

Cite this: *Dalton Trans.*, 2018, 47, 10404Received 22nd April 2018,
Accepted 10th May 2018

DOI: 10.1039/c8dt01607k

rsc.li/dalton

Reactivity studies of an imine-functionalised phosphalkene; unusual electrostatic and supramolecular stabilisation of a $\sigma^2\lambda^3$ -phosphorus motif *via* hydrogen bonding†

Daniel Morales Salazar, * Arvind Kumar Gupta and Andreas Orthaber *

A P=C heavy-alkene analogue that is unreactive towards the addition of strong acids on its double-bond is presented; instead, a strategically located imine nitrogen on the periphery forms protonated adducts displaying hydrogen bonding interactions. These materials are significantly more stable than the parent species, demonstrating an unprecedented approach towards the stabilisation of a multiple-bonded heavy main group fragment, in this case, a phosphalkene. An HCl adduct self-assembles with H₂O into a dimeric network displaying a discrete quadrilateral hydrogen-bonded arrangement.

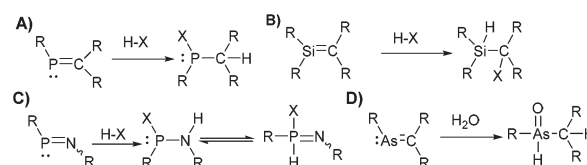
The study of molecular systems incorporating multiple-bonded heavy p-block elements has challenged chemists for decades. The high reactivity exhibited by heavy multiple bonds (E=C, E=E, E=C; E: third to sixth-row element from group 13–16) renders these species increasingly interesting at the fundamental and applied level.¹

Early on, breaking of the double-bond-rule with reports on the synthesis of stable species containing P=C, P=N, Si=C, Si=Si, As=C, and other multiple bonds, were accompanied by studies with small molecules (*e.g.* HCl, H₂O, O₂, Br₂, MeOH, MeI) to confirm the sensitivity and reactivity of the multiple bonds.² For example, the addition of HX (X: Hal⁻, Nuc⁻) to P=C compounds (Scheme 1) is an archetypical example showcasing their increased reactivity. For other species, similar pathways (hydrolysis, oxidation, addition) lead to decomposition products in most reactions with small molecules.³ In sporadic cases, a multiple-bonded fragment is kept upon reaction with small molecules *via* rearrangement,⁴ substitution/addition reactions,⁵ or due to increased stability of the unusual bonding by other means (*e.g.* aromaticity in phosphinine).⁶ For example, dicoordinate phosphorus species display

increased stability to small molecules in some examples, which is expressed in the ability to avoid protonation or alkylation.^{5,7}

The initially suggested instability of these species led to a naturally apparent dichotomy in which efforts have focused on either the stabilisation and isolation of the exotic motif as final materials⁸ (*e.g.* polymer chemistry and materials science), or their utilisation as highly-reactive synthons⁹ that can act as intermediates in driving unique chemical transformations (*e.g.* small-molecule activation,¹⁰ unique reactivity,¹¹ catalysis,¹² polymer-precursors,¹³ high-spin materials¹⁴). Regarding the former direction, finding ways to stabilise systems featuring multiple bonding to heavier elements are among the crucial goals in the modern main group community; increased stability to small molecules should broaden the scope of applying these fascinating materials in catalysis and optoelectronic materials.

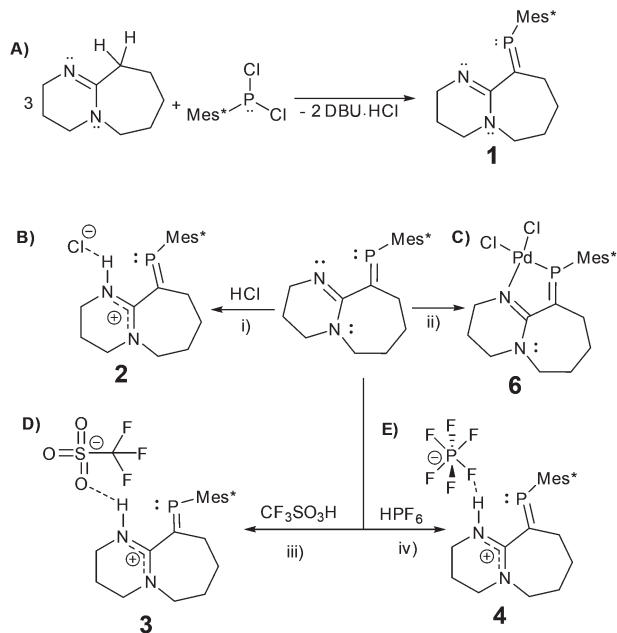
In here, we explore the reactions of the imine containing phosphalkene (**1**)¹⁵ with a variety of strong acids (Scheme 2). Despite being a sensitive compound under atmospheric conditions, when **1** reacts with hydrogen chloride (HCl), trifluoromethanesulfonic acid (HOTf), and hexafluorophosphoric acid (HPF_{6(aq.)}) under inert conditions, the P=C bond remains unchanged. The resulting protonated derivatives are significantly stabilised in comparison to **1** as demonstrated by simple decomposition experiments followed *via* ³¹P-NMR spectroscopy. Remarkably, reacting **1** and HCl with subsequent



