ChemComm

Even the normal is abnormal: N-heterocyclic carbene C2 binding to a phosphaalkene without breaking the P=C π-bond

Journal:	*ChemComm*
Manuscript ID	CC-COM-09-2015-008181.R1
Article Type:	Communication
Date Submitted by the Author:	09-Nov-2015
Complete List of Authors:	Gates, Derek; University of British Columbia, Chemistry Department Streubel , R.; University of Bonn, Chemistry Kenepohl, Pierre; The University of British Columbia, Chemistry Majhi, Paresh; University of Bonn, Chemistry Chow, Keith; The University of British Columbia, Chemistry Hsieh, Tom; The University of British Columbia, Chemistry Bowes, Eric; The University of British Columbia, Chemistry Schnakenburg, Gregor; Universitat Bonn, Institute of Inorganic Chemistry

ChemComm

RSCPublishing

COMMUNICATION

Even the normal is abnormal: N-heterocyclic carbene C^2 binding to a phosphaalkene without breaking the P=C π-bond†

Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

www.rsc.org/

Paresh Kumar Majhi,[a,b] Keith C. F. Chow,[b] Tom H. H. Hsieh,[b] Eric G. Bowes,[b] Gregor Schnakenburg,[a] Pierre Kennepohl,[b,*] Rainer Streubel[a,*] and Derek P. Gates[b,*]

Abstract. The reaction of $MesP{=}CPh_2$ with the least sterically demanding N-heterocyclic carbene (NHC = IMe) results in formation of the 'abnormal' (C^4-substituted) 4-phosphino-NHC (1). In contrast, reaction with Me_2IMe gives the unprecedented 'normal' C^2 adduct, $Me_2IMe{\rightarrow}P(Mes){=}CPh_2$ (2). Particularly striking is the asymmetric and weak bonding of the NHC to the P=C moiety in 2. DFT calculations indicate that the P=C natural bond order in 2 (1.54) still reflects significant π-character to the bond (cf. $MesP{=}CPh_2$: NBO = 1.98). Further computational analysis suggests that π-delocalization into the remote C-phenyl substituents is key to stabilizing the NHC adduct.

In just a few decades, *N*-heterocyclic carbenes (NHCs), the most important of which are the imidazol-2-ylidenes,[1] have risen from relative obscurity to becoming competitive with phosphines as important ligands in organometallic chemistry and catalysis.[2] The carbene carbon at the C^2 position in such an NHC (Fig. 1) is by far the most reactive site (so-called "classical" or "normal" binding).[3]

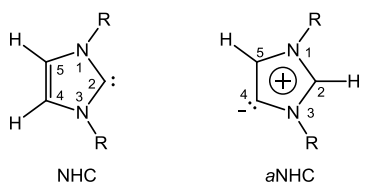


Fig. 1 Structures and numbering scheme for normal (NHC) and abnormal imidazol-2-ylidenes (aNHC).

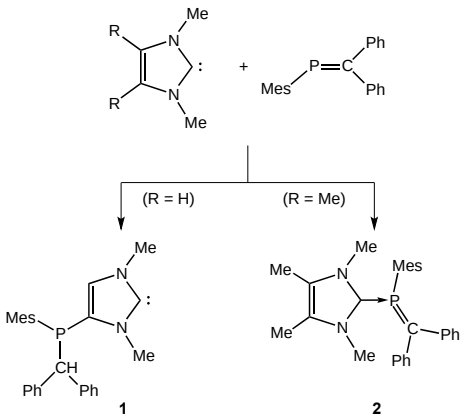
A growing number of NHCs have been observed to react through the C^4 position (so-called "mesoionic" or "abnormal" binding).[4-8] To obtain abnormal N-heterocyclic carbenes (*a*NHCs), the C^2-position is usually blocked and the C^4-postion bound to a d- or f-block element. For example, the isolation of the first free aNHC by Bertrand and co-workers required phenyl moieties at both the C^2 and C^5 positions.[5] In 2009, we reported the "abnormal" reaction of the unblocked 1,3-dimesityl-imidazol-2-ylidene (IMes) with the phosphalkene $MesP{=}CPh_2$ to afford the first example of an NHC with a phosphine substituent at C^4.[9,10] The direct functionalization of unprotected NHCs with p-block elements at the C^4 position has grown to include: halogenation,[11,12] deuteration,[13] and silylation,[14] addition of Si=N[15] and B=N[16] compounds, s-block metallation,[17,18] and borate formation.[19] An elegant method to induce *a*NHC reactivity involves temporarily blocking C^2 with an electrophile to permit base-assisted functionalization selectively at C^4, thereby affording NHCs with C^4 substituents such as: Br, Cl, C(O)R, OTf, PPh_2, $SiMe_3$.[20-22]

