A Thermally Stable Magnesium Phosphaethynolate Grignard Complex

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ABSTRACT. The 2-phosphaethynolate (OCP) anion has found versatile applications across the periodic table but remains underexplored in group 2 chemistry due to challenges in isolating thermally stable complexes. By rationally modifying their coordination environments using 1,3-dialkyl-substituted *N*-heterocyclic carbenes (NHCs), we have now isolated and characterized thermally stable, structurally diverse and hydrocarbon soluble magnesium phosphaethynolate complexes (**2**, $\mathbf{4^{Me}}$, **8-10**), including the novel phosphaethynolate Grignard reagent ($\mathbf{2^{iPr}}$). The methylmagnesium phosphaethynolate and magnesium diphosphaethynolate complexes readily activate dioxane with subsequent H-atom abstraction to form $[(NHC)MgX(\mu\text{-}OEt)]_2$ [X = Me (**3**), OCP (**8**, **9**)] complexes. Their reactivities increased with the Lewis acidity of the Mg^{2+} cation, and may be attenuated by Lewis base saturation or a slight increase in carbene sterics. Solvent effects were also investigated, and led to the surreptitious isolation of an ether-free sodium phosphaethynolate $(NHC)_3Na(OCP)$ (**6**), which is soluble in aromatic hydrocarbons and can be independently prepared by the reaction of NHC and $[Na(dioxane)_2][OCP]$ in toluene. Under

forcing conditions (105 °C, 3 d), the magnesium diphosphaethynolate complex $(NHC)_3Mg(OCP)_2$ (**10**) decomposes to a mixture of organophosphorus complexes, among which a thermal decarbonylation product $[(NHC)_2P^I][OCP]$ (**11**) was isolated.

INTRODUCTION

During the last decade, the 2-phosphaethynolate (OCP) anion has developed into an important building block for the synthesis of phosphorus-containing molecules.[1, 2] This nucleophile is isoelectronic to the cyanate ion, and can access two major resonance forms (i.e., $^{-}$O–C≡P ↔ O=C=P^{-}) for ambidentate reactivity.[3] Although the first structurally authenticated phosphaethynolate complex dates back nearly 30 years with the isolation of $[Li(DME)_2][OCP]$,[4] its thermal instability hampered extensive investigation. However, the emergence of stable $[Na(ether)_x][OCP]$ complexes (ether = DME or dioxane) in 2011[5, 6] enabled rapid development of the chemistry of the OCP anion.[1, 2] Indeed, stable element–OCP/PCO complexes across the periodic table may be obtained by a simple salt metathesis reaction between Na(OCP) and ligand-stabilized element–halides.

In contrast to the stability and versatility of sodium and potassium phosphaethynolate complexes,[5-8] their group 2 counterparts (Mg, Ca, Sr, Ba) are unstable in solution, thus difficult to study.[9, 10] One rationale for their instability is the weak nature of the phosphaalkyne (C≡P) bond.[8, 11] Since *s*-block elements are highly oxophilic, they favor the oxyphosphaalkyne isomer (i.e., $^{-}$O–C≡P), whereby the OCP anion is prone to decomposition through oxidation and self-oligomerization.[1, 8] The highly electropositive character of sodium and potassium cations allows for pronounced charge separation in their M(OCP) salts, which results in increased columbic repulsion between the OCP anions and discourages oligomerization.[1] The "free" OCP anion in these complexes is stabilized by delocalization of electron density from O to C≡P π*, thereby reducing the bond order and consequent reactivity of the C–P bond and concomitantly increasing the bond order and thermodynamic stability of the C–O bond. Conversely, phosphaethynolate salts of the less electropositive group 2 elements are thus far prone to rapid decomposition in the same coordination environments as the alkali metal salts. Nevertheless, group 2 phosphaethynolate complexes are desirable reagents due to their potential for Lewis acid reactivity profiles,[12] in contrast to the archetypal reactivity of group 1 organometallic reagents as strong nucleophiles.

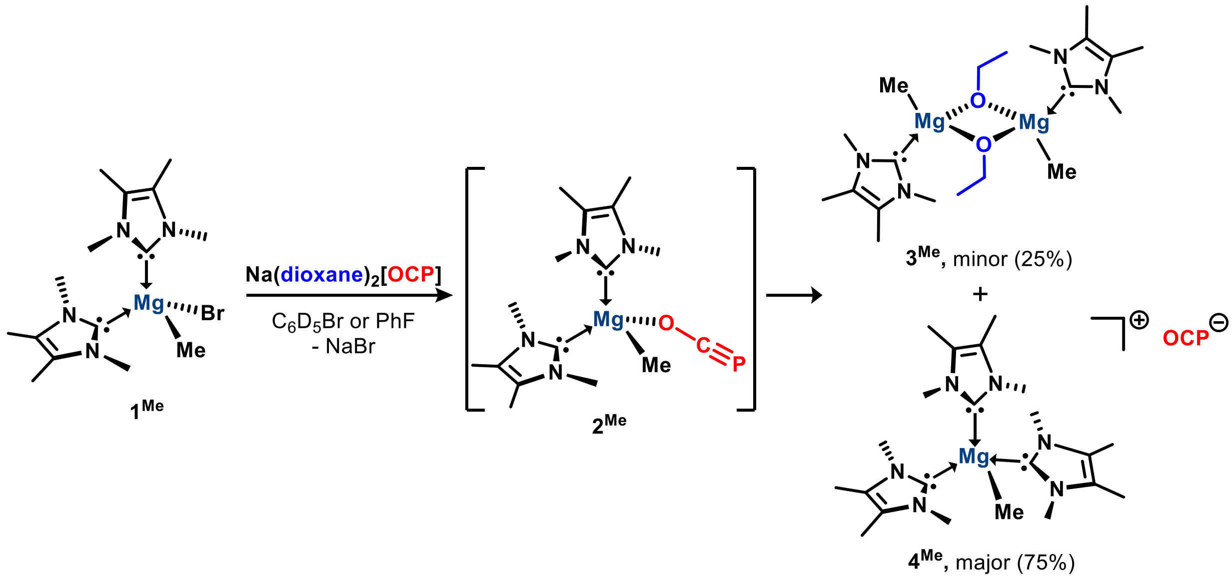
Being mindful of the critical importance of coordination environments in *s*-block phosphaethynolate chemistry, we hypothesized that the electronic influence of *N*-heterocyclic carbenes (NHCs) may enable the isolation of thermally stable alkaline earth phosphaethynolates. NHCs have become indispensable in *p*- and *d*-block organometallic chemistry as tunable donor-acceptor ligands.[13-16] However, they are relatively underexplored in *s*-block chemistry, partly because hard-soft acid-base effects can result in the destabilization of reactive species due to dynamic NHC coordination.[16] We recently discovered that such destabilizing effects can be mitigated by bis- or tris-NHC coordination in neutral and cationic magnesium complexes,[17-20] and were encouraged to apply similar principles towards magnesium phosphaethynolates. Herein, we report the isolation, characterization (NMR, IR, X-ray), and reactivity of structurally diverse NHC-stabilized magnesium phosphaethynolate complexes, including a novel phosphaethynolate-containing Grignard reagent. Unlike the majority of known *s*-block element phosphaethynolates, these complexes are remarkably soluble and thermally stable in aromatic hydrocarbon solvents.