Scheme 1 Selected reactivity of main group compounds with double bonding to a heavier element. Hydrogen halide addition on (A) P=C (classically polarised) (B) Si=C or Si=Si bonds, (C) P=N bonds, (D) and hydrolysis of As=C.

Molecular Inorganic Chemistry, Department of Chemistry - Ångström Laboratories, Uppsala University, Sweden. E-mail: andreas.orthaber@kemi.uu.se, daniel.salazar@kemi.uu.se

† Electronic supplementary information (ESI) available. CCDC 1828164–1828169. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt01607k



Scheme 2 Simplified synthetic procedures: (A) **1**; THF, $-78\text{ }^{\circ}\text{C}$ (B) **2**; (i) anhydrous HCl (2 M, THF), THF, $-78\text{ }^{\circ}\text{C}$. (C) **6**; (ii) $[\text{Pd}(\text{MeCN})_2\text{Cl}_2]$, DCM, rt. (D) **3**; (iii) $\text{CF}_3\text{SO}_3\text{H}$ (neat), MS (3 Å), THF, $-78\text{ }^{\circ}\text{C}$. (E) **4**; (iv) HPF_6 (60% aq.), MS (3 Å), THF, $-78\text{ }^{\circ}\text{C}$.

exposure to the atmosphere, leads to a hydrogen-bonded dimer ($2\cdot\text{H}_2\text{O}$) as verified by X-ray diffraction, FTIR, NMR and elemental analysis, offering an example of a multiple bonded heavier main group compound ($\text{RP}=\text{CR}_2$) involved in supra-molecular chemistry *via* hydrogen bonding (*i.e.* HB) interactions.¹⁶

The reaction of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) with $\text{Mes}^*\text{P}(\text{Cl})_2$ ($\text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) leads to phosphalkene **1**, previously reported based on spectroscopic data.¹⁷ Despite potential stabilisation of **1** *via* π -conjugation and charge delocalisation, (Fig. S1[†]), the $\text{P}=\text{C}$ bond is highly air/moisture sensitive, and decomposition products are spectroscopically visible after a few minutes of exposure to atmospheric conditions (Fig. S2[†]).

After several attempts, single-crystals of **1** were obtained by diffusion of hexanes into dichloromethane (DCM) under inert conditions (Fig. 1). The crystal structure of **1** displays bond lengths reflecting $\text{P1}=\text{C3}$, $\text{N1}=\text{C2}$ double bonds and $\text{N2}-\text{C2}$, $\text{C2}-\text{C3}$ single bonds, the latter is somewhat long for two singly bonded C_{sp^2} centres (1.494(4) Å), thus the bicyclic torsional strain frustrates the possibility to achieve electronic delocalisation across the $\text{P}=\text{C}$ to $\text{N}=\text{C}-\text{N}$ pathway. The $\text{P}=\text{C}$ bond length (1.676(3) Å) and low-field ^{31}P -NMR ($\delta = 254$ ppm) indicate **1** is a “classically polarised” phosphalkene ($\text{P}^{\delta+}\text{C}^{\delta-}$)¹⁸ with a proximal, but non-conjugated imine functionality. The π -accepting nature of the sp^2 hybridised P and N atoms as well as their proximity renders **1** interesting as an ancillary ligand as reported for other systems (*vide infra*). The reactivity of **1** with anhydrous HCl was tested, and a downfield shift of ~ 60 ppm in the ^{31}P -NMR spectrum was observed (Fig. S2[†]);