It was proposed that the sterically demanding N-Mes substituents of IMes might impede the formation of the "normal" (C^2) product in the reaction with phosphaalkenes thus leading to the "abnormal" (C^4) 4-phosphino-NHC.[23] To evaluate this hypothesis, we sought to probe the reactivity of less sterically-demanding NHCs with the phosphaalkene $MesP{=}CPh_2$.

Significantly, we have now isolated the "abnormal" product **1** and the "normal" adduct **2**, both of which have been crystallographically characterized (**1** as its BH_3 complex, **1**·BH_3). Adduct **2** is particularly remarkable in that the metrical data along with DFT calculations reveal that the NHC binds to the phosphaalkene π* with a low degree of disruption of the P=C π-bond.

1,3-Dimethyl-imidazol-2-ylidene (IMe) was generated in situ in THF[24] and treated with $MesP{=}CPh_2$ (1 equiv) at –78 °C followed by warming to room temperature (Scheme 1). Analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed that the signal for $MesP{=}CPh_2$ ($\delta^{31}P$ = 234 ppm) was not

present and a new signal at –37.2 ppm had appeared, assigned to **1**. Importantly, the chemical shift of this new signal is comparable to the abnormal product derived from IMes and MesP=CPh$_2$ (δ = -37.3 ppm).[9] The isolated product (yield 78 %) was analyzed by $^{13}C\{^1H\}$ NMR spectroscopy in THF-d^8 to reveal a broad resonance at δ = 222.5 ppm, assigned to the carbene carbon (C^2) atom of **1**; the $^3J_{P,C}$ coupling constant could not be resolved.



Scheme 1 Synthesis of compounds **1** and **2**.

In order to obtain X-ray crystallographic confirmation of **1**, several complexes **1**·ML$_n$ [ML$_n$ = BH$_3$, Rh(cod)Cl, Cr(CO)$_5$, Mo(CO)$_5$, W(CO)$_5$] were prepared. The C^2 bound complexes were characterized by ^{31}P, ^1H, $^{13}C\{^1H\}$ NMR spectroscopy[25] and mass spectrometry (see SI). In the case of **1**·BH$_3$, single crystals suitable for X-ray crystallography were obtained from a saturated THF solution at –20 °C. The molecular structure (Fig. 2) confirms the formulation as the 4-phosphinyl-substituted NHC borane complex **1**·BH$_3$. The metrical parameters in **1**·BH$_3$ do not differ significantly from those of IMe·BH$_3$[26] and, hence, shall not be discussed further.

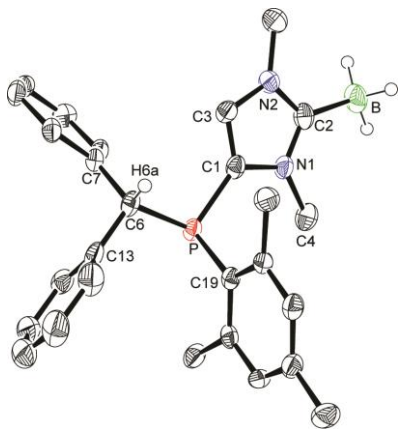


Fig. 2 Molecular structure of complex **1**·BH$_3$. Disordered solvent molecule (THF) and hydrogen atoms (except B-H and C(6)-H) have been omitted for clarity (50 % probability level). Selected bond distances (Å) and angles (°): C(2)-B 1.609(4), C(2)-N(1) 1.343(3), C(2)-N(2) 1.357(3), C(1)-C(3) 1.352(3), C(1)-P 1.817(3), C(6)-P 1.881(2), C(1)-N(1) 1.407(3), C(3)-N(2) 1.374(3); N(1)-C(2)-N(2) 104.7(2), N(1)-C(2)-B 128.9(2), N(2)-C(2)-B 126.4(3), N(1)-C(1)-P 121.21(18).

