Theoretical investigation of main-group element hydride insertion into phosphorus-heterocyclic carbenes (PHCs)

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**Abstract**

Initial reports of ring expansion reactions (RER) of N-heterocyclic carbenes (NHCs) with main-group element hydrides has led to several synthetic and theoretical investigations, including reports of insertion by Be, B, Al, Si, and Zn hydrides. The RERs generally lead to insertion of the heteroatom into the endocyclic C–N bond with formation of an expanded heterocyclic ring. Following the recent isolation of a P-heterocyclic carbene (PHC), here we report results from a computational study (RI-SCS-MP2/def2-TZVP//M06-2X/def2-TZVP) of RERs with a series of PHCs for the ring-insertion of silicon (SiH4, SiH2Ph2) and boron (BH3, BH2NMe2) hydrides. In order to explore the roles of both electronic and steric effects on PHCs and their reactivity, a series of P-substituent PHCR (R = H, Me, Ph and bulky Ar groups) were investigated. Bulky R groups serve to maximise ring planarity and the σ-donating capability of the PHC. For RER, the PHC analogues exhibit facile initial hydride transfer from the main-group hydrides to the carbene carbon, with barriers that are substantially lower than with NHCs. However, the full ring insertion mechanisms for PHCs are, in general, kinetically unfavourable due to a large barrier associated with the ring-expansion step. While bulky P-substituents maximise heterocycle planarity towards that of NHCs, the RER reactivity with bulky PHCs does not reflect that of an NHC.

**Key words**

Ring expansion reactions, phosphorus heterocyclic carbenes, DFT

**Introduction**

The isolation of a stable N-heterocyclic carbene (NHC) in 1991 by Arduengo[1] heralded significant developments across the breadth of modern coordination chemistry. The application of NHCs as robust and efficient -donating ligands [2] has grown rapidly in main group element chemistry,[3-4] transition-metal chemistry,[5] as well as in the field of catalysis.[6] Furthermore, NHCs have been employed in the stabilization and isolation of low-valent main group element compounds,[7-9] in element–element bond activation reactions,[10] and in the synthesis of NHC-based frustrated Lewis pairs.[11-12] However, it has become increasingly clear that NHCs can undergo ring expansion reactivity (RER) under appropriate conditions.[13-26] Following an initial report by Grubbs in 2006 of nickel insertion into an NHC,[13] Radius,[17-18] Rivard,[15] Inoue,[16] and Hill[14] have described the ring expansion of NHCs through reaction with hydridic E-H bonds of main group element hydride compounds of Be, B, and Si (Figure 1). Following theoretical predictions from our group,[24] the insertion of an aluminium hydride into NHC was recently reported by Hill.[19] Furthermore, ring expansion of a ring-expanded NHC was reported by Hill in 2017.[25]



**Figure 1.** Reported examples of main group element hydride insertion into N-heterocyclic carbenes (NHCs).

Our group[20-25, 27] and others[28-30] have investigated the mechanism of ring expansion of NHCs from theoretical studies, yielding a similar reaction pathway for all element hydrides (Figure 2). A number of factors affecting insertion reactivity have been explored, including steric and electronic parameters of the heterocyclic carbene,[20-21] and the nature of the main-group element hydride.[22-24] The rate-limiting step of the reaction is generally the initial hydride migration from the hydridic E-H bond to the carbene carbon, associated with T1.



**Figure 2**. Generalised reaction mechanism for insertion of main group element hydrides (EH2R*n*, e.g. SiH4, BH2NH2) into N-heterocyclic carbene (NHC).

Modification of the NHC scaffold is an important means to tune its electronic and -donating properties.[31] Replacement of an N atom with C leads to the cAAC framework, which was first isolated by Bertrand in 2005,[32] and has become a widely utilized heterocyclic carbene in both catalysis and main-group chemistry due to its increased -donating and -accepting ability. There has been no report of RER with cAAC, which has been rationalized by theoretical studies as a kinetic effect.[27-28] Our group has explored the potential for ring insertion in analogues of NHC formed by replacement of a single N atom by C, P, O, or S,[27] from which RER is predicted to be feasible for heterocyclic carbenes containing O and S heteroatoms.