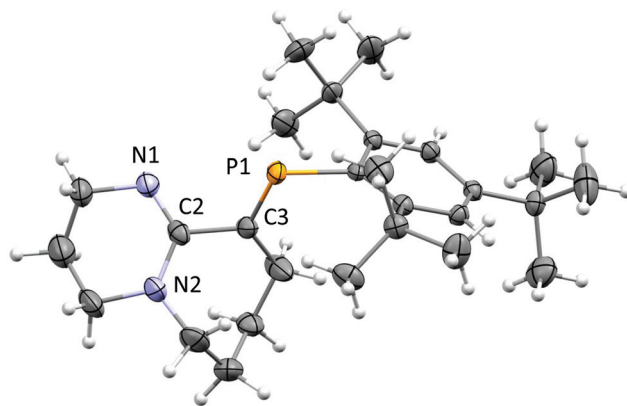


Fig. 1 ORTEP representation of **1**.²⁰ Ellipsoids are plotted at 50% probability levels. Selected interatomic distances (Å): $\text{P1}=\text{C3}$, 1.676(3). $\text{N1}=\text{C2}$, 1.285(4). $\text{N2}-\text{C2}$, 1.370(4). $\text{C2}-\text{C3}$, 1.496(4). See Table S1.[†]

such perturbation is not related to bond length changes (*vide infra*) on the environment around the phosphorus. We were unable to obtain single crystals of **2** under inert conditions, but only when left crystallising under ambient conditions, resulting in the hydrated form $2\cdot\text{H}_2\text{O}$ (Fig. 2A). Structural analysis of $2\cdot\text{H}_2\text{O}$ shows the formation of a dimeric hydrochloride hydrate salt, which self-assembled from $2 + \text{H}_2\text{O}$. The crystallisation was attempted twice again with slight variations of the conditions, and yet, the same crystal structure was obtained, which indicated the motif is energetically preferential. The reproducibility is interesting from a crystal-engineering perspective where the desire for the rational design of systems leading to discrete structures prevails.¹⁹ The molecular structure of $2\cdot\text{H}_2\text{O}$ was solved in the monoclinic space group $C2/c$. Heavy atoms were refined anisotropically, and hydrogen atoms were placed at geometric positions with fixed C–H distances, except for the N–H and water hydrogen atoms, which were located on the electron difference map. The asymmetric unit consists of the cationic fragment $[\mathbf{1} + \text{H}]^+$, as well as a hydrogen bonded chloride anion and a water molecule.

As a hydrogen-bond network, (Fig. 2A & S3[†]) the quadrilateral centred ring ($\sim 0.11\text{ nm}^2$) with the two peripheral iminium hydrogen donors is leading to a significant stabilisation as rationalised by the repeated crystallisations. A search on the Cambridge Structural Database (CSD) of the $\text{Cl}\cdots(\text{H}_2\text{O})_2\cdots\text{Cl}$ arrangement without constraints, yielded 1512 hits; restricting the search to the isolated dimeric motif observed in $2\cdot\text{H}_2\text{O}$ (a ring; with two chloride anions as HBA from three donors each, and two H_2O molecules as doubly HBD each) gave no results. A few isostructural arrangements, but with slightly different hydrogen bond coordination numbers on the HB network exist (see Fig. S3[†]). The discrete nature of the central HB motif in $2\cdot\text{H}_2\text{O}$ epitomises the small-limit of such water/chloride hydrogen-bonded cluster, in this case, embedded in a hydrophobic environment.²¹ Regardless of the interpretation, the study of hydrate and chloride containing rings and other topological arrangements is fundamentally important due to the ubiqui-



