Carbene insertion into a P−H bond: Parent phosphinidene-carbene ad-ducts from PH3 and bis(phosphinidene) mercury complexes

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Carbene insertion into a P–H bond: Parent phosphinidene-carbene adducts from PH₃ and bis(phosphinidene) mercury complexes

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1   Table of contents entry

The insertion of an *N*-heterocyclic carbene into a P–H bond is the first step in a new synthesis of parent phosphinidene-carbene adducts from PH₃. These adducts are used to generate bis(phosphinidene) mercury(II) complexes.
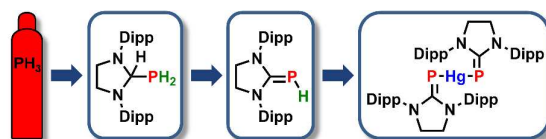
2   Abstract

PH₃ reacts with the *in situ* generated *N*-heterocyclic carbene DippNHC* (DippNHC* = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene) to give the phosphanyl-imidazolidine [^{Dipp}NHC*-H]-[PH₂]. Upon treatment with an ortho-quinone, [^{Dipp}NHC*-H]-[PH₂] is dehydrogenated to give the parent phosphinidene-carbene adduct ^{Dipp}NHC*=PH. Alternative routes to [^{Dipp}NHC*-H]-[PH₂] and ^{Dipp}NHC*=PH employ NaPH₂ and (TMS)₃P₇ (TMS = trimethylsilyl), respectively, as phosphorus sources. The adduct ^{Dipp}NHC*=PH and the related adduct ^{Dipp}NHC=PH (^{Dipp}NHC = bis(2,6-diisopropylphenyl)imidazol-2-ylidene) possessing an unsaturated NHC backbone both react with HgCl₂ to give the bis(carbene-phosphinidenyl) complexes [(^{Dipp}NHC*=P)₂Hg] and [(^{Dipp}NHC=P)₂Hg].

3   Introduction

Phosphorus can be regarded as a "carbon copy" due to the carbon-phosphorus diagonal relationship. Indeed there is some similarity between the chemistry of low coordinate phosphorus and unsaturated carbon compounds,[1] but there are significant differences. Whereas some free carbenes are relatively persistent compounds and can be isolated in substance if they possess a singlet ground state,[2] the phosphorus analogues, phosphinidenes, eluded isolation so far. This is likely due to the fact that phosphinidenes much prefer a triplet ground state and oligomerize to cyclophosphanes in

an almost barrier-less reaction, n R–P → (RP)$_n$, even in the presence of trapping reagents.[3] The singlet ground state of phosphinidenes can be stabilized by strong π-donor substituents (R = -NR$_2$, -N=CR$_2$, -PR$_2$, -SR) and although these compounds have the best chance of being isolated, no stable derivative is known to date.[4] In 1997, Arduengo and co-workers showed that substituted phosphinidenes can be stabilized by adduct formation with N-heterocyclic carbenes (NHC).[5,6] Recently, Bertrand and co-workers used the ^{31}P-NMR shifts of such NHC=PR adducts as an indicator of the π-accepting properties of the NHC.[7] They observed that adducts with saturated NHCs bearing a CH$_2$–CH$_2$ bridge between the two nitrogen centers in the ring as in ^{Dipp}NHC* show less shielded ^{31}P-NMR resonances (by approximately Δδ = 9 ppm) than those with an unsaturated CH=CH bridge as in ^{Dipp}NHC (see Figure 1). This phenomenon is attributed to the better π-accepting property of saturated NHCs.[7]

The nature of the parent NHC=PH adducts has been investigated using theoretical methods,[8] but experimental data was reported only recently. Robinson and co-workers were able to obtain carbene-stabilized diphosphorus **1** by reduction of the NHC→PCl$_3$ adduct with potassium graphite[9] and further reduction with lithium metal afforded the lithiated parent phosphinidene-carbene adduct **2** (Figure 1).[10] Similarly, Bertrand and co-workers described a diphosphorus fragment stabilized by cyclic (alkyl)(amino)carbenes (CAAC) and its one-electron oxidations, giving rise to a stable P$_2$-radical cation.[11]

