COMMUNICATION

Synthesis of metallophosphaalkenes by reaction of organometallic nucleophiles with a phosphaethynolato-borane

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We describe the reaction of a phosphaethynolato-borane [B]OCP ([B] = *N*,*N*'-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-1,3,2-diazaboryl) with the organometallic nucleophile Na[Cp*Fe(CO)$_2$] (Cp* = pentamethylcyclopentadienyl). The electrophilic character of [B]OCP allows for a new route towards the formation metal–phosphorus bonds affording a metallophosphaalkene that can be functionalised at both the oxygen and phosphorus atoms depending on the reagents employed.

Phosphaalkynes (R–C≡P) are heavier analogues of nitriles (R–C≡N) and, as such, their reactivity is largely dominated by their inherent nucleophilicity.[1] The parent compound, H–C≡P; methylidynephosphine (or phosphaacetylene), was first reported in 1950,[2] and unambiguously characterised in 1961.[3] Pioneering work on the synthesis and characterization of R–C≡P type compounds by Becker, Nixon, Regitz (and others) culminated with the isolation of the first kinetically stabilized phosphaalkyne ^{t}Bu–C≡P in 1981.[1,4] Since then, numerous metal complexes of these interesting species have been isolated, exhibiting a wealth of coordination modes.[5] In selected cases, the metal centres facilitate oligomerization of the phosphaalkynes to give rise to cyclic species such as diphosphacyclobutadienes and 1,3,5-tri-phosphabenzene derivatives.[6] More recently, the nucleophilicity of phosphaalkynes was exploited to afford 1*H*-phosphindoles by protonation of a ruthenium complex containing $(C_6H_5)_3C$–C≡P.[7]

Much less explored is the reactivity of phosphaalkynes as electrophiles. The reverse polarity of the carbon–pnictogen bond relative to nitriles, i.e. $^{\delta-}$C≡P$^{\delta+}$ vs. $^{\delta+}$C≡N$^{\delta-}$, suggests that nucleophilic reagents should react with the phosphorus atom. Cowley and co-workers explored this hypothesis by reacting Mes*–C≡P (Mes* = 2,4,6-^{t}Bu$_3$C$_6$H$_2$) with MeLi and were able to show that the methyl functionality associates with the phosphorus centre to afford ArHC=PMe (after addition of H_2O to the reaction mixture).[8] However, to our knowledge, this report constitutes one of the few examples where the reactivity of phosphaalkynes towards nucleophiles has been explored as a way of accessing novel organophosphorus compounds.[9]

We recently reported on the isolation of a novel phosphaethynolato-borane by reaction of a cyclic bromoborane with sodium salts of the phosphaethynolate anion (PCO$^-$).[10,11] This species, [B]OCP ([B] = *N*,*N*'-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaboryl), is valence isoelectronic with phosphaalkynes and formally contains a C≡P triple bond. [B]OCP is unstable in the presence of Lewis bases leading to dimerization in donor solvents (such as THF). Moreover, we demonstrated that [B]OCP reacts with strong nucleophiles such as LiMes with concomitant functionalization at the phosphorus atom. These findings suggest that [B]OCP is significantly electrophilic. This is due to a low-lying LUMO with π* character and a significant contribution from a phosphorus atom p-orbital. Herein we report some preliminary findings exploiting this reactivity pathway, which have led to a novel way of accessing metallophosphaalkenes.[12]

While [B]OCP can be considered a phosphaalkyne, its physical and chemical properties differ from that of more classical R–C≡P systems (where R = H, alkyl or aryl). For example, the ^{31}P{^{1}H} NMR resonance observed for [B]OCP (–285.9 ppm) is notably upfield compared to ^{t}Bu–C≡P (–69.2 ppm) and H–C≡P (–32 ppm),[4,13] and even more so when compared to silyl- or aryl-functionalised species such as Me$_3$Si–C≡P (+96 ppm).[14] This chemical shift, and the structure of [B]OCP, in which the boryl ring and the phosphaethynolate moiety are co-planar, indicate a significant degree of electron delocalization over the totality of the [B]OCP π-manifold. This results in greater electropositive character at the phosphorus atom, implying that [B]OCP is a relatively strong electrophile.