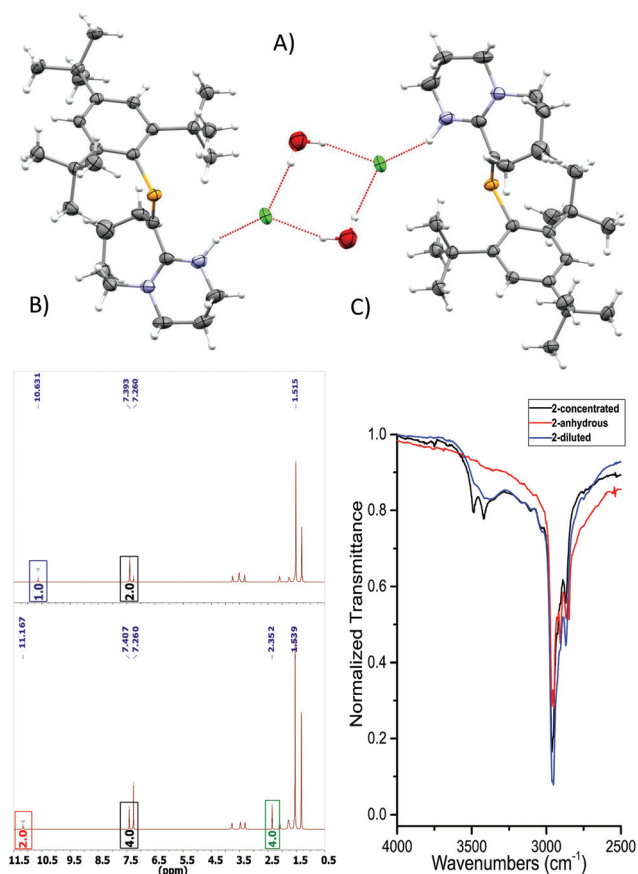


Fig. 2 (A) ORTEP representation of $2 \cdot \text{H}_2\text{O}$. Ellipsoids are plotted at 50% probability levels. (B) ^1H -NMR spectra of **2** and $2 + \text{H}_2\text{O}$. Top: Anhydrous. Bottom: H_2O titrated **2**. Red and blue box: N–H signal, green box: H_2O signal shifted due to the presence of HB. Bottom integrals assume a dimeric species. (C) FTIR: –OH region expansion of **2** and $2 + \text{H}_2\text{O}$ experiments (ESI/ Fig. S6†).

tous nature of HB interactions involving water and halides.²² We hypothesise that the addition of a water molecule *via* hydrolysis to an otherwise reactive $\text{P}=\text{C}$ double bond as seen in **1**, is attenuated due to the strategic location of the iminium–chloride pair (**2**), which leads to hydrogen bonding interactions ($2 \cdot \text{H}_2\text{O}$); further stabilisation *via* HB networks is favoured over decomposition of the functional $\text{P}=\text{C}$ centre, explaining the increased stability of both **2** (anhydrous) and $2 \cdot \text{H}_2\text{O}$ over **1** (see Fig. S4†). Substantial changes in the atomic orbital contributions to the FMO densities of **1** vs. $2/2 \cdot \text{H}_2\text{O}$ were ruled out by DFT calculations. Protonation of an imine over reaction at the multiple bonded heavier group 15 element was only recently reported for the first time, however not altering the stability of the phosphinine in this case.^{6b}

An insignificant elongation of the $\text{P}=\text{C}$ bond to 1.679(3) Å (ref. 23) from **1** to $2 \cdot \text{H}_2\text{O}$ contrasts with the $\text{N1}=\text{C2}-\text{N2}$ motif, which switches from a localised double/single bond towards a delocalized cationic situation with 1.325(4) and 1.318(4) Å bond lengths, respectively. Despite the significant separation of N2 and Cl1 from P1 (>3 Å), partial π -bond delocalisation

and other weak electrostatic interactions such as London dispersion may assist in stabilising HB interactions (Fig. S5†). Solution NMR experiments were performed (pages S18–S22†) to demonstrate the prevalence of HB in **2** and $2 + \text{H}_2\text{O}$ (not exclusively of the dimer). For example, titration of **2** (Fig. 2B) with a stoichiometric amount of deoxygenated water, resulted in downfield shifts of the N–H and H_2O signals strongly suggesting that a hydrogen bonded equilibrium is cooperatively established. Additional experiments (*e.g.* concentration dependency) in which specific experimental conditions led to expected chemical shift changes of the N–H, and the appearance of minor species in ^{31}P -NMR from complex equilibria (ion-pairs, hydrogen-bonded adducts, and others), validated the presence of HB in solution (see ESI†). The same type of evidence has been consistently used to demonstrate the presence of HB in the past.²⁴

The HB situation of **2** was further studied *via* infrared spectroscopy (Fig. 3C and Fig. S6 and S7†). The anhydrous form of **2** (red curve) lacks any –OH stretches at $>3300 \text{ cm}^{-1}$. On the other hand, measurements obtained from a dilute sample of **2** in DCM (0.5% H_2O), shows the arising of a discrete band at $\sim 3384 \text{ cm}^{-1}$, which corresponds to a HB –OH vibrational mode (blue curve). A three-fold concentration increase of **2** (*i.e.* more likely to participate in HB) to yield an approximate equimolar $2/\text{H}_2\text{O}$ mixture, led to the black spectrum featuring two, well-resolved discrete bands at 3490 and 3421 cm^{-1} . These vibrations occur at approximately 250 cm^{-1} lower wavenumbers than the –OH stretches of free H_2O in CCl_4 , indicating HB interactions. The two –OH resonances separated by only 69 cm^{-1} from the other reliably confirm the self-assembly of the dimeric motif in solution (Fig. S6 and S7† for details)²⁵ and correlate well with solid-state IR-data. Theoretically, QTAIM molecular graphs (Bader analysis) verifies the HB interactions of this cluster (Fig. S8†).²⁶ Examples of hydrogen bonding in compounds containing unsaturated/multiple bonded heavy main group motifs are rare.^{16a,c,27}