The first parent phosphinidene-carbene adduct **3** was prepared by Driess and co-workers employing H–P transfer from a phosphasilene to a NHC.[12] Our group published the facile synthesis of **3** from the easily accessible phosphorus sources (TMS)$_3$P$_7$ or Na(OCP) and the corresponding imidazolium salt.[13] Tamm and co-workers described an alternative route to **3** using P(TMS)$_3$ as a phosphorus source and a difluoroimidazoline to generate the carbene-P(TMS) adduct **4**, followed by desilylation in methanol. Starting from **4**, they have also been able to generate carbene-phosphinidene ruthenium and rhodium complexes.[14]
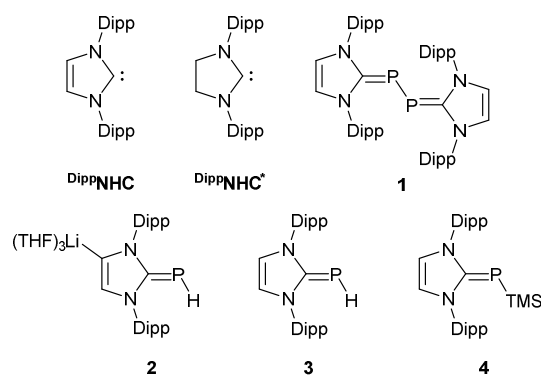
Figure 1: Unsaturated and saturated N-heterocyclic carbenes and known phosphinidene-carbene adducts (Dipp = 2,6-diisopropylphenyl).

Building upon our preliminary results, we were interested in exploring alternative synthetic routes into phosphinidene-carbene adducts. Bearing in mind the low atom-efficiency of some of the phosphorus sources employed so far, we decided to investigate the use of phosphine gas. PH_3 has been shown to be a versatile precursor for the atom-efficient synthesis of organophosphorus compounds.[15] However, the reactivity of PH_3 towards imidazolium salts and NHCs has not been investigated previously. Herein, we describe the insertion of a carbene into a P–H bond, giving access to a phosphanyl-imidazolidine, which upon dehydrogenation yields the NHC=PH adduct in high yield. Furthermore, we describe bis(carbene-phosphinidenyl)mercury(II) complexes.

4   Results and Discussion

4.1   Formation of the phosphanyl-imidazolidine from PH_3

We have studied the reactivity of different NHCs towards PH_3. The NHCs were generated *in situ* from the corresponding imidazolium salt and sodium *tert*-butoxide in THF.[16] A suspension of the imidazolium salt **5** and sodium *tert*-butoxide in THF was exposed to PH_3 for several hours and the reaction followed by ^{31}P-NMR spectroscopy. Whereas the unsaturated ^{Dipp}NHC showed no reactivity, the saturated ^{Dipp}NHC* was cleanly converted to a single product (see Figure 1 for a definition of the abbreviations ^{Dipp}NHC and ^{Dipp}NHC*). Upon evaporation of the solvent and extraction of the product with *n*-hexane, a white powder was obtained and identified as the phosphanyl-imidazolidine [^{Dipp}NHC*-H]-[PH$_2$] (**6b**), which is the result of the insertion of the carbene into the P–H bond of PH_3 (Scheme 1a, left; spectroscopic yield: 100%, isolated: 64%). The insertion of NHCs and CAACs into a P–H bond of phenylphosphane and diphenylphosphane has been demonstrated previously by Bertrand and co-workers,[17] but this is the first report of this rare type of reactivity with a P–H bond of PH_3. The ^{31}P-NMR spectrum exhibits a triplet of doublets at $\delta = -139.7$ ppm, a $^1J_{PH}$ coupling of 187 Hz and a $^3J_{PH}$ coupling of 15 Hz. An alternative route to **6b** is a reaction between the sodium *tert*-butoxide/ sodium dihydrogenphosphide aggregate