The influence of subtle changes in carbene stereoelectronics on their stability and reactivity is also evaluated.

RESULTS AND DISCUSSION

As a starting point for this synthetic investigation, the carbene-stabilized Grignard reagent $(^{Me}NHC)_2MgMeBr$ (**1^{Me}**, ^{Me}NHC = 1,3,4,5-tetramethylimidazol-2-ylidene) was prepared by the reaction of MeMgBr (3 M in Et_2O) and two equivalents of ^{Me}NHC in THF, and isolated as a colorless solid in 89% yield. Plate-like crystals of **1^{Me}** were analyzed by single-crystal X-ray diffraction (SC-XRD), which revealed a mononuclear complex (Figure S1) structurally analogous to our previously reported $(^{iPr}NHC)_2MgMeBr$ (**1^{iPr}**; ^{iPr}NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene).[17] Compound **1^{Me}** is stable indefinitely under inert conditions in the solid-state and up to 3 months in anhydrous aromatic or ethereal solvents, leading us to hypothesize that the electronic influence of two sterically unhindered NHCs may similarly stabilize a phosphaethynolate-containing Grignard complex [e.g., $(^{Me}NHC)_2MgMe(OCP)$, **2^{Me}**]. An NMR-monitored reaction between **1^{Me}** and $[Na(dioxane)_2][OCP]$[5] in C_6D_5Br revealed an immediate conversion to new products, indicated by two new Mg–CH_3 singlets (3:1 ratio) in the ^{1}H NMR spectrum, and one singlet at -373.5 ppm in the $^{31}P\{^1H\}$ NMR spectrum, downfield of $[Na(dioxane)_x][OCP]$ (-392.0 ppm).[5] The smaller Mg–CH_3 singlet is accompanied by downfield triplet and quartet (2:3) resonances consistent with an ethyl group. Indeed, X-ray diffraction studies on single-crystals obtained from preparative-scale reactions (Scheme 1) indicate that the observed signals are due to a methylmagnesium ethoxide $[(^{Me}NHC)MgMe(\mu\text{-}OEt)]_2$ (**3^{Me}**, Figure 1a) and a magnesium phosphaethynolate charge separated ion-pair $[(^{Me}NHC)_3MgMe][OCP]$ (**4^{Me}**, Figure 1b).

Scheme 1. Dioxane activation in the attempted synthesis of a phosphaethynolate-containing Grignard complex



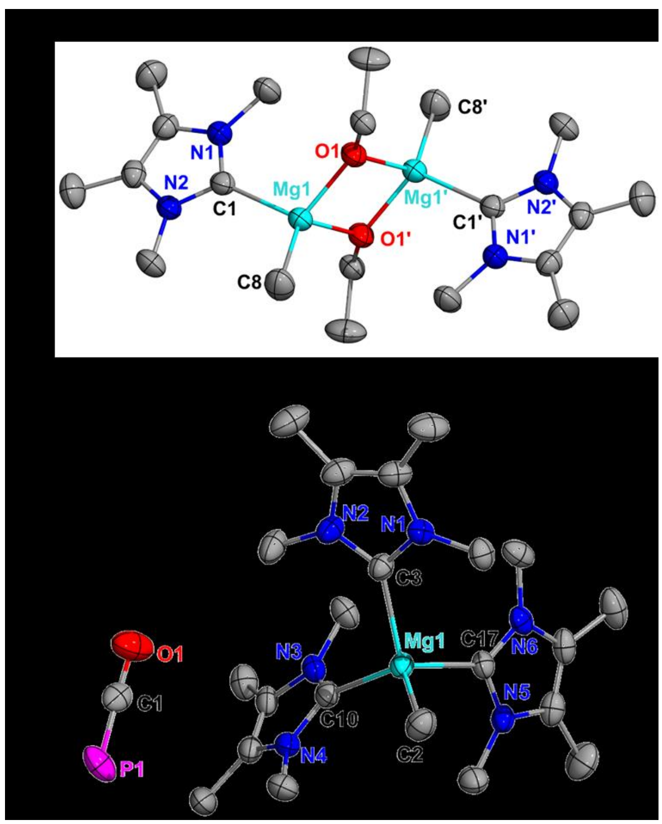
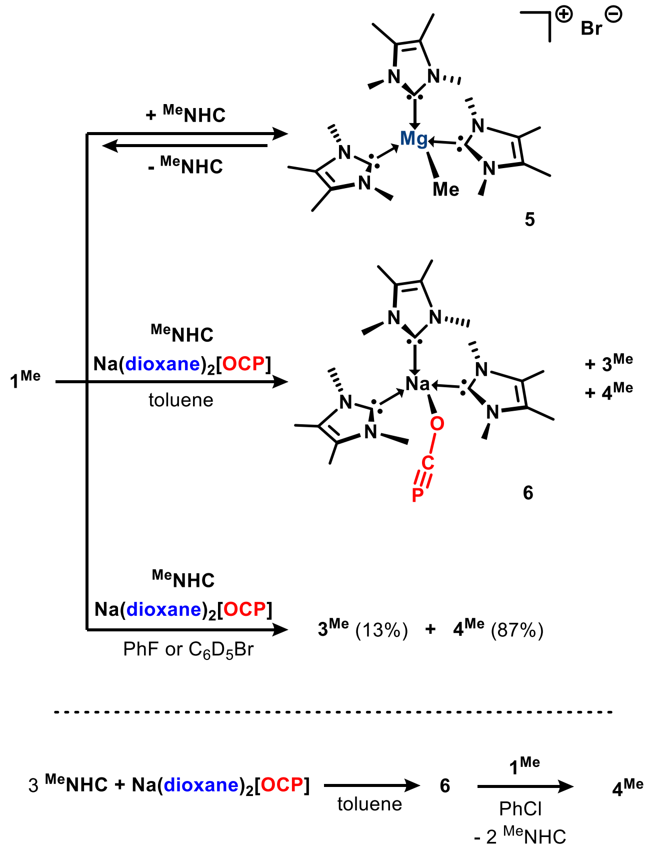