Intrigued by the stability of **1** after the reaction with HCl , its reactivity with TfOH (previously used to yield phosphonium cations from phosphalkenes)²⁸ and HPF_6 (60% aq.), acids orders of magnitude stronger than HCl , were tested. The ^{31}P -NMR spectra of **3** and **4** exhibited low-field shifts typical of phosphalkenes >300 ppm and were confirmed crystallographically (Fig. 3). Dicoordinate phosphonium cations also

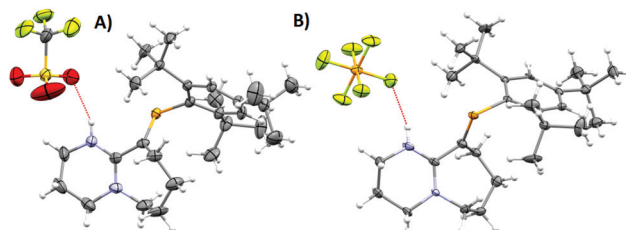


Fig. 3 ORTEP representations of (A) **3** (B) **4** (only one of the two independent molecules is displayed; see the asymmetric unit in Fig. S11†). Ellipsoids are plotted at 50% probability levels.



exhibit strongly deshielded ^{31}P NMR resonances and a $\Delta\delta^{31}\text{P}$ of 70 ppm and higher compared to their corresponding parent phosphalkenes;²⁹ as stated before for **1** (Fig. S1†), a resonance structure with a cationic phosphorus centre is plausible. However, the observed geometric parameters in the solid-state structures of **2**· H_2O , **3**, and **4** (*vide infra*) suggest that the charge delocalisation mainly occurs *via* the nitrogen atoms (Fig. S8†). Despite the pronounced effect on the ^{31}P chemical shifts for all adducts, we believe that the observed species are typical of customarily polarised phosphalkene units. The solid-state structures of **3** and **4** (Table S1†) show similar geometric parameters for the P=C unit in comparison to **2**· H_2O . The N1–C2–N2 motif displays similar bond lengths, whereas the P=C distances are slightly longer in **3** (1.689(4) Å) and **4** (1.695(5)/1.688(5) Å) in comparison to **2**· H_2O and **1**. In both cases, strong HB interactions between the cationic iminium and the anion are observed.³⁰ The donor–acceptor distances are in the range of 2.932(7)–3.097(3) Å, thus significantly shorter than in the DBU-HCl adduct (**5**) (3.156(6) Å), (Table S2†). DBU salts together with other adduct derivatives and its parent compound DBU are widely relevant in various areas such as catalysis, ionic liquids, organic synthesis, and others,³¹ however, the single crystal structure of this organic hydrochloride salt was reported for the first time (Fig. S9†). These hydrogen bonds are fundamentally interesting because they lie at the Brønsted acid/base and HB interface.³²

Additionally, single crystals of the Pd(II) complex (**6**) from the reaction of **1** with $[\text{PdCl}_2(\text{MeCN})_2]$ were obtained (Fig. S10†); as previously observed, the resulting P=C bond length shortened upon metal coordination (1.648(7) Å),³³ and as a result of the formation of the square planar complex, the torsion angle between the P=C and N=C is reduced (**6**: 12.3(7)°) with respect to the other species (52–57°) (Table S1†). The relative donor strengths of the N and the P binding sites are reflected by the Pd–Cl distances of 2.296(2) and 2.335(2) Å to the *trans*-chlorides, respectively suggesting stronger P binding.

In summary, a broad set of fascinating P=C containing systems obtained from the reactions of **1** with very strong acids and a Pd(II) precursor (**1**, **2**· H_2O , **3**, **4**, **6**), as well as the structurally unreported hydrochloride salt of DBU (**5**), are presented. The protonated derivatives are significantly stabilised towards decomposition of their phosphalkene in comparison to **1**, proving a vital role of both the anionic fragments and of HB interactions in suppressing undesired processes. The HCl adduct self-assembles into a dimeric species selectively, and exhibits a novel HB type of quadrilateral arrangement stabilised by two HB donor-only water molecules and two triply HB accepting chloride anions as the smallest water–chloride cluster of that type. The potential use of these systems as supramolecular precursors, in catalysis, and other applications may be envisioned. The introduction of this concept incentivises the use of rational design towards compounds that incorporate formidable multiple bonding to heavier p-block elements by strategically positioning saviour atoms on the periphery of the main group scaffold.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to thank the Swedish research council (Vetenskapsrådet 2017-03727), the EU COST action on Smart Inorganic Polymers (SIPs), and the Olle-Engkvist foundation for their support.