Despite monitoring the abnormal reaction of IMe with MesP=CPh$_2$ by ^{31}P NMR spectroscopy at variable temperatures (–80 to 25 °C), no P-containing intermediates have been observed. In contrast, Braunschweig and co-workers have detected a "normal" C^2-adduct as a short-lived intermediate in the abnormal reaction of IPr with the iminoborane, tBuB=NtBu.[16] In an effort to see whether the formation of the normal C^2 adduct was possible with phosphaalkenes, the C^4/C^5-blocked 1,3,4,5-tetramethyl-imidazol-2-ylidene (Me$_2$IMe)[27] was treated with MesP=CPh$_2$ in Et$_2$O. $^{31}P\{^1H\}$ NMR spectroscopic analysis of the reaction mixture revealed that the signal for MesP=CPh$_2$ (δ = 234) had been replaced by a broad signal at δ = 206.1 ($w_{1/2}$ = 124 Hz) along with about 7% of unidentified products. Interestingly, the chemical shift is highly dependent on the solvent in which the reaction is conducted (THF: δ = 185.1, $w_{1/2}$ = 608 Hz; Toluene: δ = 213.4, $w_{1/2}$ = 122 Hz). Given the similarity in chemical shift to that of MesP=CPh$_2$, we suspected that the product, regardless of solvent, retains significant P=C bond character. In addition, the phosphaalkene is released from **2** upon the addition of boranes [BR$_3$ = BPh$_3$, B(C$_6$F$_5$)$_3$] to yield a mixture of MesP=CPh$_2$ and Me$_2$IMe·BR$_3$.

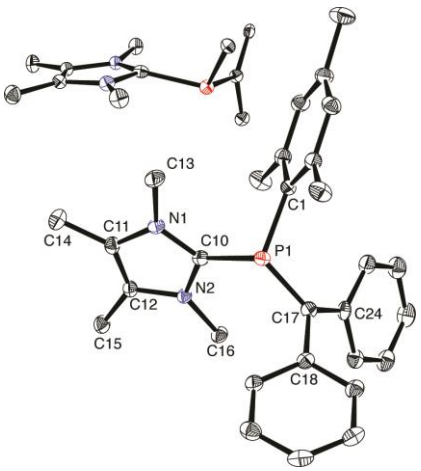


Fig. 3 Molecular structure of complex **2.** Hydrogen atoms have been omitted for clarity (50 % probability level); side view on the reduced structure (top left). Selected bond distances (Å) and angles (°): P(1)-C(10) 1.8512(18), P(1)-C(17) 1.7420(19), P(1)-C(1) 1.8416(17), N(1)-C(10) 1.354(2), N(2)-C(10) 1.345(2), C(17)-C(18) 1.479(2); N(1)-C(10)-N(2) 106.14(15), N(1)-C(10)-P(1) 121.94(14), N(2)-C(10)-P(1) 128.95(13), C(10)-P(1)-C(1) 100.98(7), C(10)-P(1)-C(17) 112.73(9), C(18)-C(17)-C(24) 118.57(16).

X-ray crystallography permitted the product described above to be identified as the unprecedented NHC-phosphaalkene adduct **2** (Fig. 3). This "normal" NHC adduct **2** features a short the P–C bond [P(1)-C(17) = 1.7420(19) Å] that is closer to that of a double bond (e.g. for MesP=CPh$_2$ [1.692(3) Å][28]) than that of a typical P–C single bond (1.85 Å).[29] In addition, the carbon atom C(17) retains a planar geometry $\Sigma\angle$C(17) = 359.7°, which is consistent with retention of its sp^2 hybridization. The distortion of the P=C bond upon binding of NHC is small with a 36.4° twisting of the C(1)–P(1)–C(10) plane with respect to the C(18)–C(17)–C(24) plane; for comparison, the same angle in MesP=CPh$_2$ is 0.9°[30] or 7.5°.[31] Particularly striking is the almost perpendicular position of the NHC donor with respect to the best plane of P=C bond (102.6° is max. angle between NHC–P bond and P=C best plane). In addition, the C(10)–P(1) single bond length [P(1)-C(10) = 1.8512(18) Å] is long. These observations stand in stark contrast to the Me$_2$IPr adduct of Mes*N=PCl[32] which displays

significant torsion of the C_{Mes*}–N=P–Cl unit and in the Me_2IPr adduct of tBuN=BtBu[16] where C_{tBu}–N=B–C_{tBu} and C^2 are coplanar. The molecular structures of related NHC-complexes to E=E bonds also exhibit significant distortions at the E=E bond.[33] The above metrical data for **2** combined with the ^{31}P chemical shift and the ready displacement of the NHC with electrophiles are all consistent with the interpretation of the NHC as a weak σ-donor in **2**.