We set out to probe this hypothesis by reacting [B]OCP with the archetypal transition metal reagent Na[Cp*Fe(CO)$_2$] (Cp* = pentamethylcyclopentadienyl), which is known to act as a nucleophile in, for example, S$_N$2 reactions.[15] The reaction of [B]OCP with one equivalent of Na[Cp*Fe(CO)$_2$] was found to afford a novel anionic metallophosphaalkene in which the Cp*Fe(CO)$_2$ unit (Fp*) associates with the phosphorus centre

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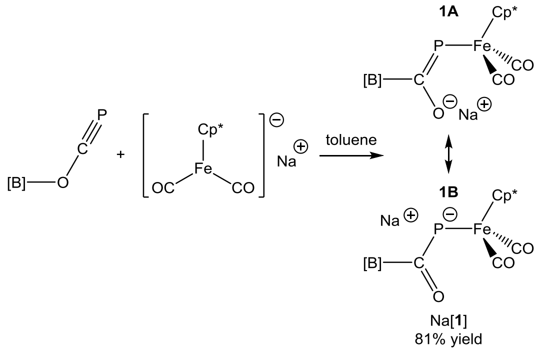
to afford {[B](NaO)C=PFp*}$_2$ ({Na[**1**]}$_2$; as pictured in Scheme 1). To the best of our knowledge, this reaction is the first example of a phosphaalkyne being used as an electrophile for the formation of a metal–phosphorus bond.[16]

Conversion to **1** was observed in the ^{31}P{^{1}H} NMR spectrum of the reaction mixture which exhibits a downfield-shifted singlet resonance at 188.6 ppm. The ^{1}H NMR spectrum in consistent with the presence of one Fp* and one boryl moiety, while the ^{13}C{^{1}H} NMR spectrum reveals a single resonance at 222.05 ppm for the central carbonyl carbon atom, shifted relative to that of the [B]OCP precursor (140.15 ppm). It is noteworthy that in this reaction, as in the reaction with LiMes, the boryl group migrates from the oxygen to the carbon atom of the phosphaethynolate.



Scheme 1. Synthesis of Na[**1**] from reaction of [B]OCP with Na[Cp*Fe(CO)$_2$]. [B] = *N*,*N*'-bis(2,6-diisopropylphenyl)-2,3-dihydro-1*H*-1,3,2-diazaboryl.

Slow evaporation of a toluene solution of the reaction mixture afforded red crystals of {Na[**1**]}$_2$ suitable for single crystal X-ray diffraction in high yield (81%). The single crystal structure of {Na[**1**]}$_2$ reveals a tight ion pair featuring two metallophosphaalkene moieties bridged by the same number of sodium cations. For clarity bond metric data will only be discussed for one of these units (Figure 1).

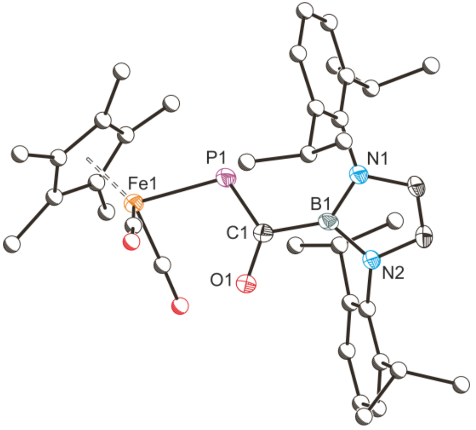
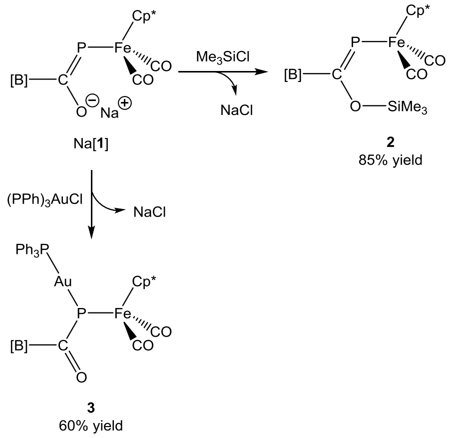


Figure 1. Molecular structure of **1**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity. Atoms of the Fp* moiety (with the exception of Fe) and the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: Fe1–P1 2.322(1), P1–C1 1.725(3), C1–O1 1.315(3), C1–B1 1.578(4), B1–N1 1.438(4), B1–N2 1.436(4); Fe1-P1-C1 111.03(9), P1-C1-O1 129.7(2), P1-C1-B1 113.68(19), O1-C1-B1 116.4(2), C1-B1-N1 130.8(3), C1-B1-N2 124.9(3), N1-B1-N2 104.2(2).