Notes and references

- (a) R. C. Fischer and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877–3923; (b) R. West, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1201–1211; (c) J. I. Bates, J. Dugal-Tessier and D. P. Gates, *Dalton Trans.*, 2010, **39**, 3151–3159; (d) C. Präsang and D. Scheschkewitz, *Chem. Soc. Rev.*, 2016, **45**, 900–921.
- (a) J. Heinicke and A. Tzschach, *Phosphorus Sulfur Relat. Elem.*, 1984, **20**, 347–356; (b) R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731–744; (c) R. Appel, G. Maier, H. P. Reisenauer and A. Westerhaus, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 197–197; (d) A. H. Cowley and S. K. Mehrotra, *J. Am. Chem. Soc.*, 1983, **105**, 2074–2075; (e) D. Gudat, M. Nieger and E. Niecke, *J. Chem. Soc., Dalton Trans.*, 1989, 693–700; (f) T. C. Klebach, R. Lourens and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1978, **100**, 4886–4888; (g) K. Sugamata, T. Sasamori and N. Tokitoh, *Chem. Lett.*, 2013, **43**, 95–96; (h) J. I. Bates and D. P. Gates, *J. Am. Chem. Soc.*, 2006, **128**, 15998–15999.
- (a) T. C. Klebach, R. Lourens and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1978, **100**, 4886–4888; (b) T. A. Van der Knaap, T. C. Klebach, R. Lourens, M. Vos and F. Bickelhaupt, *J. Am. Chem. Soc.*, 1983, **105**, 4026–4032; (c) M. J. Fink, D. J. De Young, R. West and J. Michl, *J. Am. Chem. Soc.*, 1983, **105**, 1070–1071; (d) P. Rosa, C. Gouverd, G. Bernardinelli, T. Berclaz and M. Geoffroy, *J. Phys. Chem. A*, 2003, **107**, 4883–4892; (e) R. West, *Polyhedron*, 2002, **21**, 467–472; (f) L. Weber, S. Buchwald, A. Rühlicke, H.-G. Stammer and B. Neumann, *Z. Anorg. Allg. Chem.*, 1993, **619**, 934–942; (g) V. K. Greenacre, I. J. Day and I. R. Crossley, *Organometallics*, 2017, **36**, 435–442; (h) C. Moser, M. Nieger and R. Pietschnig, *Organometallics*, 2006, **25**, 2667–2672; (i) O. C. Presly, T. J. Davin, M. Green, R. J. Kilby, S. M. Mansell, J. E. McGrady and C. A. Russell, *Eur. J. Inorg. Chem.*, 2008, **2008**, 4511–4515.
- M. Driess, H. Pritzkow and M. Sander, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 283–285.
- E. Niecke and D. Gudat, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 217–237.
- (a) Y. Zhang, F. S. Tham, J. F. Nixon, C. Taylor, J. C. Green and C. A. Reed, *Angew. Chem., Int. Ed.*, 2008, **47**, 3801–3804;



