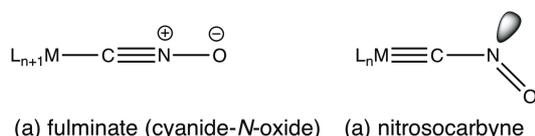


In Search of Fulminate Analogues: $L_nM\equiv CP=NR$ Benjamin J. Frogley,^[a] Anthony F. Hill,^[a,*] Rong Shang,^[b] Manab Sharma^[a] and Anthony C. Willis^[a]

Abstract: The ‘CPNR’ ligand may be viewed as being isolobal with fulminate, CNO, however attempts to prepare a complex of such a ligand resulted instead in a range of novel imino and aminophosphinocarbyne complexes. Sequential treatment of $[Mo(\equiv CBr)(CO)_2(Tp^*)]$ (Tp^* = hydrotris(dimethylpyrazolyl)borate) with tBuLi and $CIP=NMes^*$ ($Mes^* = C_6H_2^tBu_{3-2,4,6}$) afforded mixtures of the complexes $[Mo(\equiv CP^tBuNHMes^*)(CO)_2(Tp^*)]$ and traces of the bimetallic products $[Mo_2(\mu_2-C_2P_2O(NHMe)_2)(CO)_2(Tp^*)_2]$ and $[Mo_2(\mu_2-C_2PNHMe)(CO)_2(Tp^*)_2]$. The reaction of $[W(\equiv CBr)(CO)_2(Tp^*)]$ with tBuLi and $CIP=NMes^*$ afforded predominately the mononuclear carbyne $[W(\equiv CP(=NMes^*)^tBu_2)(CO)_2(Tp^*)]$ and traces of the binuclear complex $[W_2(\mu-C_2PNHMe)(CO)_4(Tp^*)_2]$ which is also obtained when tBuLi is used. Although not isolable, the intended complexes $[M(\equiv CPNMes^*)(CO)_2(Tp^*)]$ could be generated *in situ* and spectroscopically characterized via the reactions of the stannyl carbynes $[M(\equiv CSn^tBu_3)(CO)_2(Tp^*)]$ and $CIP=NMes^*$. The preceding observations are mechanistically interpreted with reference to a computational interrogation of the model complex $[Mo(\equiv CP=NCH_3)(CO)_2(Tp^*)]$, the LUMO of which has considerable phosphorus character.

Introduction

Metal fulminates, $M-CNO$, represent one of the oldest classes of organometallic compounds that feature covalent metal-carbon bonds,¹ though of course they were not recognised as such at their time of inception. Covalent molecular fulminate complexes remain rare and the few structurally authenticated examples² adopt essentially linear $M-C-N-O$ linkages, such that a cyanide-*N*-oxide description seems appropriate (Scheme 1a). It should however be noted that these examples involve metal centres (Co^{III} , Ni^{II} , Hg^{II} , Ag^I , Au^I , Pt^{II}) for which little or effectively no π -retrodonation from the metal is to be expected.

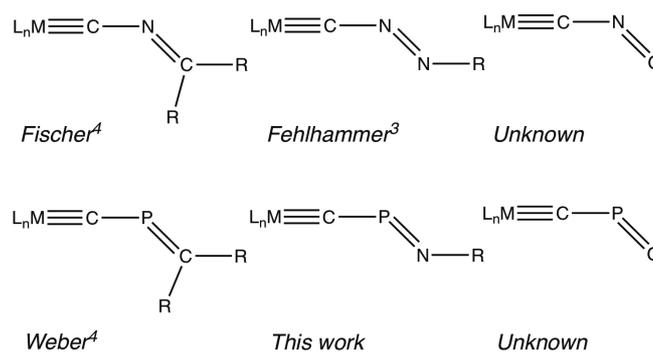


Scheme 1. Known and hypothetical fulminate coordination modes.

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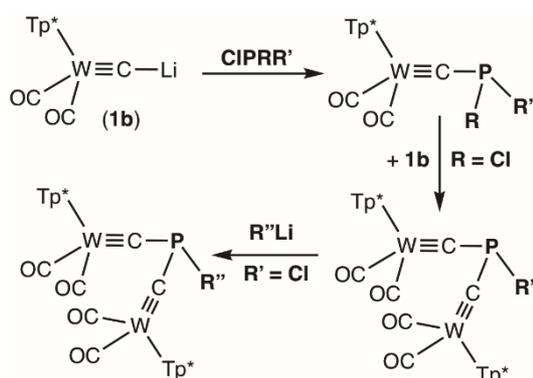
It stands to reason that coordination of a fulminate to a π -basic metal might well perturb the bonding such that a nitrosocarbyne description might increase in relevance (Scheme 1b). This supposition does not appear to have been explored, however simple isoelectronic/isolobal relationships between nitrogen and phosphorus as well as between oxo, imino and alkylidene units suggest some parallels (Scheme 2). Fehlhhammer has described a nitrile imine complex $[Cr(CNNH)(CO)_5]^-$ generated *in situ* by deprotonation of its conjugate acid,³ and H. Fischer has described a range of iminocarbyne complexes⁴ e.g., $[(OC)_5W\equiv C-N=CR_2]^+$. The alkylidene-phosphanylcarbyne class of ligand⁵ (and an arsenic analogue^{5d,6}) has enjoyed extensive studies by Weber *et al.* The complexes $[M\{\equiv CA=C(NR_2)_2\}(CO)_2(Tp^*)]$ ($M = Mo, W$; $R = Me, Et, A = P, As$) display bent $C-A=C$ spines and short $M\equiv C$ bonds, in addition to nucleophilic character at ‘A’, consistent with their description as, albeit somewhat exotic, carbyne complexes.

