Main-Group Chemistry

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Abnormal Reactivity of an N-Heterocyclic Carbene (NHC) with a Phosphaalkene: A Route to a 4-Phosphino-Substituted NHC**

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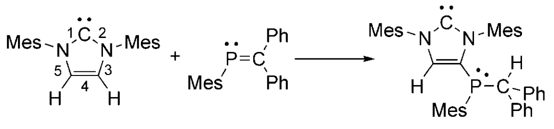
The development of "bottleable" uncomplexed carbenes is a landmark achievement[1] that has prompted a surge of interest in the study of the properties and reactivity of these once-elusive species.[2] Perhaps the most widely studied are the N-heterocyclic carbenes (NHCs), in which the divalent carbon moiety is flanked by two π-donor nitrogen atoms within a five-membered N_2C_3 heterocycle. As a consequence of the strong σ-donating and weak π-accepting properties of NHCs, they are, like phosphines, excellent ligands for d-block metals. Much of the interest in NHC–metal complexes has been driven by the fact that they are highly effective in catalyzing organic transformations. Although not as extensively studied, the role of NHCs in p-block chemistry has recently been the subject of increased attention.[2c,3–6]

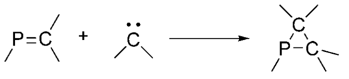
One general characteristic of NHCs is their tendency to bind electrophiles at the 2-position of the N_2C_3 ring (that is, at the carbene center). Given the vast body of research regarding NHCs over the past two decades, they are rarely observed to react at any other position. Nonetheless, the so-called abnormal NHCs, for which reactions occur at the 4- or 5-positions, are reasonably well-established in d- and f-block chemistry.[7,8] In contrast, the abnormal behavior of an NHC in p-block chemistry is rarely observed, especially when the 2-position is not blocked or bound to a metal.[9–12] The prospect of directly functionalizing a free NHC at the 4- and 5-positions with p-block moieties is exciting as it could enable the synthesis of ligands with unique electronic and coordination properties.

Herein, we report the unexpected abnormal reaction of the unprotected NHC, 1,3-dimesitylimidazol-2-ylidene (IMes, **1**), with the phosphaalkene, MesP = CPh_2 (**2**). The product **3** is the first reported NHC bearing a phosphine at the 4-position, and furthermore, is a novel bifunctional ligand. Remarkably, free carbene **1** reacts exclusively with **2** at the 4-position leaving the divalent 2-position intact in the product.

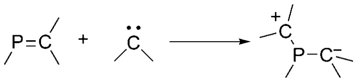


1 **2** **3**

Our interest in the addition polymerization reactions of P=C bonds prompted us to thoroughly investigate the reactions of phosphaalkenes with potential initiators. P=C bonds have been polymerized successfully using radical or anionic initiators.[13] The potential cationic polymerization of P=C bonds is particularly intriguing owing to the putative involvement of a phosphenium cation (R_2P^+) as the propagating species.[14] We have previously reported that treating *t*BuP=CH*t*Bu (2 equiv) with trifluoromethanesulfonic acid affords an asymmetric diphosphiranium cation containing a P_2C heterocycle.[15] The mechanism is believed to involve the formal cycloaddition of the phosphenium triflate *t*Bu(*t*BuCH_2)POTf to the P=C bond. Given that the phosphenium ion (R_2P^+) and carbene (R_2C) are isovalent, we postulated that a similar cycloaddition reaction may be observed when a phosphaalkene is treated with a carbene [Eq. (1a)]. Phosphaalkenes are known to react with fleeting carbenes to afford phosphiranes,[16] however their reactions with NHCs have not been reported.[17] An alternative to cyclization involves the nucleophilic addition of an NHC across the P=C bond to generate a zwitterionic species [Eq. (1b)], in much the same way as has been observed for anionic polymerization. Some multiple-bond-containing phosphorus compounds, such as phosphaalkynes[18] and iminophosphines,[19] are known to react in this way with NHCs, although in the case of phosphaalkynes, subsequent cyclizations are often observed.



(1a)



(1b)

To examine the reaction of a phosphaalkene with an N-heterocyclic carbene, IMes (**1**) and MesP=CPh_2 (**2**) were dissolved in THF and heated for several hours. Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed that the signal for the starting material **2** ($\delta = 233$ ppm) was no longer present, and had been replaced by one signal at -37.3 ppm. The upfield chemical shift suggests that the P=C bond in **2** was

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no longer present following treatment with **1**. At first glance, this may suggest that the phosphorous atom is in a similar chemical environment to Mes(Me)P–CPh_2Li ($\delta = -44.3$ ppm),[20] and possibly a zwitterionic species is formed [Eq. (1b)]. However, close examination of the ^1H NMR spectrum ruled out this possibility, as the signal assigned to vinylic protons of the C_3N_2 ring integrated for one, rather than two, hydrogen atoms. Perhaps most enlightening was the $^{13}C\{^1H\}$ NMR spectrum, which clearly showed a doublet at 220.3 ppm ($^3J_{CP} = 4.5$ Hz). Remarkably, this observation suggested that that the free carbene moiety was still present after the reaction.