The recent isolation of a P-heterocyclic carbene (PHC) (**1**, Figure 3)[31, 33] extends the NHC framework by replacement of both N atoms with P, which has led to a number of theoretical[27, 34-37] studies exploring the properties and reactivity of PHCs. A number of other carbenes containing P in place of nitrogen have been isolated, including both cyclic and non-cyclic amino-phosphinocarbenes (**2**,**3**),[31, 38] phosphinosilylcarbene (**4**),[39] and cyclic azavinylidenephosphoranes (**5**).[40]



**Figure 3.** Isolated heterocyclic carbenes containing phosphorus. Mes = 1,3,5-trimethylphenyl (mesitylene), Dipp = 2,6-diisopropylphenyl.

It is well-established that the unusual stability and -donation properties of NHCs are primarily due to the ability of nitrogen atoms to act as π-donors, which decreases the electron deficiency at the adjacent carbene center.[41] In the cAAC framework donation from N is reduced, leading to the ligand with superior π-accepting ability. The π-donor capabilities of the heavier elements are considered to be as large or even larger than their second row homologues,[42] which suggests a design strategy to identify desirable structural elements of novel PHCs.[43] This new class of ligand displays a high degree of structural versatility when compared to amino carbenes, which may be utilized in tuning the properties and reactivity of the carbene.[44] However, phosphorus centres are strongly pyramidalized, which weakens P-C π-donation compared to the nitrogen centres in planar NHCs.[45]

Tricoordinate pyramidal phosphorus can potentially be planarized by utilizing bulky substituent groups,[46-47] evidenced by the recent isolation of a stable PHC analogous to Enders' NHC using sterically demanding 2,4,6-tri-tert-butyl-phenyl substituents at phosphorus.[48] Such PHCs have been shown to be strong σ-donors towards transition metals, while the electrophilic phosphorus atoms appear to govern the reactivity of the carbenes.[49] Current research is focused on investigating PHCs as catalysts for the activation of single and multiple bonds,[50] with calculations indicating that PHCs have substantially lower activation barriers than NHCs for breaking bonds R–H and C–halogen single bonds, and π-bonds in benzene, ethylene and acetylene. It has been hypothesized that the greater reactivity of PHCs is due to their energetically lower-lying LUMO in comparison with NHCs.[50]

Prompted by the continued discovery of new and novel P-containing heterocyclic carbenes together with the structural versatility of PHCs, it is of interest to explore the properties and reactivity of PHCs. We have considered a series of PHCR (R = H, Me, Ph, Ar) to assess the effect of sterically demanding substituents at phosphorus (Figure 4).[48] A C=N(Me) heterocycle backbone has been utilized, consistent with the PHC isolated by Bertrand. For comparison we have considered an analogous NHCMe compound with the same backbone.

 

PHCR NHCMe

**Figure 4.** PHC and NHC compounds considered in this study (R = H, Me, Ph, Ar).

Here we report the results of a computational investigation of the electronic structure of PHCR compounds, and their propensity to undergo ring-expansion. We have considered boron and silicon hydrides due to these elements being diagonal in the second and third periods of the periodic table (they have similar atomic properties of electronegativity and atomic radii and should behave similarly). It can be expected that the conclusions can be expected to be broadly applicable to other element hydrides.

**Computational details**

Unless noted, gas phase electronic structure calculations were performed using Gaussian 09.[51] Geometry optimisations were carried out to determine both minima and transition state structures using the M06-2X density functional[52] and def2-TZVP basis set.[53-56] For molecules with the larger aryl group the smaller 6-31+G(d) basis set was employed. Harmonic vibrational frequencies were calculated analytically at the same level of theory in order to characterize stationary points as minima or transition states and to evaluate the corresponding thermochemical data within the harmonic limit (standard state of T = 298.15 K and p = 1 atm). Single-point calculations with RI-SCS-MP2[57] and def2-TZVP basis sets were performed within Orca 4.0.1[58-59] using the M06-2X optimized geometries. All tabled RI-SCS-MP2are presented as *G* values, which combine the RI-SCS-MP2/def2-TZVP electronic energies and M06-2X/def2-TZVP thermochemical corrections (M06-2X/6-31+G(d) for P-Ar molecules). For all transition states, intrinsic reaction coordinate (IRC)[60] calculations were carried out to ensure connectivity between the local minima along the reaction pathway. Molecular orbital (MO) and natural bond orbital (NBO)[61-62] analysis was carried out at the BP86/def2-TZVP level of theory.