The fascinating metrical parameters in **2** led us to probe the nature of bonding in this compound and in MesP=CPh_2 by computational methods (DFT-B3LYP/TZVP). The optimized gas phase geometry was in good agreement with the solid state molecular structure (see SI) and natural bond orbital (NBO) analysis suggests that both P(1) and C(17) retain significant π-bond character. On first glance, the data is consistent with adduct formation between the C^2 lone pair of Me_2IMe and the P=C π* orbital of MesP=CPh_2. Surprisingly, this adduct formation only leads to a small increase in the π* population in **2** (by 0.08 e^- compared to MesP=CPh_2) and displays a concomitant decrease in the NBO P=C bond order (from 1.98 to 1.54). The P=C π bond polarizes substantially upon binding of Me_2IMe (Fig. 4); the phosphorus natural hybrid orbital (NHO) shows increased 3d character in the π_{PC} bond leading to pd hybridization, and this pd hybrid functions as the acceptor orbital for the Me_2IMe→P σ bond. Nevertheless, the actual contributions from the putative pd hybrid NHOs in both the $\pi_{P(1)\text{-}C(17)}$ and the $\sigma_{P(1)\text{-}C(10)}$ orbitals are quite small (11% and 23%, respectively).

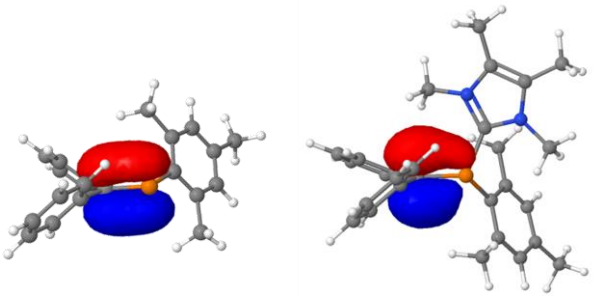


Fig. 4 NBO representation of the NBO-derived π_{PC} orbital in MesP=CPh_2 (left) and **2** (right). Orbital surfaces are plotted at 0.05 $e^-/Å^3$ using WebMO.

The calculated atomic charges obtained by natural population analysis (NPA) are shown in Table 1 and the changes (Δ*q*) reveal the overall effect of adduct formation. Predictably, there is an electron redistribution towards the carbon of the phosphaalkene moiety that is accompanied by a concomitant decrease in charge at phosphorus. The significant redistribution of charge density from the NHC to the remote phenyl substituents was unanticipated, particularly when noting the asymmetry in negative charge accumulation between the two substituents (see Δ*q* for Ph_{cis} vs. Ph_{trans} in Table 1). However, these observations are in agreement with the different angles between the P=C bond plane and each phenyl substituent in **2** (*cis*, 17.5°; *trans*, 51.9°); the metrical data contrasts the analogus angles within the free MesP=CPh_2[34] (Ph_{cis}>Ph_{trans}). This finding is consistent with asymmetric allylic π-delocalization across the CPh_2 moiety. In fact, a comparison to the hypothetical Me_2IMe adduct of MesP=CMe_2 shows that the phenyl substituents are critical to stabilizing **2**. Namely, the dimethyl derivative exhibits a much longer P-C_{NHC} bond (2.00Å vs. 1.86Å) and this bond has a significantly lower bond dissociation energy (~45 kJ/mol lower than that for **2**).

Table 1. Calculated NPA atomic and fragment charges for MesP=CPh_2, Me_2IMe, and the resultant adduct **2**. Δ*q* is the change in charge between **2** and the sum of the charges in the reactants.

	NPA atomic/fragment charges					
	Mes	IMe_4	P	CPh_2	Ph_{cis}	Ph_{trans}
MesP=CPh_2	-0.30	-	0.66	-0.38	0.02	0.01
IMe_4	-	0.00	-	-	-	-
2	-0.32	0.35	0.90	-0.65	-0.16	-0.13
Δ*q*	-0.01	0.35	0.24	-0.26	-0.18	-0.14

Analysis by natural resonance theory (NRT) suggests that the major contributors to the canonical forms of **2** (R = Ph) are the simple adduct (**2A**) and the asymmetric allylic form (**2B**) (Fig. 5). It is interesting that the structure **2B** showing π-delocalization to Ph_{cis} is considerably more important than that involving Ph_{trans} (**2D**). Importantly, this result is consistent with the crystal structure data described above. Moreover, this analysis confirms that significant P=C character remains even though charge is highly delocalized. Overall, the results are consistent with an interpretation of the bonding within **2** where the $\pi_{P=C}$ bond is perturbed by the NHC donor but is not broken entirely resulting in the unique geometry of the isolated adduct.