- (b) H. Huang, G. Tao, Z. Wei, J. Hou, M.-c. Wang, Z. Duan and F. Mathey, *Organometallics*, 2018, **37**, 464–468.
- 7 S. Loss, C. Widauer and H. Grützmacher, *Angew. Chem., Int. Ed.*, 1999, **38**, 3329–3331.
- 8 (a) M. Kobayashi, N. Hayakawa, T. Matsuo, B. Li, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka and K. Tamao, *J. Am. Chem. Soc.*, 2016, **138**, 758–761; (b) K. Tamao, M. Kobayashi, T. Matsuo, S. Furukawa and H. Tsuji, *Chem. Commun.*, 2012, **48**, 1030–1032; (c) K. Duck, B. W. Rawe, M. R. Scott and D. P. Gates, *Angew. Chem., Int. Ed.*, 2017, **56**, 9507–9511; (d) R. C. Smith and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 2004, **126**, 2268–2269; (e) D. Morales Salazar, E. Mijangos, S. Pullen, M. Gao and A. Orthaber, *Chem. Commun.*, 2017, **53**, 1120–1123.
- 9 (a) R. J. Gilliard, D. Heift, Z. Benkő, J. M. Keiser, A. L. Rheingold, H. Grützmacher and J. D. Protasiewicz, *Dalton Trans.*, 2018, **47**, 666–669; (b) G.-L. Hou, B. Chen, W. J. Transue, Z. Yang, H. Grützmacher, M. Driess, C. C. Cummins, W. T. Borden and X.-B. Wang, *J. Am. Chem. Soc.*, 2017, **139**, 8922–8930; (c) A. Hinze and J. M. Goicoechea, *Angew. Chem., Int. Ed.*, 2016, **55**, 15515–15519.
- 10 (a) Y. Peng, B. D. Ellis, X. Wang, J. C. Fettinger and P. P. Power, *Science*, 2009, **325**, 1668–1670; (b) 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**, 13453–13457.
- 11 P. K. Majhi, K. C. Chow, T. H. Hsieh, E. G. Bowes, G. Schnakenburg, P. Kennepohl, R. Streubel and D. P. Gates, *Chem. Commun.*, 2016, **52**, 998–1001.
- 12 (a) S. Ito, T. Shinozaki and K. Mikami, *Eur. J. Org. Chem.*, 2017, 6889–6900; (b) H.-o. Taguchi, D. Sasaki, K. Takeuchi, S. Tsujimoto, T. Matsuo, H. Tanaka, K. Yoshizawa and F. Ozawa, *Organometallics*, 2016, **35**, 1526–1533; (c) A. J. Arduengo, J. C. Calabrese, A. H. Cowley, H. V. R. Dias, J. R. Goerlich, W. J. Marshall and B. Riegel, *Inorg. Chem.*, 1997, **36**, 2151–2158.
- 13 B. W. Rawe, C. M. Brown, M. R. MacKinnon, B. O. Patrick, G. J. Bodwell and D. P. Gates, *Organometallics*, 2017, **36**, 2520–2526.
- 14 (a) X. Pan, X. Wang, Z. Zhang and X. Wang, *Dalton Trans.*, 2015, **44**, 15099–15102; (b) G. Tan, S. Li, S. Chen, Y. Sui, Y. Zhao and X. Wang, *J. Am. Chem. Soc.*, 2016, **138**, 6735–6738; (c) G. Tan, J. Li, L. Zhang, C. Chen, Y. Zhao, X. Wang, Y. Song, Y.-Q. Zhang and M. Driess, *Angew. Chem., Int. Ed.*, 2017, **56**, 12741–12745.
- 15 R. Appel and L. Krieger, *J. Organomet. Chem.*, 1988, **354**, 309–312.
- 16 (a) Y. Mao, K. M. H. Lim, Y. Li, R. Ganguly and F. Mathey, *Organometallics*, 2013, **32**, 3562–3565; (b) G. Becker, *Z. Anorg. Allg. Chem.*, 1981, **480**, 38–48; (c) G. Becker, M. Rössler and G. Uhl, *Z. Anorg. Allg. Chem.*, 1982, **495**, 73–88.
- 17 R. Appel and L. Krieger, *J. Organomet. Chem.*, 1988, **354**, 309–312.
- 18 L. Weber, *Eur. J. Inorg. Chem.*, 2000, **2000**, 2425–2441.
- 19 G. R. Desiraju, *Angew. Chem., Int. Ed.*, 2007, **46**, 8342–8356.
- 20 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565–565.
- 21 (a) J. H. Loehlin and A. Kvik, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1978, **34**, 3488–3490; (b) M. N. Hoque, A. Basu and G. Das, *Cryst. Growth Des.*, 2012, **12**, 2153–2157; (c) A. Basu and G. Das, *Chem. Commun.*, 2013, **49**, 3997–3999; (d) D.-X. Wang, S.-X. Fa, Y. Liu, B.-Y. Hou and M.-X. Wang, *Chem. Commun.*, 2012, **48**, 11458–11460.
- 22 (a) G. A. Jeffrey, *Crystallogr. Rev.*, 2003, **9**, 135–176; (b) T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76; (c) Q. He, P. Tu and J. L. Sessler, *Chem*, 2018, **4**, 46–93; (d) J. E. Combariza, N. R. Kestner and J. Jortner, *J. Chem. Phys.*, 1994, **100**, 2851–2864; (e) N. Agmon, *J. Phys. Chem. A*, 1998, **102**, 192–199; (f) W. H. Thompson and J. T. Hynes, *J. Am. Chem. Soc.*, 2000, **122**, 6278–6286; (g) J. N. Moorthy, R. Natarajan and P. Venugopalan, *Angew. Chem., Int. Ed.*, 2002, **41**, 3417–3420.
- 23 (a) D. Nauroozi and A. Orthaber, *Eur. J. Inorg. Chem.*, 2016, **2016**, 709–717; (b) S. Shah, T. Concolino, A. L. Rheingold and J. D. Protasiewicz, *Inorg. Chem.*, 2000, **39**, 3860–3867.
- 24 (a) P. L. Wash, E. Maverick, J. Chiefari and D. A. Lightner, *J. Am. Chem. Soc.*, 1997, **119**, 3802–3806; (b) C. Reichardt and T. Welton, in *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 7–64; (c) M. Fleischmann, D. Drettwan, E. Sugiono, M. Rueping and R. M. Gschwind, *Angew. Chem., Int. Ed.*, 2011, **50**, 6364–6369; (d) E. E. Simanek, M. I. M. Wazeer, J. P. Mathias and G. M. Whitesides, *J. Org. Chem.*, 1994, **59**, 4904–4909; (e) R. Wyler, J. de Mendoza and J. Rebek, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1699–1701.
- 25 A. Maeda, J. Sasaki, Y. Shichida and T. Yoshizawa, *Biochemistry*, 1992, **31**, 462–467.
- 26 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893–928.
- 27 (a) G. Becker, *Z. Anorg. Allg. Chem.*, 1977, **430**, 66–76; (b) S. G. Ruf, J. Dietz and M. Regitz, *Tetrahedron*, 2000, **56**, 6259–6267; (c) X. Chen, S. Alidori, F. Puschmann Florian, G. Santiso-Quinones, Z. Benkő, Z. Li, G. Becker, H. F. Grützmacher and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2014, **53**, 1641–1645; (d) R. Suter, Y. Mei, M. Baker, Z. Benkő, Z. Li and H. Grützmacher, *Angew. Chem., Int. Ed.*, 2016, **56**, 1356–1360.
- 28 (a) D. Gudat, E. Niecke, B. Krebs and M. Dartmann, *Chimia*, 1985, **39**, 277–279; (b) J. I. Bates and D. P. Gates, *Chem. – Eur. J.*, 2012, **18**, 1674–1683; (c) L. Weber, S. Kleinebeckel and T. Haase, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1857–1862.
- 29 (a) A. H. Cowley, M. C. Cushner and J. S. Szobota, *J. Am. Chem. Soc.*, 1978, **100**, 7784–7786; (b) N. Burford, T. S. Cameron, J. A. Clyburne, K. Eichele, K. N. Robertson, S. Sereda, R. E. Wasylshen and W. A. Whitla, *Inorg. Chem.*, 1996, **35**, 5460–5467; (c) D. Gudat, *Coord. Chem. Rev.*, 1997, **163**, 71–106.