$\{[Na(O^tBu)]_x[Na(PH_2)]\}$ (x ≈ 2.5)[18] and the imidazolium chloride **5b** in which **6b** could be isolated as the sole product in 80% yield (Scheme 1a, right). Similar to the reaction with PH_3, exposure of the unsaturated imidazolium chloride **5a** to $\{[Na(O^tBu)]_x[Na(PH_2)]\}$ (x ≈ 2.5) did not give the desired unsaturated [^{Dipp}NHC-H]-[PH_2] (**6a**) but as of yet unidentified phosphorus containing products. These results suggest that the more strongly basic saturated carbene obtained by deprotonation of **5b** interacts first with PH_3 via a C···H–P bridge followed by simultaneous proton transfer and addition of the PH_2^- unit to the carbon center. A related mechanism was computed for the interaction of imidazolium salts with the OCP^- anion.[13] Single crystal X-ray diffraction was used to unambiguously identify the compound (Figure 2).
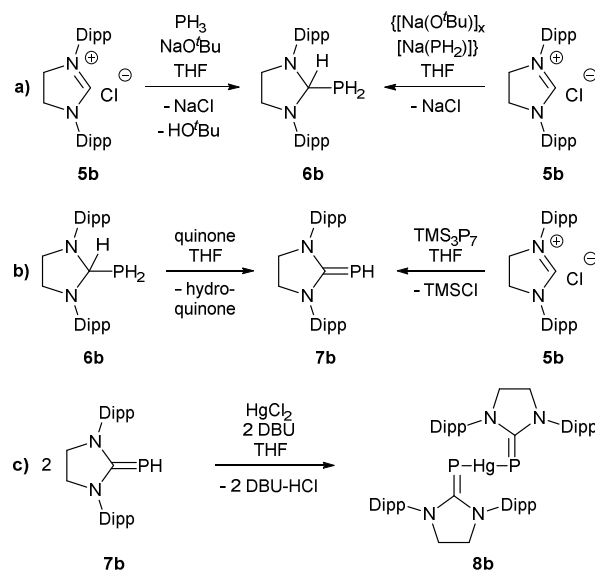
Scheme 1: a) Synthesis of [^{Dipp}NHC*-H]-[PH_2] (**6b**) using either PH_3 (left) or $\{[Na(O^tBu)]_x[Na(PH_2)]\}$ (x ≈ 2.5) (right) as a phosphorus source. b) Synthesis of ^{Dipp}NHC*=PH (**7b**) from **6b** and 9,10-phenanthrenequinone (left) and from [^{Dipp}NHC*-H]-[Cl] (**5b**) and (TMS)$_3$P$_7$ (right). c) Synthesis of the mercury complex [Hg(^{Dipp}NHC*=P)$_2$] (**8b**) from **7b**. [Hg(^{Dipp}NHC=P)$_2$] (**8a**) is synthesized from ^{Dipp}NHC=PH (**7a**) in the same fashion.
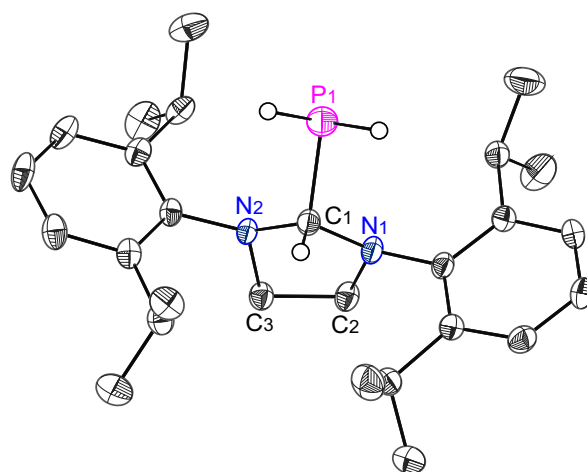
Figure 2: ORTEP plot of [$^{\text{Dipp}}$NHC*-H]-[PH$_2$] (**6b**). Hydrogen atoms apart from the phosphorus and the carbene-C bound hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

4.2 Dehydrogenation to the phosphinidene-carbene adduct

Dehydrogenation of [$^{\text{Dipp}}$NHC-H]-[PH$_2$] (**6b**) to the parent phosphinidene-carbene adduct $^{\text{Dipp}}$NHC*=PH (**7b**) was achieved using an ortho-quinone as a hydrogen acceptor. Upon exposure of **6b** to 9,10-phenanthrenequinone in THF, it was converted quantitatively to **7b** (Scheme 1b left, isolated yield: 77%). Alternatively, the compound could be obtained from (TMS)$_3$P$_7$ and the imidazolium salt analogous to the unsaturated $^{\text{Dipp}}$NHC=PH (**7a**) as described previously.[13] However, whereas **6b** is easily dehydrogenated to **7b**, exposure of **7a** and **7b** to a hydrogen pressure of 4 bar did not lead to the reformation of the phosphanyl-imidazolidine species.

$^{\text{Dipp}}$NHC*=PH (**7b**) exhibits a resonance in the ^{31}P-NMR spectrum as a doublet at $\delta = -116.7$ ppm and a $^1J_{\text{PH}}$ coupling of 162 Hz, corroborating the presence of a P–H bond. This corresponds to a shift of $\Delta\delta = 20.0$ ppm to higher frequencies as compared to **7a** ($\delta = -136.7$ ppm), relating to the increased π-accepting properties of the saturated NHC.[7] Single crystals of **7b** were investigated by X-ray diffraction, which allowed to determine the structure (Figure 3). Selected bond lengths and angles of **7a**[13] and **7b** are listed in comparison to those of **6b** in Table 1.

