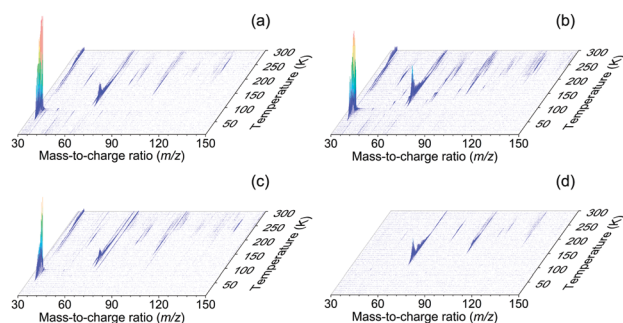


Fig. 1 Mass-to-charge dependent temperature programmed desorption (TPD) profiles obtained after photoionizing the desorbing molecules of irradiated (a) phosphine (PH_3) and carbon dioxide (CO_2) ice with 10.86 eV photons, (b) phosphine (PH_3) and [^{13}C]-carbon dioxide ($^{13}\text{CO}_2$) ice with 10.86 eV photons, (c) phosphine (PH_3) and [^{18}O]-carbon dioxide (C^{18}O_2) ice with 10.86 eV photons, and (d) phosphine (PH_3) and carbon dioxide (CO_2) ice with 9.60 eV photons.

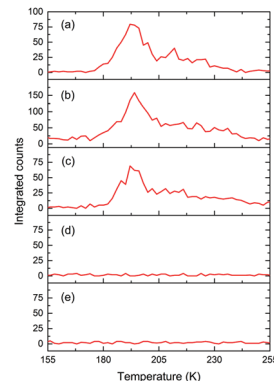


Fig. 2 Temperature programmed desorption (TPD) profiles recorded *via* PI-ReTOF-MS for (a) $m/z = 78$ ($\text{PH}_3\text{-CO}_2$ system, PI = 10.86 eV), (b) $m/z = 79$ ($\text{PH}_3\text{-}^{13}\text{CO}_2$ system, PI = 10.86 eV), (c) $m/z = 82$ ($\text{PH}_3\text{-C}^{18}\text{O}_2$ system, PI = 10.86 eV), (d) $m/z = 78$ (blank $\text{PH}_3\text{-CO}_2$, PI = 10.86 eV), and (e) $m/z = 78$ ($\text{PH}_3\text{-CO}_2$ system, PI = 9.60 eV).

To confirm that the species observed *via* $m/z = 78$ are linked to a molecule with the formula PH_3CO_2 , two additional isotopic experiments were carried out by replacing carbon dioxide with [^{13}C] and [^{18}O] carbon dioxide in separate experiments. Here, the TPD profiles recorded at $m/z = 79$ and 82 (Fig. 2(b) and (c)) – shifted by 1 amu and 4 amu in the [^{13}C] and [^{18}O] carbon dioxide experiments, respectively. These findings reveal that the product molecules have one carbon atom and two oxygen atoms, a finding which is consistent with the molecular formula PH_3CO_2 . It is worth mentioning that we also conducted a control experiment, that is, an experiment under identical conditions with phosphine (PH_3) and carbon dioxide (CO_2), but without exposing the ice to energetic electrons. In this control study, no signal was observed at $m/z = 78$ (Fig. 2(d)), which demonstrates that the PH_3CO_2 product is the result of the radiolysis of the ices, but not an artifact from the photoionization laser and/or gas phase ion–molecule reactions of the precursors.