**Results and discussion**

### 1. Free PHC carbenes

The optimized geometries of the singlet ground state carbenes (PHCH, PHCMe, PHCPh, PHCAr, and NHCMe) with M06-2X/def2-TZVP (Figure 5) are in agreement with previous reported theoretical results, whereby replacement of the nitrogen by phosphorus causes a loss of ring planarity.[24] Each PHC can potentially have four diastereomers due to the two distinct chiral P centres. Negligible differences were found between stereoisomers, and thus only results are for all *(S)* stereoisomers are presented (see ESI for relative energies). Interestingly, PHCPh exhibits a minimum energy structure with the phenyl ring attached to PN being nearly co-planar with the PHC ring, while for PHCAr the phenyl rings are perpendicular to the PHC ring. All attempts to locate a PHCPh minima with perpendicular Ph rings relaxed to the structure in Figure 5.





**Figure 5**. Optimized geometries of PHCH, PHCMe, PHCPh, PHCAr, and NHCMe, illustrating the non-planarity of the PHC ring.

**Table 1**. Structural and electronic properties of free PHCs.a

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Bond distance (Å) | | Bond Angle (o) | | | () b | | H-L gap c | S-T gap d |
| Carbene | C1-PN | C1-PC | PN-C1-PC | N=C-PC-C1 | PC-C=N-PN | PC | PN | (eV) | (eV) |
| PHCH | 1.713 | 1.678 | 99.0 | 10.5 | -14.8 | 347 | 326 | 2.81 | 2.41 |
| PHCMe | 1.718 | 1.665 | 99.3 | 8.6 | -13.3 | 351 | 328 | 2.90 | 2.76 |
| PHCPh | 1.645 | 1.635 | 98.5 | 13.6 | -10.7 | 321 | 358 | 2.61 | 2.56 |
| PHCAr | 1.666 | 1.693 | 98.0 | 8.1 | -8.8 | 351 | 354 | 3.25 | 3.06 |
| NHCMe | 1.370 | 1.339 | 100.2 | 0.0 | 0.0 | 360 | 360 | 4.60 | 4.41 |

a M06-2X/def2-TZVP results except for PHCAr, which are M06-2X/6-31+G(d) results.

b Sum of bond angles around the phosphorus atom.

c HOMO-LUMO (H-L) gap at the BP86/def2-TZVP level of theory (PHCAr is BP86/6-31+G(d)).

d Vertical singlet-triplet (S-T) gap calculated at the singlet state geometry.

From the results in Table 1, the P-substituent has a significant impact on P-C bond distances and the sum of bond angles around the phosphorus atoms (321o to 358o). The P-C1 bond distances in PHCR are longer than the N-C1 distances in NHCMe than, which indicates a stronger donation of the nitrogen lone pair into the vacant carbene orbital compare with those at phosphorus in PHCR. The PC-C=N-PN dihedral angle indicates a tendency for phosphorus to pyramidalize with less bulky substituents (PHCH, PHCMe) that is successively reduced with heavier substituents and (PHCPh, PHCAr) that leads to greater ring planarity. The bulky substituents at the phosphorus atoms tend to adopt a bisected orientation with respect to the plane of the five-membered ring. Pyramidalization is a result of the phosphorus lone pair being less capable of π-donation into the vacant carbene p-orbital than is the case with nitrogen. The electrophilicity of PHCs strongly depends on pyramidalization at the carbene centre, which will subsequently be expected to be influenced by different P substituents.