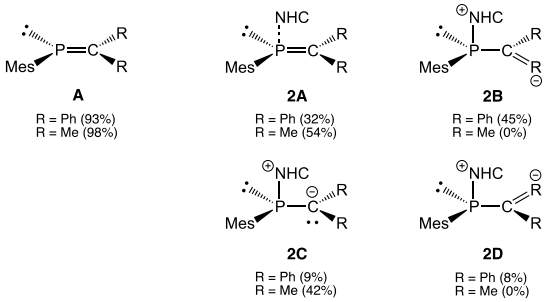


Fig. 5 Generalized canonical forms illustrating the bonding within of MesP=CR_2 (**A**, R = Ph or Me) and a NHC→MesP=CR_2 (**2A-D**, R = Ph or Me). The percent contributions are obtained from an NRT analysis of the NBO computational results (see SI for details).

Herein, we have shown that steric bulk at the N-substituents of NHCs is not required for abnormal products to be formed in their reactions with phosphaalkenes. By contrast, we find that blocking the $C^{4,5}$ positions of the NHC leads to the formation of an unprecedented weakly bound C^2-adduct that retains significant P=C double bond character. The formation of such adducts is predicated on the ability for charge delocalization in the substituents of the phosphaalkene and suggests that modulation of the stability of the NHC adduct is strongly dependent on the nature of the phosphaalkene.

DG and PK are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support of this work. RS thanks the Deutsche Forschungsgemeinschaft (DFG) SFB 813 “Chemistry at Spin

Centers" and the COST action (CM1302). RS and PKM are grateful to the DAAD PPP Program for Canada. Computation work was enabled by support by WestGrid (www.westgrid.ca) and Compute Canada Calcul Canada (www.computecanada.ca).

Notes and references

[a] Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany. Email: r.streubel@uni-bonn.de.

[b] Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, V6T 1Z1. Email: dgates@chem.ubc.ca.

† Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data, X-ray data, DFT procedures and results, selected spectra. For crystallographic data, see: CCDC 1428162 (**1**·BH_3) and CCDC 1428161 (**2**). See DOI: 10.1039/c000000x/

1 A. J. Arduengo III, R. L. Harlow, and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361.

2 M. N. Hopkinson, C. Richter, M. Schedler, and F. Glorius, *Nature*, 2014, **510**, 485.

3 D. Bourissou, O. Guerret, F. P. Gabbai, and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39.

4 S. Grundemann, A. Kovacevic, M. Albrecht, J. W. Faller Robert, and H. Crabtree, *Chem. Commun.*, 2001, 2274.

5 E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, and G. Bertrand, *Science*, 2009, **326**, 556.

6 O. Schuster, L. Yang, H. G. Raubenheimer, and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445.

7 P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596.

8 J. B. Waters and J. M. Goicoechea, *Coord. Chem. Rev.*, 2015, **293**, 80.

9 J. I. Bates, P. Kennepohl, and D. P. Gates, *Angew. Chem. Int. Ed.*, 2009, **48**, 9844.

10 NHCs bearing an anionic PR-substituent at C^4 have subsequently been reported: P. K. Majhi, G. Schnakenburg, Z. Kelemen, L. Nyulaszi, D. P. Gates, and R. Streubel, *Angew. Chem. Int. Ed.*, 2013, **52**, 10080.

11 A. J. Arduengo III, F. Davidson, H. V. R. Dias, J. R. Goerlich, D. Khasnis, W. J. Marshall, and T. K. Prakasha, *J. Am. Chem. Soc.*, 1997, **119**, 12742.

12 M. L. Cole, C. Jones, and P. C. Junk, *New J. Chem.*, 2002, **26**, 1296.

13 M. K. Denk and J. M. Rodezno, *J. Organomet. Chem.*, 2001, **617-618**, 737.

14 H. Cui, Y. Shao, X. Li, L. Kong, and C. Cui, *Organometallics*, 2009, **28**, 5191.

15 R. S. Ghadwal, H. W. Roesky, M. Granitzka, and D. Stalke, *J. Am. Chem. Soc.*, 2010, **132**, 10018.

16 H. Braunschweig, W. C. Ewing, K. Geetharani, and M. Schafer, *Angew. Chem., Int. Ed.*, 2015, **54**, 1662.

17 Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer, P. v. R. Schleyer, and G. H. Robinson, *J. Am. Chem. Soc.*, 2010, **132**, 14370.