Figure 1. Molecular structures of $\mathbf{3^{Me}}$ (a) and $\mathbf{4^{Me}}$ (b). Thermal ellipsoids set at 50% probability. H atoms are omitted for clarity, and only major occupied positions for the disordered OCP anion in $\mathbf{4^{Me}}$ are shown. Selected bond distances (Å) and angles (deg): $\mathbf{3^{Me}}$: Mg1–O1, 1.9659(13); Mg1–O1', 1.9868(13); Mg1–C1, 2.2649(18); Mg1–C8, 2.145(2), Mg1---Mg1', 2.9722(11); C1–N1, 1.354(2); O1–Mg1–O1', 82.48(5); O1–Mg1–C1, 109.72(6); O1–Mg1–C8, 119.67(8). $\mathbf{4^{Me}}$: C1–P1, 1.574(14); O1–C1, 1.208(10); Mg1–C2, 2.156(4); Mg1–C3, 2.226(3); Mg1–C10, 2.230(4); Mg1–C17, 2.259(4); O1–C1–P1, 177.1(9); C2–Mg1–C17, 111.65(15); C2–Mg1–C10, 118.81(16).

The metathical exchange of a bromide ligand in $\mathbf{1^{Me}}$ to the softer OCP anion results in a more electrophilic Mg^{2+} cation in the transient phosphaethynolate-containing Grignard reagent ($\mathbf{2^{Me}}$). As we have previously observed in similar $(NHC)_2MgRX$ complexes,[18] the increased electrophilicity results in a spontaneous NHC rearrangement to $\mathbf{4^{Me}}$, enabling the formation of an unobserved (^{Me}NHC)(dioxane)MgMe(OCP) intermediate, which decomposes to $\mathbf{3^{Me}}$ via dioxane activation. However, the ether activation mechanism is poorly understood.[21, 22] The direct action of $\mathbf{2^{Me}}$ on dioxane is similarly likely, and the significantly higher yield of $\mathbf{4^{Me}}$ from this reaction (75% NMR conversion compared to 25% of $\mathbf{3^{Me}}$) suggests that NHC rearrangement outcompetes dioxane activation. Indeed, $\mathbf{4^{Me}}$ is unreactive to ether cleavage, and no further conversion of dioxane to ethoxide was observed after the initial formation of $\mathbf{3^{Me}}$ and $\mathbf{4^{Me}}$ in the NMR experiment. Furthermore, the reaction of $\mathbf{1^{Me}}$ and $[Na(dioxane)_2][OCP]$ in toluene (6 h, RT) afforded $\mathbf{3^{Me}}$ in 57% isolated yield, in contrast to a 25% NMR yield from the same reaction in C_6D_5Br. Hence, the influence of weakly coordinating halogenated solvents on the intermediary Lewis acidic species significantly attenuates their electrophilicity[23, 24] and consequent reactivity.

In the direct synthesis of compound **4^Me^**, equimolar amounts of **1^Me^**, ^{Me}NHC and [Na(dioxane)$_2$][OCP] were sequentially combined in C_6D_5Br or fluorobenzene to yield the desired product (Scheme 2), albeit with minor amounts of **3^Me^** (1:7 ratio of **3^Me^**:**4^Me^** in C_6D_5Br, Figure S7). After workup, **4^Me^** was obtained as an off-white solid in 39% yield. NMR studies suggest that a dynamic equilibrium between multiple MeMg(OCP) species is present in solution. At room temperature, the ^{1}H NMR spectrum revealed two overlapping singlets in the Mg–CH_3 region, and one set of ^{Me}NHC peaks with the C(CH_3) singlet slightly broadened. In the ^{31}P{^{1}H} NMR spectrum, the OCP singlet (δ -382.0 ppm) was also broadened, and shifted upfield (with further broadening) at lower temperatures but did not resolve into unique resonances (VT-NMR, 243 – 333 K, C_6D_5Br). The Mg–CH_3 singlets coalesced at 60 ºC with equivalent intensities for the ^{Me}NHC singlets. At the same temperature, a previously unresolved C≡P doublet in the ^{13}C{^{1}H} NMR spectrum was observed at 166.8 ppm ($^1J_{CP}$ = 48.1 Hz), and the corresponding ^{31}P{^{1}H} resonance (δ -378.3 ppm) is slightly shifted downfield. Notably, the observation of a $^1J(^{13}C–^{31}P)$ coupling information is without precedent for group 2 phosphaethynolate complexes due to rapid solution-state decomposition of previously reported complexes.[9, 10] However, this coupling constant is smaller than reported values for "interaction free" OCP anions (range 62.0 – 63.2 Hz),[7, 25, 26] and in the range of contacted OCP moieties in the s-block.[4, 5] In the solid-state IR spectrum, two overlapping bands (vs) at 1800 cm^{-1} and 1770 cm^{-1} were attributed to the OCP asymmetric stretch, and are in the range of uncoordinated OCP anions.[26, 27] Thus, **4^Me^** is best described as a charge-separated ion-pair in the solid-state, although bound [Mg]–OCP forms may exist in solution.