Having established the formation of a new molecule with the molecular formula PH_3CO_2 (78 amu) along with its ^{13}C and ^{18}O substituted counterparts, we are shifting our attention now to the identification of the PH_3CO_2 product isomer(s). This objective is achieved by selectively photoionizing specific structural isomers based on their ionization energies. Our electronic structure calculations expose the existence of ten closed shell local minima, whose adiabatic ionization energies and relative energies obtained at the CCSD(T)/CBS level with B3LYP/cc-pVTZ zero-point vibrational energy corrections are presented in Fig. 3. These species can be arranged in three groups: the thermodynamically most stable phosphino formic acid isomers (H_2PCOOH ; **1a–1b**) [IE = 9.74–9.75 eV; $\Delta E = 0.00\text{--}0.20$ eV], its enol tautomers (HPC(OH)_2 ; **2a–2d**) [IE = 8.23–8.42 eV; $\Delta E = 0.85\text{--}1.10$ eV], and the formic phosphinous anhydride species (HCOOPH_2 ; **3a–3d**) [IE = 9.34–9.50 eV; $\Delta E = 0.00\text{--}0.16$ eV]; the ionization energies of these three groups are well separated by about >0.24 eV (group I and III) and 1.1 eV (group II and III). At a photon energy of 10.86 eV, all isomers can be ionized (Fig. 2(a)). A photoionization energy of 9.60 eV allows only the ionization of isomers belonging to group II and III; considering the ionization energy of 9.74–9.75 eV, phosphino formic acid (H_2PCOOH ; **1a–1b**) cannot be ionized by 9.60 eV photons.

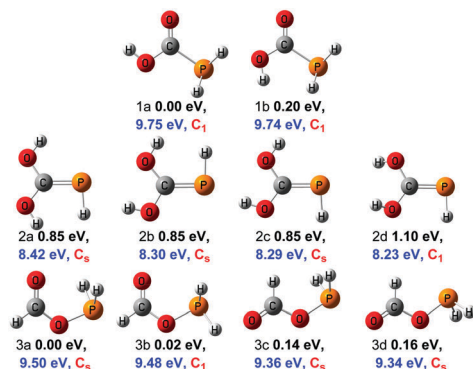
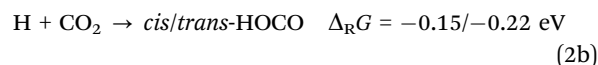
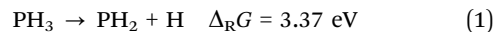


Fig. 3 Molecular structures of H₂PCOOH isomers along with relative energies in eV (black), adiabatic ionization energies in eV (blue), and point groups (red).

The TPD profile of the 9.60 eV experiments is depicted in Fig. 2(e) and does not show any ion counts at $m/z = 78$. Therefore, we can conclude that isomers belonging to group II and III are not ionized at 9.60 eV, and that signal at $m/z = 78$ in the 10.86 eV experiment is linked solely to the previously elusive phosphino formic acid (H₂PCOOH), but not to HPC(OH)₂ or HCOOPH₂.

It is interesting to rationalize the exclusive synthesis of the phosphino formic acid isomer (H₂PCOOH). Upon interaction of energetic electrons, the phosphine molecule (PH₃) can undergo a unimolecular decomposition to form predominantly the phosphino (PH₂) radical plus suprathreshold atomic hydrogen (H) (reaction (1)).^{6,21} The suprathreshold hydrogen atom can add to the carbon or oxygen atom of the carbon dioxide (CO₂) molecule.^{22–24} These pathways lead to the formyloxyl (HCOO) and *cis/trans*-hydroxycarbonyl (HOCO) isomers, respectively, with the latter being more stable by 0.51/0.59 eV (reaction (2)). Recent experiments in carbon dioxide–methane²³ and carbon dioxide–water²⁴ ices confirm a preferential hydrogen atom addition to the oxygen atom of carbon dioxide, and solely the *cis/trans*-hydroxycarbonyl (HOCO) radical was detected spectroscopically. In the low temperature carbon dioxide–phosphine ices, the *cis/trans*-hydroxycarbonyl (HOCO) radical could recombine without barrier with the phosphino (PH₂) radical forming the experimentally detected phosphino formic acid isomer (H₂PCOOH) (reaction (3)) if both radicals hold a favorable recombination geometry. Note that any synthesis of the non-detected formic phosphinous anhydride species (HCOOPH₂) requires the formation of the formyloxyl (HCOO) radical intermediate, which then recombines with the phosphino (PH₂) radical. However, the aforementioned discussion excluded the formation of the formyloxyl (HCOO) radical, which in turn eliminates the synthesis of the formic phosphinous anhydride species (HCOOPH₂). Finally, the failed detection of the enol tautomer (HPC(OH)₂) deserves some attention. Previous studies on the acetaldehyde (CH₃CHO)–vinyl alcohol (H₂CCH(OH)) keto–enol isomer pair in electron irradiated carbon monoxide–methane ices suggests that the enol tautomer is formed *via* atomic hydrogen shift from the carbon to the oxygen atom in acetaldehyde upon radiolysis of the latter.¹⁵ The non-detection of the enol tautomer (HPC(OH)₂) in the present experiments proposes that the keto–enol tautomerization is absent possibly due to yields of the phosphino