The electronic stability of the PHCs is also reduced compared to NHCMe, with smaller HOMO-LUMO (H-L) gaps and singlet-triplet (S-T) gaps. The results are consistent with other research,[63] which found that the LUMO orbital is energetically lower-lying in PHCR compared to NHCR. Interestingly, both the H-L and S-T gaps both generally increase with increasing substituent bulk. Here PHCPh is an outlier as a result of the LUMO energy being stabilised relative to the other PHCs. The largest aryl substituent produces the most stable PHCR ligand (largest H-L and S-T gaps), which in general correlates with heavier substituents leading to greater ring planarity (and greater delocalisation of electron density in the ring).

Closer inspection of the MOs illustrates the electronic structure of PHCs and their difference to NHCs (Table 2). It is well known that the HOMO of NHC is a directional σ-donor MO (rationalizing NHCs as strong -donors), however with the exception of PHCMe, for PHCR the carbene σ-donor MO is a lower-lying HOMO-1 orbital. PHCMe is the exception with a σ-symmetry HOMO (see ESI). Moreover, while the HOMO-1 of NHCMe has π-character delocalized on the ring, with PHCR the analogous MO is predominantly a P-centred lone-pair. The energy gap between HOMO and HOMO-1 is 1.20 eV with NHCMe, but is smaller for PHCH (0.52 eV) and monotonically decreases with larger substituents to PHCAr (0.14 eV). The LUMO of NHCs is a π-symmetry MO located on the carbene carbon (C1, Figure 4), which rationalizes the strong π-accepting character of NHCs. For PHCR, the LUMO is similarly associated with the empty carbene π-symmetry MO for the smaller substituents, however in PHCAr the accepting carbene π-symmetry MO is actually the LUMO+2 orbital. Hence, while bulky P-substituents are required to stabilize and planarize the PHC, it would appear that one consequence is a loss of π-accepting character.

**Table 2**. BP86/def2-TZVP molecular orbitals of NHCMe and PHCR (R = H, Me, Ph, Ar).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | NHCMe | PHCH | PHCMe | PHCPh | PHCAr |
| LUMO |  |  |  |  |  |
| HOMO |  |  |  |  |  |
| HOMO-1 |  |  |  |  |  |

**2. Ring expansion reactivity**

The RER mechanism of PHCR with main-group hydrides was postulated to be similar to that for NHC (Figure 2). The nature of the RER is expected to depend on numerous factors, including the Lewis-acidic element hydride and substituents on main group element hydride.[20-24] The discussion that follows is organised to consider reactivity of PHCR with each of SiH4, SiH2Ph2, BH3, and BH2NMe2 element hydrides.

Results for the RER of SiH4 with PHCR are presented in Figure 6 as reaction coordinate potential energy plots (note that A refers to the free reactants). Cartesian coordinates and energies of each species are given in the Supporting Information. One key difference between the RER mechanism of PHCs and NHCs is that the initial NHC-SiH4 adduct A (Figure 2) is not located with PHCs. Rather, initial adduct formation and H-migration from the silane to the NHC carbene-carbon atom occur together in a concerted step (T1). This trend has been noted previously for PHCH and a mixed-PN heterocyclic carbene.[27, 63] The character of the T1 complexes are considered in detail later. The potential energy reaction coordinates for the PHCs are similar with the exception of PHCAr, which is potentially related to the different geometry of free PHCAr, and the increased steric bulk relative to PHCPh. For NHCs, the rate-determining step is calculated to be T1, however with PHCs the largest barrier is calculated for T2 (PHCH, PHCMe, PHCPh) or T3 (PHCAr). The initial step for reaction of SiH4 with PHCH, PHCMe, PHCPh, and PHCAr requires considerable energy of 110.4, 124.4, 117.5, 157.4 kJ/mol, respectively, although it is generally less than 156.5 kJ/mol calculated for NHCMe. The largest barriers for PHCs (T2 or T3) are above 200 kJ/mol, which indicates that ring-expansion to produce a six-membered ring (D) is not kinetically feasible, despite the overall reaction being thermodynamically favoured.