Scheme 2. Fulminate Isolobes.³⁻⁵

Herein we describe an exploration of the synthesis and spectroscopic characterisation of previously unknown iminophosphanylcarbyne complexes, ‘ $L_nM\equiv CP=NR$ ’ and whilst these defied isolation, they serve as intermediates *en route* to a range of novel unsaturated phosphorus functionalised carbyne complexes.

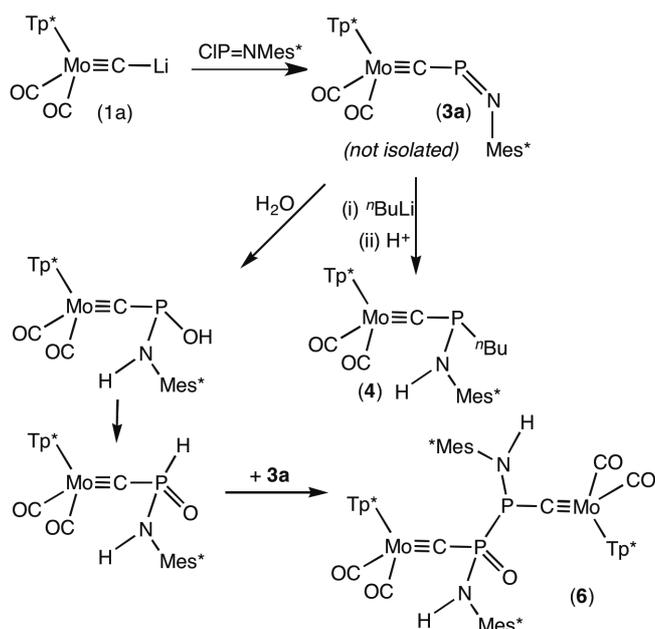
Results and Discussion

The lithiocarbynes $[M(\equiv CLi)(CO)_2(Tp^*)]$ ($M = Mo$ **1a**, W **1b**) may be conveniently generated *in situ* from $[M(\equiv CBr)(CO)_2(Tp^*)]$ via lithium-halogen exchange with tBuLi .^{7,8} These serve as carbon-based nucleophiles for the synthesis of a wide range of heteroatom-functionalised carbynes through reactions with suitable electrophiles.^{7,9} Of particular relevance here are the reactions with halophosphines that give rise to mono- and binuclear phosphinocarbynes (Scheme 3).¹⁰ We have therefore considered the reactions of **1** with *P*-halo-iminophosphanes as a possible route to complexes of the form L_nMCPNR .



Scheme 3. Synthesis of phosphinocarbynes via bromocarbyne lithiation.¹¹

With the exception of Cl–P=NMe^{s*} (**2**; Me^{s*} = C₆H₂’Bu₃-2,4,6)¹¹ *P*-haloiminophosphanes are generally dimeric in nature, e.g., “CIPN’Bu” actually exists as a head-to-tail cyclic dimer P₂N₂Cl₂’Bu₂,¹² which undergoes a range of nucleophilic halide substitution reactions in which the P₂N₂ ring ultimately remains intact. Treating a freshly generated THF solution of **1a** with a stoichiometric amount of **2** at –78 °C results in the formation of a deep green solution that rapidly discolours to orange-brown. On warming to room temperature, infrared spectroscopy suggests the presence of a major (ν_{CO} : 2012, 1932 cm⁻¹) and two minor products (ν_{CO} : 1999/1915 and 1992/1904 cm⁻¹). Repeated chromatography provided initially an orange compound, the spectroscopic data for which were not consistent with the desired complex [Mo(≡CP=NMe^{s*})(CO)₂(Tp^{*})] (**3a**), but rather the aminophosphinocarbyne [Mo(≡CPⁿBuNHMe^{s*})(CO)₂(Tp^{*})] (**4**, Scheme 4).



Scheme 4. Attempted synthesis of an iminophosphanylcarbyne (Me^{s*} = C₆H₂’Bu₃-2,4,6).