Scheme 2. Dynamic carbene coordination and solvent effects in the direct synthesis of 4^Me^



The observed ether cleavage implicates **2^{Me}** as an intermediary species in the direct synthesis of **4^{Me}**, and motivated an investigation into the reaction of ^{Me}NHC and **1^{Me}** prior to the formation of phosphaethynolate complexes. The reaction of **1^{Me}** and ^{Me}NHC yielded a new product presumed to be [(^{Me}NHC)$_3$MgMe][Br] (**5**) based on a 3:1 ^{1}H NMR integral ratio for the characteristic ^{Me}NHC and Mg–CH_3 peaks (Scheme 2 and Figure S14). Attempts to obtain single crystals of **5** for structural elucidation by SC-XRD yielded **1^{Me}** instead, and VT-NMR studies on **5** (Figure S15) suggest a dynamic process between multiple Mg–CH_3-containing species. Theoretical studies suggest that while NHC complexation is facile, cationization is endergonic and favors neutral complexes in the equilibrium.[18] Having realized that the tris(NHC)-stabilized species **4^{Me}** and **5** are prone to dynamic ligand coordination in solution, we investigated solvent effects. The reaction of $\mathbf{1^{Me}}$, ^{Me}NHC and [Na(dioxane)$_2$][OCP] in toluene yielded a complex mixture of products including $\mathbf{3^{Me}}$, $\mathbf{4^{Me}}$ and (^{Me}NHC)$_3$Na(OCP) (**6**) (Figure 2). Clearly, the absence of weakly coordinating solvents resulted in pronounced ligand scrambling and loss of selectivity for the desired product. Nevertheless, the serendipitous isolation of **6** afforded a rare ether-free, hydrocarbon-soluble alkali metal phosphaethynolate complex.

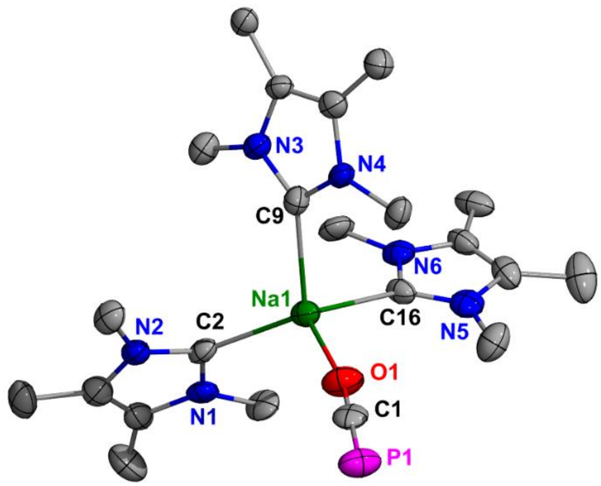
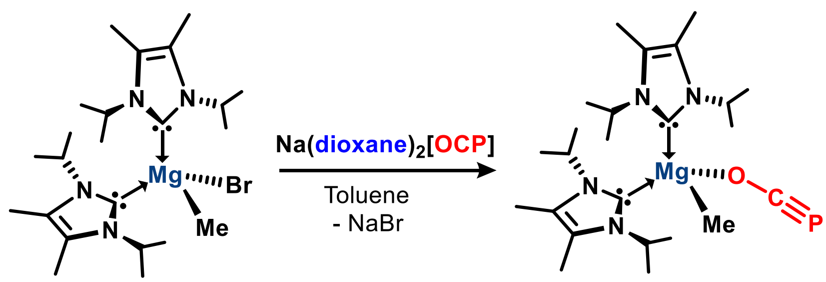


Figure 2. Molecular structure of **6** (thermal ellipsoids set at 50% probability; H atoms and co-crystallized toluene solvent are omitted for clarity). Only one of two crystallographically independent but chemically equivalent molecules in the asymmetric unit is represented. Selected bond distances (Å) and angles (deg): Na1–O1, 2.247(5); O1–C1, 1.215(5); C1–P1, 1.578(7); Na1–C2, 2.505(7); Na1–C9, 2.476(7); Na1–C16, 2.513(6); Na1–O1–C1, 167.2(5); O1–C1–P1, 179.2(6).

Compound **6** was directly prepared from the addition of three equivalents of ^{Me}NHC to [Na(dioxane)$_2$][OCP] in toluene, and isolated as a light yellow solid in 66% yield (Scheme 2, bottom). The OCP singlet resonance in the ^{31}P{^{1}H} NMR spectrum (δ -388.4 ppm) is downfield of [Na(dioxane)$_{2.5}$][OCP] (δ -392.0 ppm).[5] Single-crystal X-ray diffraction studies on **6** reveals a mononuclear molecule, whereby the terminal M–OCP bend angle (Na1–O1–C1: 167.2(5)º) is considerably wider than those of [(THF)Na(dibenzo-12-crown-6)][OCP] (138.1(2)º),[9] but is comparable to [Li(DME)$_2$][OCP] (170.7º).[4] The O–C≡P bond lengths in **6** (C–O, 1.215(8) Å; C≡P, 1.578(7) Å) are comparable to those of structurally authenticated Na(OCP) complexes,[5, 9] but the Na–O bond distance (2.247(5) Å) is the shortest reported value to date, although only slightly shorter than [(THF)Na(dibenzo-12-crown-6)][OCP] (2.290(2) Å). Highlighting the practicality of **6** for ether-free synthesis, the reaction of $\mathbf{1^{Me}}$ and **6** in chlorobenzene cleanly affords $\mathbf{4^{Me}}$ in 58% yield.