**Figure 6**. Insertion pathway for SiH4 with PHCR (R = H (blue), Me (green), Ph (yellow) and Ar (orange)) and NHCMe (red). RI-SCS-MP2/def2-TZVP//M06-2X/def2-TZVP calculated relative free energies (kJ/mol); PHCAr results are RI-SCS-MP2/def2-TZVP//M06-2X/6-31+G(d).

Reaction of PHCs with SiH2Ph2 was subsequently investigated, since it has previously been noted that SiH4 provides an upper bound of barriers compared to the experimentally relevant SiH2Ph2.[21-22] Plots of the reaction coordinate energy are given in Figure 7, with the PHCAr system omitted due to the computational expense. Here the additional phenyl groups on the silicon centre cause a reduction in the energy barriers compared to SiH4 – the T1 barriers are 103.4, 120.7, and 96.4 kJ/mol for PHCH, PHCMe, and PHCPh, respectively. The T1 barriers with PHCs are all smaller than the 133.6 kJ/mol calculated for NHCMe, which mirrors the results for SiH4 that initial hydride-transfer is more favourable for PHCs than NHCs. However, the largest barrier remains the T2 barrier, which is above 170 kJ/mol for all PHCs considered here. These barriers are too large to expect subsequent RER leading to isolation of a six-membered ring, and hence minimum B is the expected product for the reaction of PHCs with silanes.

**Figure 7**. Insertion pathway for SiH2Ph2 with PHCR (R=H (blue), Me (green) and Ph (yellow)) and NHCMe (red). RI-SCS-MP2/def2-TZVP//M06-2X/def2-TZVP calculated relative free energies (kJ/mol).

The stability and electronic structure of the first transition state complexes (T1) of PHCR with both silane substrates was additionally investigated with natural bond orbital (NBO) analysis. For comparison, Wiberg bond indices (WBI), important geometrical parameters, and barrier heights are collated in Table 3. As noted above, with NHCs (Figure 2) an initial NHC-EH2Rn adduct forms with a C-Si bond subsequently leading to T1 (H-migration from Si to C), which is reflected in the C-Si, Si-H, and C-H bond distances in T1 with NHCMe all three being quite similar for SiH4 (1.82-1.88 Å) and SiH2Ph2 (1.68-1.87 Å). Moreover, the WBI values for C-Si bonds are 0.75-0.77, which reflects the appreciable C-Si bonding with NHCMe. For PHCR, the R substituent has a significant influence on the character of T1.

For the lighter R (H, Me) T1 exhibits a quasi-linear C-H-Si framework without a C-Si bond, evidenced by the C-Si distance being *ca*. 3 Å (WBI < 0.2) and close to the sum of the C-H and Si-H bond distances. However, with the increased steric bulk of the PHCAr shorter C-Si bonds of 2.02 Å (SiH4) and 2.18 Å (SiH2Ph2) are obtained that are much closer to the Si-C distance of 1.87-1.88 Å calculated for NHCMe. The longer C-Si bond in the PHCAr-SiH2Ph2 system (compared to SiH4) arises from steric repulsion between the bulky phenyl groups located on both the PHC and silane. The results for PHCPh further support this analysis. Despite the significant steric bulk of the Ph substituents on P, the co-planarity of one of the Ph groups and the heterocycle allows PHCPh to behave similarly to PHCMe in its interaction with the smaller SiH4 substrate. However, with a bulkier SiH2Ph2 substrate the PHCPh moiety cannot avoid steric repulsion and so in T1 the structure is different to PHCMe, with weaker a C-H bond and stronger C-Si bond analogous to the case of PHCAr with SiH4.

**Table 3**. Bond distances and Wiberg bond index (WBI) analysis of T1 structure in the reaction of PHCR with SiH4 and SiH2Ph2.a