Single-crystal X-ray crystallographic analysis confirmed that phosphaalkene **2** had effectively inserted into the C–H bond at the 4-position of carbene **1** to afford the phosphine-substituted NHC **3** (Figure 1).[21] Interestingly, the presence of the bulky phosphine moiety slightly perturbs the bond lengths and angles within the NHC heterocycle compared to IMes.[22] For example, the C4-C3-N2 angle in the product (104.4(2)°) is smaller than that in IMes (106.5(3)°); this contraction is accompanied by an expansion of the exocyclic angles at C3. Furthermore, the C3–N2 bond length in **3** is slightly elongated with respect to that in IMes (1.406(2) versus 1.378(4) Å). Despite the steric congestion within this molecule, the P–C bond lengths are at the shorter end of the typical range for P–C bonds and the analogous bonds in the model system Mes(Me)P–$CHPh_2$.[20]

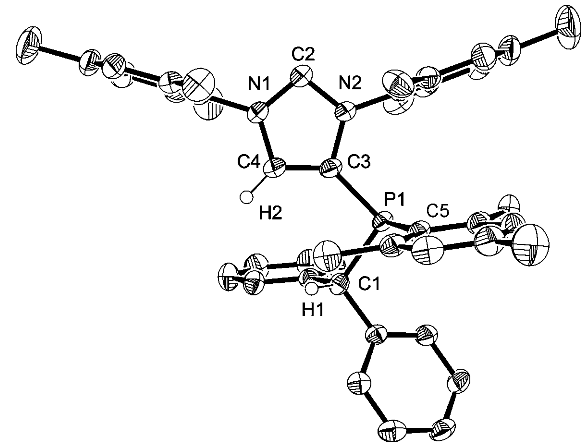

Figure 1. ORTEP of **3** (thermal ellipsoids set at 50% probability). The partial benzene atoms, and all hydrogen atoms except H1 and H2, are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.869(2), P1–C3 1.816(2), P1–C5 1.846(2), C2–N1 1.363(2), C2–N2 1.366(3), C4–N1 1.388(2), C3–N2 1.406(2), C3–C4 1.349(3); N1-C2-N2 101.2(2), C3-C4-N1 107.2(2), C4-C3-N2 104.4(2), N1-C4-C3-P1 169.7(2).

The mechanism of this unanticipated reaction between an NHC and a phosphaalkene is puzzling, and we therefore employed DFT calculations[23] to gain some insight into the possible intermediates formed in this transformation. Three plausible mechanisms were considered; the first involves initial normal nucleophilic addition of **1** to the P=C bond of **2**, followed by proton migration and subsequent rearrangement to **3** (Figure 2, path 1). This type of mechanism is believed to be involved in the selective chlorination of IMes at the 4- and 5-positions by CCl_4.[9] A second plausible mechanism involves initial proton migration within **1** to generate an abnormal carbene, which then adds across the P=C bond of **2**, and finally proton migrations within the ring afford **3** (Figure 2, path 2). A third mechanism was also considered that involves formal addition of an enamine resonance form of IMes (a formal positive charge on the nitrogen atom and a formal negative charge on the C4 carbon atom) to **2**, affording a zwitterionic species (formal charges: positive on the nitrogen atom, negative on the CPh_2 carbon). This electrophilic aromatic substitution-type mechanism appears to be involved in the reported deuteration of I*t*Bu at the 4- and 5-positions by [D_6]DMSO.[10] Preliminary calculations using IMes (**1**) and phosphaalkene **2** showed that the initial addition to the P=C bond at the 4-position of IMes did not lead to a stable geometry for such an intermediate. Therefore, this mechanism was not considered further.

The results of the DFT calculations for the two proposed mechanisms, modeled in the dielectric field of THF, are depicted in Figure 2. All the calculations were performed using optimized geometries, and for **1**, **2**, and **3** the results were in general agreement with the molecular structures obtained from X-ray crystallography. The difference in energy between the starting reagents and the product is $-47.0\ kJ\,mol^{-1}$ in THF, which suggests that the overall reaction is exothermic. As can be clearly seen from Figure 2, path 2, which involves isomerization to the abnor-