On the basis of these observations, we turned our attention to the slightly more sterically encumbered 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (^{iPr}NHC) to stabilize the desired Grignard complex. The reaction of (^{iPr}NHC)$_2$MgMeBr ($\mathbf{1^{iPr}}$)[17] and [Na(dioxane)$_2$][OCP] was monitored in C_6D_6, and the immediate formation of (^{iPr}NHC)$_2$MgMe(OCP) ($\mathbf{2^{iPr}}$) followed by its slow conversion to [(^{iPr}NHC)MgMe(μ-OEt)]$_2$ ($\mathbf{3^{iPr}}$)[20] was observed. A preparative scale reaction in toluene affords $\mathbf{2^{iPr}}$ as a colorless crystalline solid in 70% yield (Scheme 3). In the ^{31}P{^{1}H} NMR spectrum, the OCP singlet resonates at -366.8 ppm, which is comparable to (THF)$_4$Mg(OCP)$_2$ (δ -367.9 ppm).[9] A doublet in the ^{13}C{^{1}H} NMR spectrum (δ 162.4 ppm) is attributed to the OCP resonance, and the remarkably small $^1J(^{13}C–^{31}P)$ coupling constant (25.4 Hz) is outside the range for *s*-block OCP complexes (41.5 – 62 Hz), and comparable to (salen)(THF)Al(OCP) (24.5 Hz).[28] Notably, smaller coupling constants are indicative of more phosphaalkyne (C≡P) than phosphaketene (C=P) bonding in solution, due to a greater contribution of the P 3*s* orbital to the C–P bond in the latter.[1] The solid-state IR spectrum of $\mathbf{2^{iPr}}$ provides further evidence for a phosphaethynolate anion with a very strong band at 1740 cm^{-1} for the OCP asymmetric stretch, which is comparable to $(THF)_4Mg(OCP)_2$ (1759 cm^{-1}).[9] In the ^1H NMR spectrum, the Mg–CH_3 resonance of **2^{iPr}** (δ -0.67 ppm) is upfield of **1^{iPr}** (δ -0.45 ppm), which suggests a more nucleophilic methyl group since the softer OCP anion results in increased cationic character for the Mg^{2+} center.[18]

Scheme 3. Synthesis of a stable magnesium phosphaethynolate Grignard complex



The molecular structure of **2^{iPr}** was unambiguously determined by X-ray diffraction on a single-crystal obtained from a saturated toluene/hexanes (3:1) mixture at room temperature (Figure 3). The magnesium atom is contained within a tetrahedral coordination environment comprised of two NHCs, a terminal methyl group and an O-bound OCP moiety. The Mg1–O1–C1 angle (162.4(3)°) is comparable to metal–OCP bend angles for rare earth complexes,[29, 30] and significantly wider than those of group 2 and 13 (< 154°).[9, 10, 28, 31] The O1–C1 (1.232(5) Å) and C1–P1 (1.559(5) Å) bond distances are in the expected range for an $^{-}$O–C≡P anion,[1] and the Mg1–O1 bond (1.983(4) Å) is slightly shorter than those of $(THF)_4Mg(OCP)_2$ (2.024(16) Å).[9]

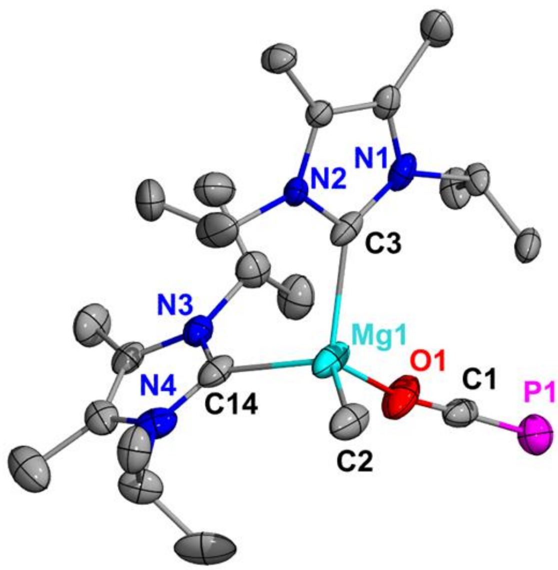


Figure 3. Molecular structure of $\mathbf{2^{iPr}}$ (thermal ellipsoids set at 50% probability; H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): Mg1–O1, 1.982(3); O1–C1, 1.232(5); C1–P1, 1.559(5); Mg1–C2, 2.143(5); Mg1–C3, 2.266(4); Mg1–C14, 2.261(4); Mg1–O1–C1, 162.4(3); O1–C1–P1, 178.7(4); O1–Mg1–C2, 113.28(17); O1–Mg1–C14, 96.16(15).

Compound $\mathbf{2^{iPr}}$ is highly soluble in non-polar solvents (e.g., toluene and benzene) and stable for several weeks under anhydrous conditions. In the solid-state, $\mathbf{2^{iPr}}$ can be stored in an inert atmosphere under ambient conditions for several months without noticeable decomposition. Compound $\mathbf{2^{iPr}}$ is also stable for several hours in refluxing benzene before decomposing to a light orange solution, which includes uncoordinated carbene and unidentified insoluble solids. Based on similar observations by others,[32] these solids are presumed to be OCP oxidation products, as the OCP anion may be easily oxidized in the presence of electrophilic metals.[1, 33, 34] Notably, $\mathbf{2^{iPr}}$ is stable in THF and does not activate the solvent under ambient conditions. The $^{31}P\{^{1}H\}$ NMR resonance for the OCP singlet of $\mathbf{2^{iPr}}$ in THF-d_8 (δ -368.7 ppm) is comparable to the same in benzene-d_6 (δ -366.8 ppm), and in the ^{1}H NMR spectrum, integral ratios suggest the same coordination environment observed in the solid state. Thus, the NHC-coordination in $\mathbf{2^{iPr}}$ is persistent even in the donor solvent, highlighting the vital role of steric protection from the ^{iPr}NHC ligands.

Table 1. Comparison of selected spectroscopic data and bond metrics[a] for the isolated phosphaethynolate complexes.