The significant contraction of the C$_1$–P$_1$ bond from 1.885(2) Å in the phosphanyl species **6b** to 1.743(2) Å in the phosphinidene species **7b** is attributable to the double bond character of the C=P bond and change of the valence electron configuration at the carbon center C$_1$ from sp^3 to sp^2 in **7b**. A comparatively long P–C bond (1.871(1) Å) is also seen in $^{\text{Dipp}}$NHC→PCl$_3$, which has a P–C single bond as well[10] (see Table 2 in the ESI for a listing of the structural parameters of various free NHCs and NHCs bound to phosphorus centers). The C$_1$–P$_1$ bond distance (1.743(2) Å) and the N$_1$–C$_1$–N$_2$ bond angle (107.4(2)°) of the PH adduct **7b** are very similar to those of the PPh adduct $^{\text{Mes}}$NHC*=PPh ($^{\text{Mes}}$NHC* = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene; C$_1$–P$_1$ = 1.754 Å,

N1–C1–N2 = 107.41°)[5] and other phosphinidene type adducts with N-heterocyclic carbenes (see Table 2 in ESI). The formation of the NHC=PH adduct leads to an increase of the N1–C1–N2 bond angle by 2.343° from 105.0(1)° in the free carbene ^{Dipp}NHC*[19] to 107.4(2)° in **7b**, which is similar to the increase of 2.87° from 101.4° in ^{Dipp}NHC[16] to 104.3(1)° in **7a**.[13] This widening of the N1–C1–N2 angle simply reflects the change from a non-bonding electron domain at C1 in the free carbenes to a partially double bonding domain in **7a** and **7b**. The slightly larger N1–C1–N2 angle in the saturated adduct **7b** (107.4(2)°) as compared to the unsaturated adduct **7a** (104.3(1)°) is a consequence of the C2H2–C3H2 bridge, which causes longer C2–N1 and C3–N2 bonds and is observed likewise in the free carbenes.[16,19] The C1–P1 bond distances in **7a** and **7b** are identical within the experimental error. Consequently, a comparison of the structural data of **7a** and **7b** does not reflect the different electronic properties of the unsaturated versus saturated NHCs.
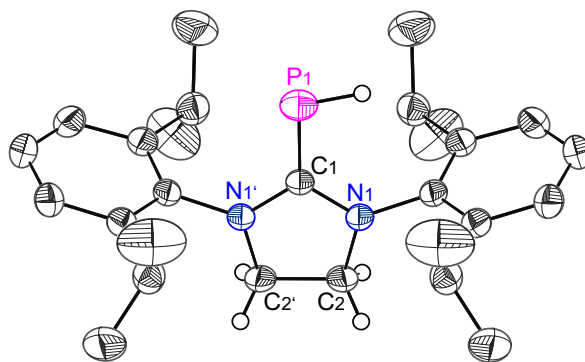

Figure 3: ORTEP plot of ^{Dipp}NHC*=PH (**7b**). Hydrogen atoms apart from the phosphorus and C–C bound hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 1: Comparison of selected bond lengths and angles of [^{Dipp}NHC-H]-[PH2] (**6b**), ^{Dipp}NHC=PH (**7a**),[13] ^{Dipp}NHC*=PH (**7b**), [(^{Dipp}NHC=P)2Hg] (**8a**) and [(^{Dipp}NHC*=P)2Hg] (**8b**). [a] Bond length given in Å. [b] Bond angle given in °.

	6b	7a	7b	8a	8b
C1–P1[a]	1.885(2)	1.752(1)	1.743 (2)	1.755(2)	1.754(6)
P1–Hg1[a]	---	---	---	2.399 (1)	2.407(1)
N1–C1[a]	1.454(2)	1.373(1)	1.357 (2)	1.384(2)	1.380(7)
N2–C1[a]	1.456(2)	1.373 (1)		1.384(2)	1.384(7)
C2–C3[a]	1.526(2)	1.341 (2)	1.511(3)	1.338(3)	1.518(8)
N1–C1–N2[b]	101.5(1)	104.3(1)	107.4(2)	103.6(1)	106.5(5)
C1–P1–Hg1[b]	---	---	---	103.6(1)	104.3(2)