formic acid isomer (H₂PCOOH) being too low to form detectable fractions of the enol tautomer of (HPC(OH)₂).



Having established the synthesis of the hitherto elusive phosphino formic acid molecule (H₂PCOOH) along with its ¹³C and ¹⁸O substituted counterparts, we are turning our attention now to the stability of this compound. Our electronic-structure calculations predict that phosphino formic acid (**1a**) can undergo unimolecular decomposition forming phosphine (PH₃) and carbon dioxide (CO₂) *via* a weakly bound van der Waals complex in an overall exoergic reaction ($\Delta_{\text{R}}G = -0.53 \text{ eV}$; $\Delta_{\text{R}}G = -51 \text{ kJ mol}^{-1}$) after isomerizing to **1b** *via* a barrier of 0.45 eV (43 kJ mol⁻¹) and passing a transition state located 1.94 eV (187 kJ mol⁻¹) above **1b** (Fig. 4(a)). These data demonstrate that although phosphino formic acid (H₂PCOOH) is less stable than the phosphine (PH₃) and carbon dioxide (CO₂) reactants, phosphino formic acid (H₂PCOOH) is kinetically stable due to the significant barrier separating the reactants and products. The features of the underlying potential energy surface toward decomposition (Fig. 4(a)) are alike to those of the surfaces of carbamic acid (H₂NCOOH)²⁵ and carbonic acid (HOCO₂), which have been isolated previously.^{26–30} The calculated phosphorus–carbon bond distance of 1.87–1.89 Å (**1a–1b**) (Table S2, ESI†) correlates with the existence of a phosphorus–carbon single bond (1.84 Å), but not with a double bond (1.71 Å), which is shorter by about 0.03–0.05 Å. On the other hand, the nitrogen–carbon bond length in the isovalent carbamic acid (H₂NCOOH) was determined to be 1.36–1.38 Å (Table S3, ESI†), *i.e.* between a typical nitrogen–carbon single (1.47 Å) and double bond (1.29 Å) due to resonance and hence partial double bond character of the –C=N– moiety. Although the replacement of the nitrogen atom by phosphorus increases the bond length to carbon from a partial double (–C=N–) to a single (–C–P–) bond, the barrier to a gas phase decomposition increases from 149 kJ mol⁻¹ to 187 kJ mol⁻¹ from carbamic acid (H₂NCOOH) to phosphino formic acid (H₂PCOOH) (Fig. 4). This unexpected enhancement of stability can be rationalized in terms of distinct partial charges distributions. Here, the nitrogen atom in carbamic acid (H₂NCOOH) holds a charge of –0.264 *e* and can easily capture the adjacent acidic proton on oxygen to pass the transition state (Fig. 4b), while the positive charges on the phosphorous atom (0.003 *e*) in phosphino formic acid (H₂PCOOH) may hinder the approach of the proton and lead to a higher barrier for the decarboxylation of phosphino formic acid (H₂PCOOH). Consequently, the replacement of single nitrogen atom by lower electronegative phosphorus enhances the stability of the molecule carrying the carbon–phosphorus bond (phosphino formic acid) compared to the carbon–nitrogen moiety (carbamic acid). Finally, considering the average velocity of 240 ms⁻¹ of the phosphino