The C=P bond in **1** is significantly elongated (1.725(3) Å) relative to that of [B]OCP (1.545(2) Å). This distance falls between the values expected for a P–C single (1.86 Å) and double bond (1.69 Å).[17,18] The sum of bond angles at the central carbon atom (359.8°) is consistent with a planar, formally sp^2 hybridised, atom. **1** can be formally discussed as an anionic metallophosphaalkene with a formal negative charge on the oxygen atom (resonance form **1A** in Scheme 1), or conversely as a phosphide bearing an acyl substituent (resonance form **1B**). Subsequent reactivity studies reveal that it can react as either depending on the reagent in question.



Scheme 2. Metathesis reactions of Na[**1**] on reaction with Me$_3$SiCl to afford **2** and with (PPh$_3$)AuCl to afford **3**.

For example, compound **1** is readily silylated by reaction with Me$_3$SiCl affording a neutral metallophosphaalkene, [B](Me$_3$SiO)C=PFp* (**2**), in quantitative yield (according to Scheme 2). The ^{31}P NMR spectrum reveals a singlet resonance at 350.6 ppm (cf. 188.6 ppm for Na[**1**]) which is consistent with other literature-reported phosphaalkenes. For example, the closely related species ^{t}Bu(Me$_3$SiO)C=PFp (Fp = CpFe(CO)$_2$) exhibits a singlet resonance in its ^{31}P{^{1}H} NMR spectrum at 215.2 ppm,[19] while (Me$_3$Si)$_2$C=PFp is observed at 641.5 ppm.[20] The ^{1}H NMR spectrum largely remains unchanged with the exception of an additional resonance at 0.15 ppm from the trimethylsilyl group. Red crystals of **2** could be isolated from a concentrated hexane solution in 85% yield (Figure 2).

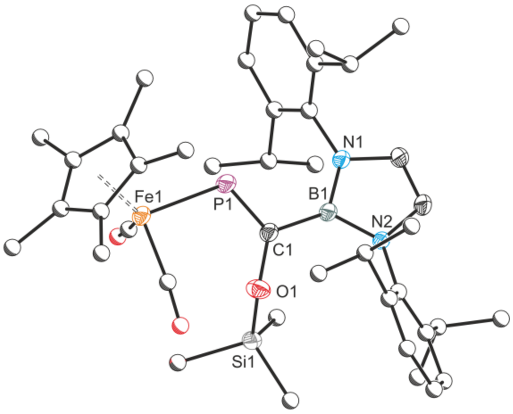


Figure 2. Molecular structure of **2**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity. Atoms of the Fp* moiety (with the exception of Fe) and the Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: Fe1–P1 2.2738(7), P1–C1 1.694(2), C1–O1 1.381(3), O1–Si1 1.651(2), C1–B1 1.568(3), B1–N1 1.440(3), B1–N2 1.448(3); Fe1-P1-C1 115.29(9), P1-C1-O1 124.10(17), P1-C1-B1 116.80(18), O1-C1-B1 118.5(2), C1-B1-N1 127.0(2), C1-B1-N2 128.8(2), N1-B1-N2 104.2(2).

Structurally there is no significant change to the metallophosphalkene core of **1** on silylation. There is a slight shortening of the C–P bond in **2** (1.694(2) compared to 1.725(3) Å in {Na[**1**]}$_2$), which is a result of increased localisation of electron density in the bond C–P π bond. This is accompanied by a shortening of the Fe–P bond on loss of any delocalised negative charge on the phosphorus atom.