4.3   Mercury complexes

The formation of the mercury complexes [(^{Dipp}NHC=P)$_2$Hg] (**8a**) and [(^{Dipp}NHC*=P)$_2$Hg] (**8b**) was achieved by slowly adding HgCl$_2$ to a solution of the phosphinidene-carbene adducts **7a** or **7b** in THF in the presence of two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Extraction with toluene afforded **8a** and **8b** as yellow, crystalline solids in over 60% yield. The bis(carbene-phosphinidenyl)mercury compounds showed singlet resonances at –56.0 ppm (**8a**) and –32.3 ppm (**8b**) respectively in the ^{31}P-NMR spectrum. This corresponds to a shift in the ^{31}P-NMR resonance of about 80 ppm to higher frequencies upon replacement of the P–H bonds by P–Hg bonds. The ^{13}C-NMR signal for the carbene carbon C1 was not detected in a standard ^{13}C-NMR experiment, but ^{13}C-HMBC experiments revealed the C1 signals in **8a** and **8b** as broad doublets at 181.8 ppm and 197 ppm with P–C couplings of 128 Hz and 256 Hz, respectively.

The solid state structures of both mercury compounds were determined by single crystal X-ray diffraction (Figure 4). Both compounds show very similar structures**Error! Reference source not found.**. The mercury centers are coordinated linearly by two phosphinidene-carbene units. There are examples of mercury(II) bis(phosphido)[20,21] and bis(phosphane) complexes;[22,23–25] however, to the best of our knowledge, these are the first examples of bis(phosphinidene) mercury compounds. Comparisons of selected bond lengths and angles of the mercury complexes and the phosphinidene-carbene adducts they are derived from are presented in Table 1.

The lengths of the Hg–P bonds (**8a**: 2.399(1) Å; **8a**: 2.407(1) Å) are in range of Hg–P bonds observed in linear Hg(II) phosphanes, [Hg(PR$_3$)$_2$][23,24,26] or Hg(II) phosphides, [Hg(PR$_2$)$_2$],[21,25] (see Table 3 in ESI). The C1–P1 distances and C1–N1–C2 angles in **8a**, **8b** are identical to the ones in **7a**, **7b** within experimental error. That is the exchange of hydrogen in **7a**, **7b** to Hg(II) in **8a**, **8b** has no significant structural consequences. On the other hand, the C–P bonds in the transition metal complexes [(^{Dipp}NHC=P)Rh(Cp*)Cl] and [(^{Dipp}NHC=P)Ru(η^6-p-cymene)Cl] are significantly longer (approximately 1.82 Å, see Table 2 in the ESI), which indicates significant σ- and π-electron donation from phosphorus to empty orbitals at the metal center consequently elongating the C–P bonds.[14]
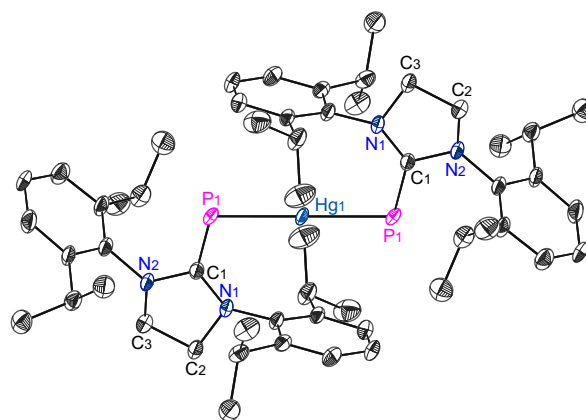
Figure 4: ORTEP plot of [($^{\text{Dipp}}$NHC*=P)$_2$Hg] (**8b**). Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. For the ORTEP plot of [($^{\text{Dipp}}$NHC*=P)$_2$Hg] (**8b**) see Figure 3 in the ESI.

5 Conclusion

By utilizing PH$_3$ as a phosphorus source the phosphanyl-imidazolidine **6b** has been synthesized. Dehydrogenation yields the parent phosphinidene-carbene adduct **7b** in good yield. The reactivity of NHCs towards PH$_3$ depends strongly on their electronic properties, specifically the nucleophilicity of the carbene is pivotal in the P–H insertion step. Furthermore, the first bis(phosphinidene) mercury(II) complexes were synthesized and structurally characterized. The structural data of **7a** and **8a** with an unsaturated NHC and of **7b** and **8b** with a saturated NHC do not allow distinguishing between the electronic properties of the NHC moieties. However, a comparison of the structures of the mercury compounds **8a**, **8b** with those of transition metal complexes with NHC=P ligands clearly reflects that these act as electronically flexible ligands, which may be exploited in the future in order to tune the reactivity of such compounds.

6 Acknowledgements

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