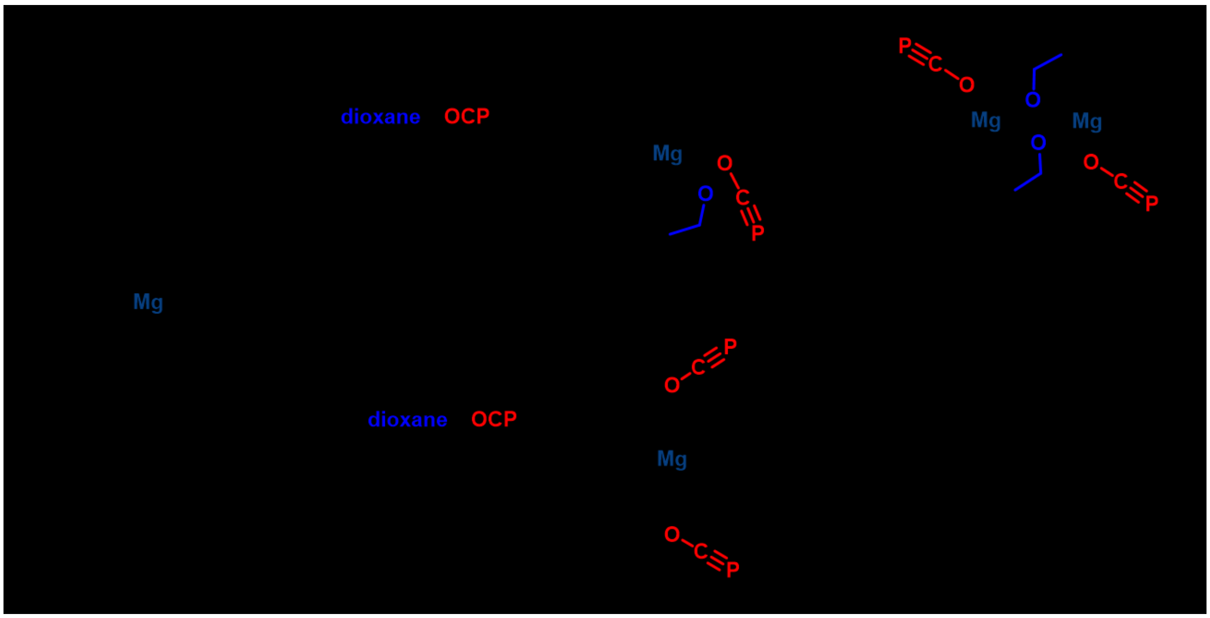
	$(^{iPr}NHC)_2Mg$ Me(OCP) ($\mathbf{2^{iPr}}$)	$(^{Me}NHC)_3MgMe$ (OCP) ($\mathbf{4^{Me}}$)	$(^{Me}NHC)_3Na$(OCP) (**6**)[a]	$(^{iPr}NHC)_nMg$(OEt)(OCP) (**8**/**9**)	$(^{Me}NHC)_3Mg(OCP)_2$ (**10**)
δ ^{31}P (ppm)	-366.8	-378.2[b]	-388.4	-364.9	-385.6
δ ^{13}C (C≡P) (ppm)	162.4	166.8[b]	168.7	161.3	169.0
$^{1}J_{C\text{-}P}$ (Hz)	25.4	48.1[b]	unresolved	unresolved	52.9
ν(OCP) (cm^{-1})	1740	1770, 1800	1761	1727	1744
M–O–C (°)	162.4(3)	N/A	167.2(5)	145.9(5)[c]	140.6(2), 147.5(3)
d(M–O) (Å)	1.982(3)	> 5.5	2.247(5)	1.938(4)[c]	2.143(2), 2.111(3)
d(O–C) (Å)	1.232(5)	1.208(10)	1.215(8)	1.254(7)[c]	1.199(5), 1.208(3)
d(C–P) (Å)	1.559(5)	1.574(14)	1.578(7)	1.545(6)	1.575(3), 1.584(6)
d(^{NHC}C–M) (Å)	2.266(4), 2.261(4)	2.226(3), 2.230(4), 2.259(4)	2.505(7), 2.476(7), 2.513(6)	2.192(6)	2.213(3), 2.216(3), 2.215(3)

[a]Values reported for only one of two chemically equivalent but crystallographically unique molecules in the asymmetric unit. [b]Data obtained at 60 °C. [c]M–OCP fragment.

Upon the successful isolation of the Grignard complex ($\mathbf{2^{iPr}}$), we explored the influence of NHCs in stabilizing the homoleptic magnesium diphosphaethynolate (Scheme 4). The reaction between $(^{iPr}NHC)_2MgBr_2$[17] ($\mathbf{7^{iPr}}$) and two equivalents of $[Na(dioxane)_2][OCP]$ yielded $(^{iPr}NHC)_2Mg(OEt)(OCP)$ (**8**) as the only isolable product. The $^{31}P\{^1H\}$ NMR resonance (δ -364.9

ppm), and the OCP asymmetric stretch in the solid-state IR (vs, 1721 cm^{-1}) are comparable to $\mathbf{2^{iPr}}$ (Table 1).

Scheme 4. Role of carbene stereoelectronics in the stabilization of a magnesium bis(2-phosphaethynolate) complex



The structural assignment of **8** is based on ^{1}H NMR integral ratios, where the characteristic NHC and ethoxide resonances are in a 2:1 ratio. The ^{iPr}NHC methine resonances are broadened in both the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, which may result from steric congestion or a potential dynamic process. Upon crystallization, **8** loses one equivalent of NHC to form $[(^{iPr}NHC)Mg(\mu\text{-}OEt)(OCP)]_2$ (**9**), whose molecular structure was authenticated by SC-XRD (Figure 4a). The Mg–O contacts in **9** (1.930(5) – 1.953(4) Å) for both the ethoxide and OCP anions are remarkably short [covalent radius R(Mg–O) = 2.02 Å[35]]. The Mg1–O1–C1 angle (145.9(5)°) is much smaller than in $\mathbf{2^{iPr}}$ (162.4(3)°), but is comparable to those of $(THF)_4Mg(OCP)_2$ (142.8(15)°).[9] The C≡P bond (1.545(6) Å) in **9** is the among shortest reported values for metal-oxyphosphaalkyne complexes (see Table

S1), and suggests a more substantial contribution of the O–C≡P resonance form in this compound than in $\mathbf{2^{iPr}}$ and $(THF)_4Mg(OCP)_2$. Notably, **9** was not observed in the NMR of the bulk material from this reaction. Multiple crystallization attempts yielded a mixture of powdery and crystalline solids, from which the crystalline material is difficult to separate and independently analyze by NMR spectroscopy. Compound **8** is stable for several weeks in anhydrous benzene and toluene, and similar to $\mathbf{2^{iPr}}$, decomposition is observed after several hours in refluxing benzene to afford free ^{iPr}NHC and unidentified solids.