18 D. R. Armstrong, S. E. Baillie, V. L. Blair, N. G. Chabloz, J. Diez, J. Garcia-Alvarez, A. R. Kennedy, S. D. Robertson, and E. Hevia, *Chem. Sci.*, 2013, **4**, 4259.

19 S. Kronig, E. Theuergarten, C. G. Daniliuc, P. G. Jones, and M. Tamm, *Angew. Chem. Int. Ed.*, 2012, **51**, 3240.

20 D. Mendoza-Espinosa, B. Donnadieu, and G. Bertrand, *J. Am. Chem. Soc.*, 2010, **132**, 7264.

21 J. Ruiz and A. F. Mesa, *Chem. Eur. J.*, 2012, **18**, 4485.

22 K. Schwedtmann, M. H. Holthausen, K.-O. Feldmann, and J. J. Weigand, *Angew. Chem., Int. Ed.*, **52**, 14204.

23 J. I. Bates and D. P. Gates, *Organometallics*, 2012, **31**, 4529.

24 A. Wacker, H. Pritzkow, and W. Siebert, *Eur. J. Inorg. Chem.*, 1998, **1998**, 843.

25 Consistent with that observed for the Rh(I) and Ir(I) complexes of 4-phosphinyl NHC derived from IMes (see ref 23), two signals were observed in the ^{31}P NMR spectra of complexes **1**·ML_n [ML_n = BH_3, Rh(cod)Cl, $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$]. Although the origin of these signals is not known, we tentatively attribute these signals to isomers .

26 P. Bissinger, H. Braunschweig, T. Kupfer, and K. Radacki, *Organometallics*, 2010, **29**, 3987.

27 N. Kuhn and T. Kratz, *Synthesis*, 1993, 561.

28 T. A. Van Der Knaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam, and M. Konijn, *Tetrahedron*, 1984, **40**, 765.

29 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J Chem Soc Perk T 2*, 1987, S1.

30 T. A. Vanderknaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam, and M. Konijn, *Tetrahedron*, 1984, **40**, 765.

31 O. Mundt, G. Becker, W. Uhl, W. Massa, and M. Birkhahn, *Z. Anorg. Allg. Chem.*, 1986, **541**, 319.

32 N. Burford, T. S. Cameron, D. J. LeBlanc, A. D. Phillips, T. E. Concolino, K. C. Lam, and A. L. Rheingold, *J. Am. Chem. Soc.*, 2000, **122**, 5413.

33 For recent examples, see: (*a*) D. Geiss, M. I. Arz, M. Strassmann, G. Schnakenburg, and A. C. Filippou, *Angew. Chem., Int. Ed.*, 2015, **54**, 2739; (*b*) S. Roy, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrada, G. Frenking, and H. W. Roesky, *J. Am. Chem. Soc.*, 2015, **137**, 150; (*c*) F. Dahcheh, D. W. Stephan, and G. Bertrand, *Chem. Eur. J.*, 2015, **21**, 199; (*d*) F. Dahcheh, D. Martin, D. W. Stephan, and G. Bertrand, *Angew. Chem., Int. Ed.*, 2014, **53**, 13159; (*e*) A. Jana, V. Huch, and D. Scheschkewitz, *Angew. Chem., Int. Ed.*, 2013, **52**, 12179.

34 M. Yam, J. H. Chong, C.-W. Tsang, B. O. Patrick, A. E. Lam, and D. P. Gates, *Inorg. Chem.*, 2006, **45**, 5225.

Journal Name RSCPublishing

COMMUNICATION

Even the normal is abnormal: N-heterocyclic carbene C^2 binding to a phosphaalkene without breaking the P=C π-bond†

Paresh Kumar Majhi,[a,b] Keith C. F. Chow,[b] Tom H. H. Hsieh, [b] Eric G. Bowes,[b] Gregor Schnakenburg,[a] Pierre Kennepohl,[b,*] Rainer Streubel[a,*] and Derek P. Gates[b,*]

Graphical Abstract: (max 3 cm x 8 cm)