- 30 (a) M. S. Miran, H. Kinoshita, T. Yasuda, M. A. B. H. Susan and M. Watanabe, *Chem. Commun.*, 2011, **47**, 12676–12678; (b) T. S. Teets, J. A. Labinger and J. E. Bercaw, *Organometallics*, 2013, **32**, 5530–5545.
- 31 (a) M. Pschenitza, S. Meister and B. Rieger, *Chem. Commun.*, 2018, **54**, 3323–3326; (b) Z. Z. Yang, L. N. He, C. X. Miao and S. Chanfreau, *Adv. Synth. Catal.*, 2010, **352**, 2233–2240; (c) P. G. Jessop, D. J. Heldebrant, X. Li, C. A. Eckert and C. L. Liotta, *Nature*, 2005, **436**, 1102–1102.
- 32 P. Gilli, L. Pretto, V. Bertolasi and G. Gilli, *Acc. Chem. Res.*, 2009, **42**, 33–44.
- 33 (a) K. Takeuchi, H.-o. Taguchi, I. Tanigawa, S. Tsujimoto, T. Matsuo, H. Tanaka, K. Yoshizawa and F. Ozawa, *Angew. Chem., Int. Ed.*, 2016, **55**, 15347–15350; (b) S. Ikeda, F. Ohhata, M. Miyoshi, R. Tanaka, T. Minami, F. Ozawa and M. Yoshifuji, *Angew. Chem., Int. Ed.*, 2000, **39**, 4512–4513; (c) M. Klein, C. Albrecht, G. Schnakenburg and R. Streubel, *Organometallics*, 2013, **32**, 4938–4943; (d) J. Dugal-Tessier, G. R. Dake and D. P. Gates, *Angew. Chem., Int. Ed.*, 2008, **47**, 8064–8067; (e) P. Le Floch, *Coord. Chem. Rev.*, 2006, **250**, 627–681; (f) S. C. Serin, F. S. Pick, G. R. Dake and D. P. Gates, *Inorg. Chem.*, 2016, **55**, 6670–6678.