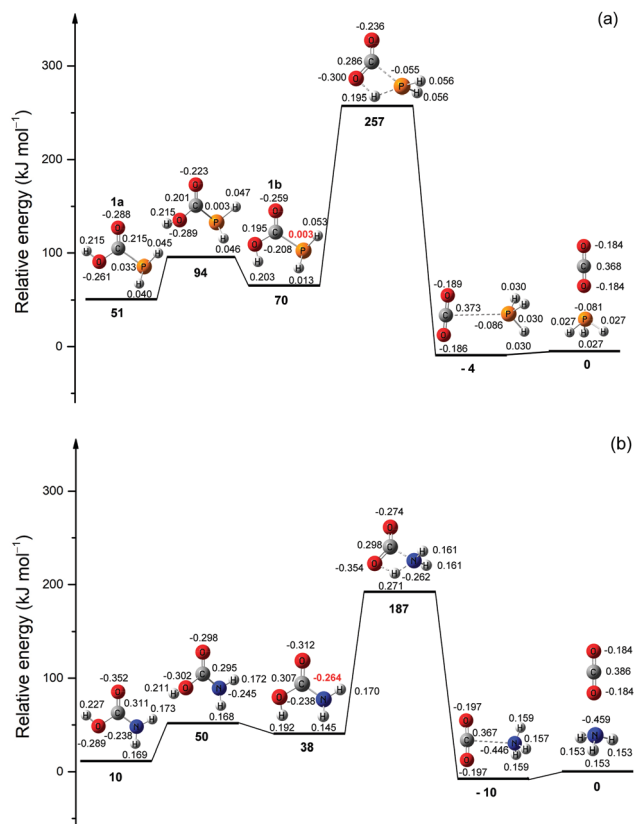


Fig. 4 Molecular decomposition pathway of phosphino formic acid (H₂PCOOH) (a) and of the isovalent formic acid (H₂NCOOH) (b). Energies were obtained at the CCSD(T)/CBS level with B3LYP/cc-pVTZ zero-point vibrational energy corrections. Partial charges (e) of the species related to the decomposition of phosphino formic acid (H₂PCOOH) and carbamic acid (H₂NCOOH) are also indicated.

formic acid (H₂PCOOH) subliming at 190 K and the distance between the ice and the photoionization laser of 2 mm, the lifetime of the subliming phosphino formic acid (H₂PCOOH) has to be at least 6 μs to survive the time between the sublimation and the photoionization event.

In conclusion, exploiting single photon vacuum ultraviolet photoionization reflectron time of flight mass spectrometry (PI-ReTOF-MS), the present study provides compelling evidence on the exclusive synthesis of the phosphino formic acid (H₂PCOOH) molecule – the hitherto elusive isovalent species of carbamic acid (H₂NCOOH). Utilizing isotopically labelled reactants, this approach allowed the determination of the molecular formula of the newly formed molecule based on the isotopic shifts and the fragment-free detection of the neutral parent molecule upon photoionization. The non-equilibrium nature of the reaction pathway *via* a phosphorus–hydrogen bond rupture in phosphine followed by addition of the suprathreshold hydrogen atom to the oxygen atom of carbon dioxide and recombination of the *cis/trans* hydroxy carbonyl (HOCO) with phosphino (PH₂) leads exclusively to a directed synthesis of the free phosphino formic acid (H₂PCOOH) molecule.

This work was supported by NASA under Grant NNX16AD27G to The University of Hawaii. The Hawaii group would also like to thank the W. M. Keck Foundation to fund the surface science machine. AHHC, BJS, and SYC thank the National Center for High-performance Computer in Taiwan for providing the computer resources for the calculations.

Conflicts of interest

There are no conflicts to declare.