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | *r*(C-H) | | *r*(Si-H) | | *r*(C-Si) | | Δ*G* (T1) |
|  | (Å) | WBI | Å | WBI | (Å) | WBI | kJ/mol |
| **SiH4** |  |  |  |  |  |  |  |
| PHCH | 1.707 | 0.22 | 1.524 | 0.73 | 3.008 | 0.14 | 110.4 |
| PHCMe | 1.503 | 0.37 | 1.571 | 0.58 | 2.885 | 0.18 | 124.4 |
| PHCPh | 1.512 | 0.36 | 1.571 | 0.58 | 2.891 | 0.18 | 117.5 |
| bPHCAr | 1.745 | 0.29 | 1.601 | 0.51 | 2.021 | 0.28 | 157.4 |
| NHCMe | 1.823 | 0.31 | 1.819 | 0.33 | 1.878 | 0.77 | 156.5 |
| **SiH2Ph2** |  |  |  |  |  |  |  |
| PHCH | 1.781 | 0.23 | 1.521 | 0.69 | 3.073 | 0.13 | 103.4 |
| PHCMe | 1.699 | 0.27 | 1.531 | 0.65 | 3.021 | 0.14 | 120.7 |
| PHCPh | 1.973 | 0.19 | 1.544 | 0.67 | 2.177 | 0.40 | 96.4 |
| NHCMe | 1.683 | 0.38 | 1.870 | 0.24 | 1.872 | 0.75 | 133.6 |

a M06-2X/def2-TZVP geometries with BP86/def2-TZVP calculated WBI.

b M06-2X/6-31+G(d) geometries with BP86/def2-TZVP calculated WBI.

The RER properties of PHCs was expanded to consider reactions with boranes (BH3, BH2NMe2), which have not previously been investigated. It has previously been demonstrated with NHCs that calculated results for BH3 represent an upper bound of barrier heights for RER of experimentally relevant BH2NHR species.[24] Here we only considered PHCMe and PHCPh as model PHC systems. The reaction energy profiles for the reaction of PHCMe and PHCPh with the two boranes are plotted in Figure 8. Analogous to the silane mechanism, no initial adduct structure could be located. Rather, adduct formation and hydride transfer (from B-H to carbene C1) occurs together in a concerted manner. For PHCMe, the initial barrier (T1) for both BH3 (36.7 kJ/mol) and BH2NMe2 (23.1 kJ/mol) is very low and would likely be overcome under mild temperatures (room temperature). With PHCPh, the bulkier P-substituent has negligible impact on the initial barrier with the BH3 substrate, however with the bulkier BH2NMe2 the barrier increases above 100 kJ/mol, which reflects the greater steric repulsion. The subsequent minima structures (B) are very stable for all reactions, being over 200 kJ/mol lower in energy than the free reactants. The barriers for ring-expansion (T2) are *ca*. 200 kJ/mol, which are kinetically unfeasible and thus make ring expansion unlikely for PHCR with both boron and silicon hydride.



**Figure 8**. General insertion pathway for BH2X. BH3 with PHCMe (blue) and PHCPh (orange), and BH2NMe2 with PHCMe (grey) and PHCPh (yellow). RI-SCS-MP2/def2-TZVP//M06-2X/def2-TZVP calculated relative free energies (kJ/mol).

**Conclusions**

A theoretical investigation of PHCs formed by the replacement two nitrogen atoms of NHCs by phosphorus atoms. It is found that PHCR have a non-planar configuration that leads to smaller HOMO-LUMO gaps than NHCMe, and *σ*-donor electronic density that is concentrated in HOMO-1 orbital. Increasing the steric bulk of the R group forces the heterocycle towards planarity. The ability of PHCR to participate in ring expansion reactivity was examined by consideration of silane and boranes substrates. A mechanism that is similar to that with NHC is predicted, with several notable differences. With all PHCs (independent of steric bulk of the P-substituent), initial PHC-substrate adduct formation and first hydride migration occurs together in a concerted manner in contrast to the two-step process with NHCs. The barrier for this initial step is typically smaller with PHCs than with NHCs. However, the T2 barrier associated with ring-opening is significantly greater with PHCs than for NHCs and is concluded to be kinetically unfavourable for PHCR with all SiH4, SiH2PH2, BH3, and BH2NMe2­ substrates that were investigated. Hence, while successively increasing the steric bulk of the P-substituent yields increased planarity of the PHC heterocycle, it is insufficient to alter the ring-expansion reactivity properties of PHCs to allow ring insertion to become favourable as is the case with NHCs.

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