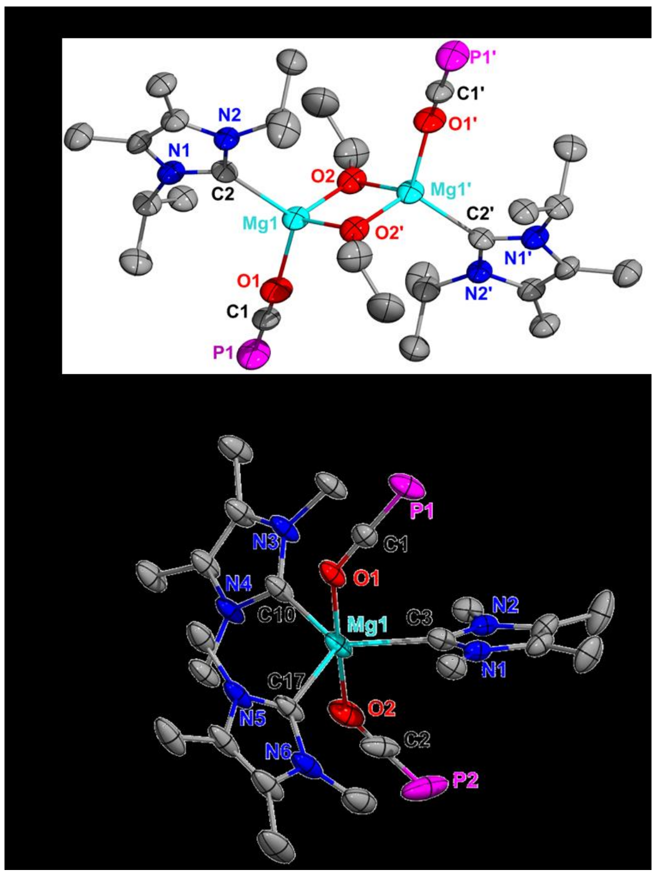


Figure 4. Molecular structure of **9** (a) and **10** (b). Co-crystallized solvent molecules for **10** and all H atoms are omitted for clarity. Thermal ellipsoids are shown at a probability level of 50% (**9**) and 30% (**10**). Selected bond distances (Å) and angles (deg): **9**: Mg1–O1, 1.938(4); Mg1–O2, 1.930(5),

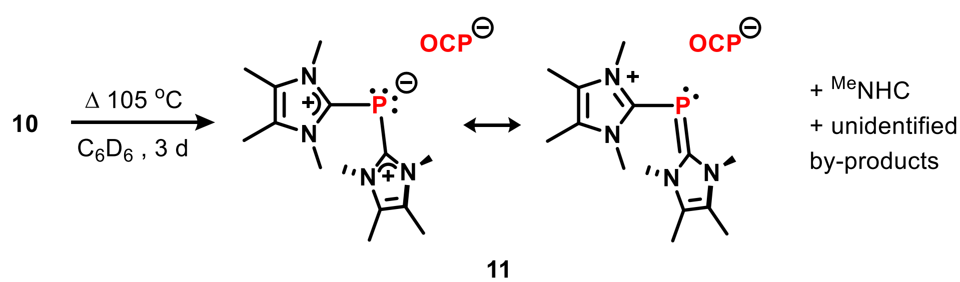
Mg1–O2', 1.953(4); O1–C1, 1.254(7); C1–P1, 1.545(6); Mg1–C2, 2.192(6); Mg1---Mg1, 2.885(4); Mg1–O1–C1, 145.9(5); O1–C1–P1, 179.3(6); O1–Mg1–C2, 112.6(2); O2–Mg1–O1, 115.2(2); O2–Mg1–O2', 84.04(19). **10**: Mg1–O1, 2.111(3); Mg1–O2, 2.143(2); Mg1–C3, 2.213(3); Mg1–C10, 2.216(3); Mg1–C17, 2.215(3); O1–C1, 1.208(3); O2–C2, 1.199(5); C1–P1, 1.575(3); C2–P2, 1.584(6); C1–O1–Mg1, 140.6(2); C2–O2–Mg1, 147.5(3); O1–Mg1–O2, 178.62(10); O2–Mg1–C3, 90.20(12); O1–Mg1–C3, 88.75(10); C17–Mg1–C3, 118.06(11); C10–Mg1–C3, 125.53(11); C17–Mg1–C10, 116.36(12).

Consistent with the reactivity profile for $\mathbf{4^{Me}}$, we anticipated that base saturation via tris-NHC coordination may stabilize the target diphosphaethynolate complex and attenuate its Lewis acid reactivity or decomposition pathways. Indeed, the reaction of equimolar amounts of $(^{Me}NHC)_2MgBr_2$, ^{Me}NHC and $[Na(dioxane)_2][OCP]$ in toluene yielded the desired product $(^{Me}NHC)_3Mg(OCP)_2$ (**10**) as a colorless crystalline solid in 35 % yield (Scheme 4). In the $^{31}P\{^1H\}$ NMR spectrum, the OCP anion resonates at δ -385.6 ppm and is significantly upfield from those of $(THF)_4Mg(OCP)_2$, $\mathbf{2^{iPr}}$ and **8** (Table 1). The C≡P resonance (δ 169.0 ppm, $^1J_{CP}$ = 52.9 Hz) in the $^{13}C\{^1H\}$ NMR spectrum is observed as a doublet with a much larger ^{13}C–^{31}P coupling constant than in $\mathbf{2^{iPr}}$. Single crystal X-ray diffraction studies reveal that **10** is mononuclear (Figure 4b). The magnesium atom resides in a trigonal bipyramidal coordination environment with three ^{Me}NHC ligands on the equatorial positions (Σ ∠C-Mg-C = 359.95º). The axial OCP anions in **10** are *cis* to the OMgO plane, in contrast to $(THF)_4Mg(OCP)_2$ for which they are *trans*. Owing to the donor effects of tris(NHC)-stabilization, the Mg–O bond lengths in **10** are 0.09 – 0.21 Å longer than those of $\mathbf{2^{iPr}}$, **9** and $(THF)_4Mg(OCP)_2$ (Table 1). The O–C≡P bond parameters in **10** are comparable to **6** and $(THF)_4Mg(OCP)_2$, with shorter O–C and longer C–P bond lengths than those of $\mathbf{2^{iPr}}$ and

9. The isolation of **10** suggests that the difficulty in stabilizing the ^{iPr}NHC adduct results from unfavorable steric congestion, which may lead to carbene dissociation and enable a more electrophilic Mg^{2+} center for dioxane activation.