References

- 1 I. Langmuir, *J. Am. Chem. Soc.*, 1919, **41**, 868–934.
- 2 D. Bellus, *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations. Guidebook*, Georg Thieme Verlag, Stuttgart and New York, 2000.
- 3 D. S. N. Parker, A. M. Mebel and R. I. Kaiser, *Chem. Soc. Rev.*, 2014, **43**, 2701–2713.
- 4 L. Rossi, *Science of Synthesis: Houben-Weyl Methods of Molecular Transformations*, Georg Thieme Verlag, Stuttgart and New York, 2005.
- 5 M. Förstel, P. Maksyutenko, B. M. Jones, B. J. Sun, S. H. Chen, A. Chang and R. I. Kaiser, *ChemPhysChem*, 2015, **16**, 3139–3142.
- 6 A. M. Turner, M. J. Abplanalp, S. Y. Chen, Y. T. Chen, A. H. Chang and R. I. Kaiser, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27281–27291.
- 7 J. B. Bossa, P. Theule, F. Duvernay, F. Borget and T. Chiavassa, *Astron. Astrophys.*, 2008, **492**, 719–724.
- 8 K. Diemert, T. Hahn, W. Kuchen and P. Tommes, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1993, **83**, 65–76.
- 9 Y. Fu, T. Q. Yu, Y. M. Wang, L. Liu and Q. X. Guo, *Chin. J. Chem.*, 2006, **24**, 299–306.
- 10 K. Diemert, T. Hahn, W. Kuchen, D. Mootz, W. Poll and P. Tommes, *Z. Naturforsch., B: Chem. Sci.*, 1995, **50**, 209–212.
- 11 K. Diemert, T. Hahn and W. Kuchen, *J. Organomet. Chem.*, 1994, **476**, 173–181.
- 12 R. Thamm and E. Fluck, *Z. Naturforsch., B: Chem. Sci.*, 1981, **36**, 910–916.
- 13 K. Diemert, T. Hahn and W. Kuchen, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1991, **60**, 287–294.
- 14 B. M. Jones and R. I. Kaiser, *J. Phys. Chem. Lett.*, 2013, **4**, 1965–1971.
- 15 M. J. Abplanalp, S. Gozem, A. I. Krylov, C. N. Shingledecker, E. Herbst and R. I. Kaiser, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**, 7727–7732.
- 16 M. J. Abplanalp and R. I. Kaiser, *Astrophys. J.*, 2017, **836**, 195.
- 17 A. Bergantini, P. Maksyutenko and R. I. Kaiser, *Astrophys. J.*, 2017, **841**, 96.
- 18 S. Góbi, A. Bergantini, A. M. Turner and R. I. Kaiser, *J. Phys. Chem. A*, 2017, **121**, 3879–3890.
- 19 S. Elbel, H. Tom Dieck, G. Becker and W. Ensslin, *Inorg. Chem.*, 1976, **15**, 1235–1238.
- 20 J. Berkowitz, L. A. Curtiss, S. T. Gibson, J. P. Greene, G. L. Hillhouse and J. A. Pople, *J. Chem. Phys.*, 1986, **84**, 375–384.
- 21 A. M. Turner, M. J. Abplanalp and R. I. Kaiser, *Astrophys. J.*, 2016, **819**, 97.
- 22 X. Song, J. Li, H. Hou and B. Wang, *J. Chem. Phys.*, 2006, **125**, 094301.
- 23 C. J. Bennett and R. I. Kaiser, *Astrophys. J.*, 2007, **660**, 1289–1295.
- 24 W. Zheng and R. I. Kaiser, *Chem. Phys. Lett.*, 2007, **450**, 55–60.
- 25 B. Ramachandran, A. M. Halpern and E. D. Glendening, *J. Phys. Chem. A*, 1998, **102**, 3934–3941.
- 26 T. Loerting, C. Tautermann, R. T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer and K. R. Liedl, *Angew. Chem., Int. Ed.*, 2000, **39**, 891–894.
- 27 R. Ludwig and A. Kornath, *Angew. Chem., Int. Ed.*, 2000, **39**, 1421–1423.
- 28 I. Kohl, K. Winkel, M. Bauer, K. R. Liedl, T. Loerting and E. Mayer, *Angew. Chem., Int. Ed.*, 2009, **48**, 2690–2694.
- 29 J. Bernard, M. Seidl, I. Kohl, K. R. Liedl, E. Mayer, Ó. Gálvez, H. Grothe and T. Loerting, *Angew. Chem., Int. Ed.*, 2011, **50**, 1939–1943.
- 30 G. Bucher and W. Sander, *Science*, 2014, **346**, 544–545.