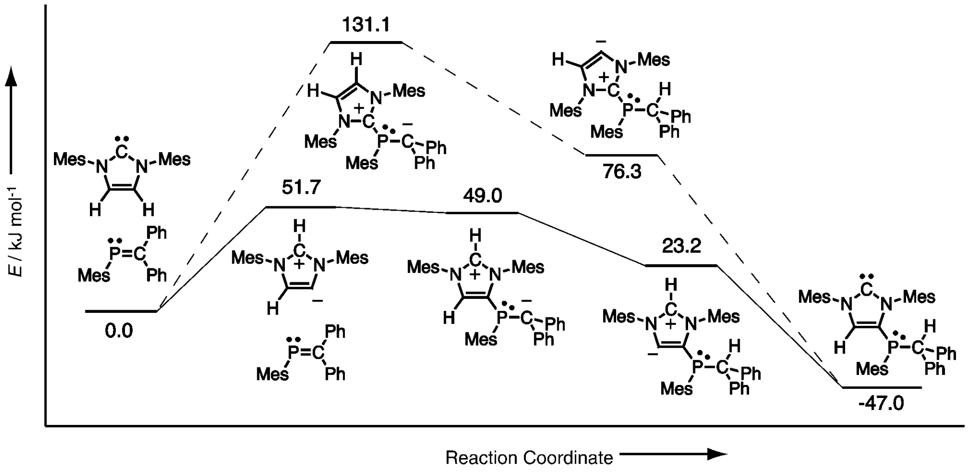

Figure 2. Results of DFT calculations, showing two plausible pathways (----- path 1, —— path 2) for the reaction between IMes (**1**) and MesP=CPh_2 (**2**), to afford 4-phosphino-2-carbene (**3**). The structures and total energy of each intermediate are given. Transition states have not been calculated.

mal carbene before P=C addition, is considerably more energetically favorable than path 1, which involves normal carbene addition. The abnormal IMes is found to be 51.7 kJ mol^{-1} higher in energy than the normal IMes; 51.7 kJ mol^{-1} is slightly lower than the values determined in previous calculations for the normal and abnormal parent carbene (that is, IH; $\Delta E = +84$ or $+73$ kJ mol^{-1}).[24,25] Therefore, we speculate that the reaction proceeds along path 2, or some variation thereof, although further experiments and calculations of the relevant transition states are necessary to confirm this postulation.

The calculated structure of **3** revealed that the carbene lone pair and the phosphorous atom lone pair are the two frontier orbitals and are very close in energy. The fact that the carbene and phosphorous lone pairs are close in energy hints at an interesting possibility to tune the donor properties of this bifunctional carbene/phosphine non-chelate ligand. Thus, a preliminary investigation of the coordinating properties of **3** with gold(I), a metal that readily binds both NHCs and phosphines, was carried out. Upon treatment of a THF solution of **3** with [(tht)AuCl] (1 equiv, tht = tetrahydrothiophene), a small shift relative to **3** was observed in the ^{31}P NMR spectrum ($\delta = -36.4$ ppm versus $\delta = -37.3$ ppm in THF). A signal was detected in the ^{13}C NMR spectrum ($\delta = 175.2$ ppm), which is similar to **3**·$(AuCl)_2$ ($\delta = 177.6$ ppm; IMes·AuCl $\delta = 173.4$ ppm).[26] Although this species was not isolated, the chemical shifts suggest that complexation to gold occurs first at the carbene center. Addition of a second equivalent of [(tht)AuCl] affords the digold complex **3**·$(AuCl)_2$ ($\delta = -0.14$ ppm) in which both the carbene and phosphine centers are coordinated to gold(I). The single crystal X-ray diffraction structure of air- and moisture-stable **3**·$(AuCl)_2$ is shown in Figure 3.

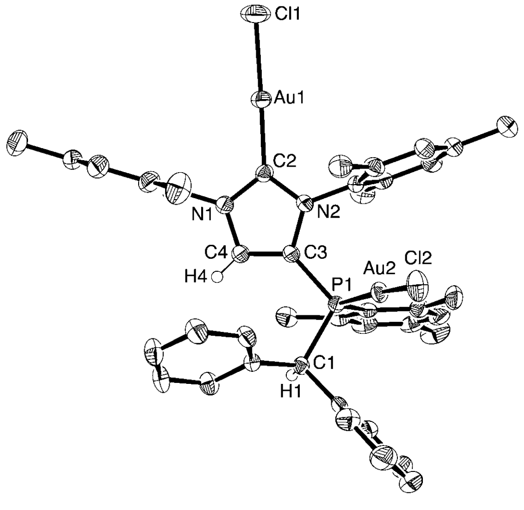

Figure 3. ORTEP of **3**·$(AuCl)_2$ (thermal ellipsoids set at 50% probability). The dichloromethane atoms and all hydrogen atoms except H1 and H4 are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.882(5), P1–C3 1.817(6), P1–C5 1.826(5), C2–N1 1.360(7), C2–N2 1.345(6), C4–N1 1.376(7), C3–N2 1.397(7), C3–C4 1.354(7), C2–Au1 1.971(5), P1–Au2 2.238(1), Au1–Cl1 2.266(2), Au2–Cl2 2.284(1); N1-C2-N2 105.1(5), C3-C4-N1 108.0(5), C4-C3-N2 105.2(5), C2-Au1-Cl1 176.9(2), P1-Au2-Cl2 171.9(1), N1-C4-C3-P1 170.2(4).

In summary, we have demonstrated that IMes will react with a phosphaalkene to give an unprecedented 4-phosphino-2-carbene, which is a highly unusual reaction for a free NHC. This work opens the door to abnormal reactions of NHCs with other unsaturated molecules, and to the development of novel bifunctional ligands for use in catalysis.[27]

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