Compound **10** is stable in refluxing benzene for several hours. However, heating a colorless C_6D_6 solution of **10** in a J-Young NMR tube for 3 days at 105 ºC yielded an orange solution, with the appearance of two new singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ -149.9 and -115.24 ppm. By layering this solution with hexanes, a few light yellow crystals were obtained and characterized by X-ray diffraction as a charge-separated bis-NHC stabilized phosphorus(I) species [(^{Me}NHC)$_2$P^I][OCP] (**11**) (Scheme 5). The bond metrics in **11** (Figure 5) are comparable to reported (NHC)$_2$P^I cations,[36-41] and justify the structural depiction in Scheme 5. Similarly, the resonances in the $^{31}P\{^1H\}$ NMR spectrum are in agreement with known P^I cations (δ -115.24 ppm, range -93 to -127 ppm[36-41]) and a non-contacted OCP anion (δ -386.1 ppm).

Scheme 5. Thermal decomposition of a magnesium diphosphaethynolate complex



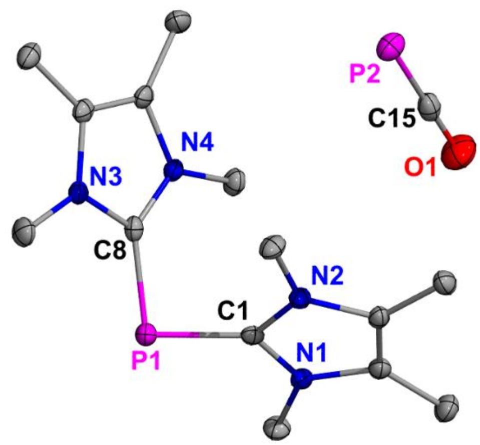


Figure 5. Molecular structure of **11** with H atoms omitted for clarity. Selected bond distances (Å) and angles (deg): P1–C1, 1.8045(18); P1–C8, 1.8055(18); C15–P2, 1.605(2); O1–C15, 1.196(2); C1–N1, 1.355(2); C1–N2, 1.390(2); C8–N3, 1.355(2); C8–N4, 1.351(2); C1–P1–C8, 96.63(8); O1–C15–P2, 179.00(17).

Upon its successful structural characterization, it becomes clear that **11** is a minor product of this transformation, and the major product remains unidentified (δ -149.9 ppm in the $^{31}P\{^{1}H\}$ NMR). Free ^{Me}NHC was identified as another by-product of this reaction, and the second major set of ^{Me}NHC resonances in the ^{1}H NMR spectrum is presumably due to **11** but could not be confidently assigned (Figure S25). Attempts to independently isolate and spectroscopically characterize **11** were unsuccessful. Nevertheless, the observation of **11** suggests that a highly unusual decarbonylation of a phosphaethynolate complex has occurred. Such reactivity is traditionally observed in the domain of phosphaketenide ($^{-}$P=C=O) complexes.[1, 2, 42-51] The $^{-}$P←:C=O resonance form is widely invoked to rationalize decarbonylation from OCP fragments, and lends credence to the intermediacy of a magnesium phosphide in this reaction. Literature precedence suggests that base transfer to the phosphorus atom or carbonyl carbon is a likely initial step in the observed decarbonylation.[26, 50-54]

CONCLUSION

Solvent-free, phosphaethynolate-containing Grignard complexes have been isolated, and the stereoelectronic influence of 1,3-dialkyl substituted NHCs on their stabilization was explored. In contrast to known alkaline earth phosphaethynolate salts which are ether-stabilized and rapidly decompose in solution, these NHC-stabilized complexes are highly soluble and thermally stable in common hydrocarbon solvents. The ability of some of these compounds to activate dioxane was attributed to enhanced metal Lewis acidity due to dynamic carbene coordination, which may render them promising reagents for bond activation at magnesium. In addition, the isolated carbene-saturated Na(OCP), which is soluble in non-polar solvents, may become a key reagent in situations where ethers must be avoided, or the solubility of ethereal solvent-coordinated Na(OCP) is problematic.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at DOI. Experimental procedures, NMR and IR spectra, molecular structure of $\mathbf{1}^{\mathbf{Me}}$, crystallographic refinement details (PDF).

Accession Codes

CCDC 2086364-2086372 and 2097942-2097943 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

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Notes

The authors declare no competing financial interest.

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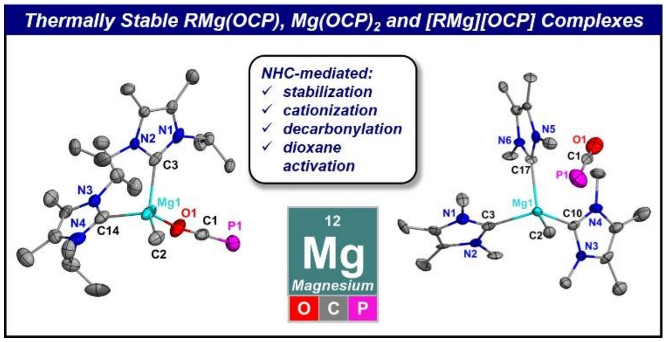

Structurally diverse, hydrocarbon soluble magnesium phosphaethynolate complexes with remarkable thermal stability have been isolated and characterized. The stereoelectronic influence of 1,3-dialkyl-substituted *N*-heterocyclic carbenes in their stabilization facilitated cationization, dioxane activation and thermal decarbonylation reactivities.