Prompted by the results obtained on silylation of **1**, we explored the reactivity of this species towards other electrophiles that would preferentially bind to the phosphorus atom. Reaction of Na[**1**] with one equivalent of (PPh$_3$)AuCl gives rise to a novel species (**3**) exhibiting two doublet resonances of equal intensity in the ^{31}P{^{1}H} NMR spectrum at 98.8 and 43.3 ppm ($^2J_{P-P}$ = 102.7 Hz). The former of these corresponds to the phosphide substituent P{C(O)[B]}Fp*$^-$, while the latter is due to the PPh$_3$ ligand coordinated to the gold centre. Recrystallisation of this compound from a concentrated toluene solution afforded orange crystals of a linear gold(I) compound in moderate yield (60%).

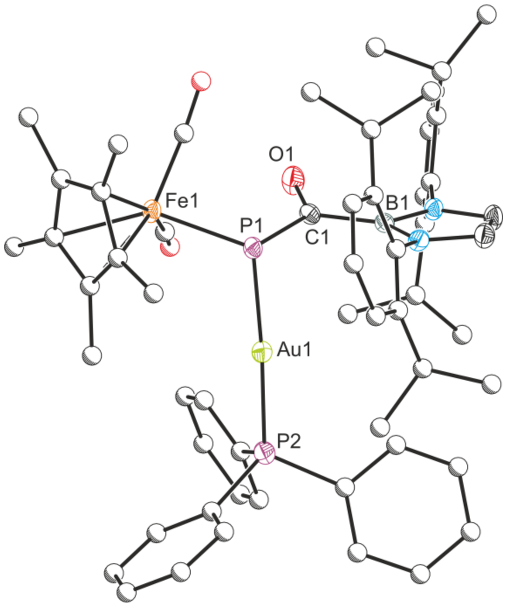


Figure 3. Molecular structure of **3**. Anisotropic displacement ellipsoids set at 50% probability. Hydrogen atoms have been omitted for clarity. Atoms of the Fp* moiety (with the exception of Fe), Ph and Dipp groups are pictured as spheres of arbitrary radius. Selected interatomic distances [Å] and angles [°]: Au1–P1 2.3282(10), Au1–P2 2.2993(11), Fe1–P1 2.3062(12), P1–C1 1.846(4), C1–O1 1.235(5), C1–B1 1.590(6), B1–N1 1.441(5), B1–N2 1.430(5); P1-Au1-P2 175.51(4), Fe1-P1-C1 107.89(14), P1-C1-O1 123.3(3), P1-C1-B1 118.1(3), O1-C1-B1 118.4(3), C1-B1-N1 130.9(3), C1-B1-N2 124.2(4), N1-B1-N2 104.7(3), Au1-P1-Fe1 107.52(4), Au1-P1-C1 94.02(13), Fe1-P1 C1 107.89(14).

The single crystal X-ray structure of **3** (Figure 3) confirms the presence of a linear gold(I) complex bonded to an anionic phosphido ligand and triphenylphosphine (P1-Au1-P2 175.51(4)°). In contrast to **2**, which can be rationalized as a *bone fide* metallophosphaalkene, in **3** there is a significant lengthening of the C–P bond (1.846(4) Å; cf. 1.694(2) Å in **2**) in line with the value expected for a single bond.[17,18] The gold-phosphorus bond distances are quite similar (Au1–P1 2.328(1) and Au1–P2 2.299(1) Å) with the bond to the triphenylphosphine substituent being somewhat shorter, presumably due to the presence of a stereochemically active lone-pair on the P{C(O)[B]}Fp*$^-$ substituent. The phosphide P1 atom is pyramidal with a sum of bond angles of 309°. Related gold(I) phosphane/phosphanido complexes,[21,22] such as (PPh$_3$)AuP(SnMe$_3$)$_2$, have been found to exhibit comparable bond metrics with the bond to the phosphide functionality (2.320(1) Å) being slightly longer than that to the phosphine (2.293(1) Å).[22]

To conclude, we describe a novel route for the formation of metallophosphaalkenes by exploiting the electrophilic character of a unique phosphaalkyne. Migration of the boryl functionality from the oxygen to the carbon atom in [B]OCP allows for the stabilization of anionic phosphaalkenes which can be further functionalized by reactions with electrophiles.

Conflicts of interest

There are no conflicts to declare.

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