The IR spectrum comprises a pair of ν_{CO} absorption bands (*n*-hexane: 1996, 1916 cm⁻¹) comparable to those reported for molybdenum phosphinocarbyne complexes, e.g., [Mo(≡CPPh₂)(CO)₂(Tp^{*})] (THF: 1995, 1913 cm⁻¹)^{10a} and [Mo(≡CPⁿBuPh)(CO)₂(Tp^{*})] (C₆H₁₄: 1995, 1912/1916 cm⁻¹).^{10e} The ³¹P{¹H} NMR spectrum of **4** showed a singlet at 78.8 ppm while the ¹H and ¹³C{¹H} NMR spectra revealed three chemically distinct pyrazolyl environments, indicating the asymmetry of the molecule due to the stereogenic phosphorus. Besides those expected for the mesityl group, signals for one *n*-butyl group and a doublet integrating for one proton at 4.87 ppm (²J_{PH} = 10 Hz) were also observed. The ¹³C{¹H} NMR spectrum included a doublet at δ_{C} = 325.7 (¹J_{CP} = 100 Hz) in a similar region to those for Weber’s alkylidenephosphanylcarbyne complexes [M(≡C–P=C(NR₂)₂)(CO)₂(Tp^{*})] (δ_{C} = 318–337, ¹J_{CP} = 101–111 Hz; M = Mo, W; R = Me, Et).⁵ Two resonances were observed for the diastereotopic carbonyl ligands at δ_{C} = 230.2 and 226.6 (d, ³J_{CP} = 4 Hz).

The formulation of **4** as an amino-butyl-phosphinocarbyne is consistent with the formation of the desired complex **3a** which subsequently reacts with adventitious ⁿBuLi followed by protic work-up (Scheme 4). This is further supported by treatment of a solution of presumed **3a**, generated *in situ*, with an alternative lithium reagent, 2,4,6-trimethylphenyllithium (mesityllithium, MesLi), which furnishes the distinct aminophosphinocarbyne [Mo(≡CPMe^{s*}NHMe^{s*})(CO)₂(Tp^{*})] (**5**). Spectroscopic data for this species are reassuringly similar to those of **4**, the only major differences resulting from the presence of a mesityl rather than *n*-butyl group on phosphorus. The molecular structure of **5** has been determined (Figure 1) and confirms the formulation as a phosphinocarbyne with Mes and NHMe^{s*} substituents about an approximately trigonal pyramidal P^{III} centre ($\Sigma^{\circ}\text{P}$ = 313.5°). Bond distances and angles are generally consistent with the small number of reported phosphinocarbynes.¹⁰ The angles about phosphorus are slightly larger than in other reported species, although this is not entirely surprising given the exaggerated steric bulk of the mesityl and super-mesityl (Me^{s*}) groups.

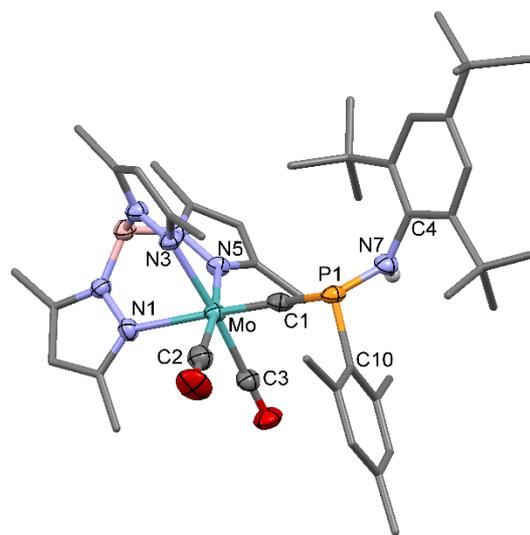


Figure 1. Molecular structure of **5** (50% displacement ellipsoids, pyrazolyl and aryl groups simplified for clarity). Selected bond lengths (Å) and angles (°): Mo–C1 1.822(3), C1–P1 1.791(3), P1–N7 1.691(3), P1–C10 1.866(3), N7–C4 1.446(4), Mo–N1 2.324(3), Mo–N3 2.246(3), Mo–N5 2.235(2), Mo–C2 2.013(4), Mo–C3 2.010(3), Mo–C1–P1 164.2(2), C1–P1–C10 98.47(14), C1–P1–N7 106.94(15), N7–P1–C10 108.13(16), P1–N7–C4 122.1(2).

A further piece of circumstantial evidence for the in situ formation of **3a** was provided by a 'rogue crystal' obtained from the first of two chromatographic purifications of **4**. Insufficient material was acquired for spectroscopic characterisation, however its molecular structure is included here (**6**, Figure 2) because it is unprecedented and it is also consistent with being the hydrolysis product of **3a** (Scheme 4). The molecular structure of **6** corresponds to a bimetallic bis(carbyne) in which both phosphorous (P^{III}) and phosphoric (P^V) centres are directly bonded within a $Mo\equiv CP(=O)(NHR)-P(NHR)C\equiv Mo$ core. The only other structure that loosely resembles the $R_2P_2O(NHR)_2$ core of **6** from the Cambridge Crystallographic Data Centre is $(Cp^*)P(=O)(NHSiMe_3)-P(NHSiMe_3)(Cp^*)$ ($Cp^* = \eta^1-C_5Me_5$), communicated by Nieger *et al.*¹³ The P1–P2 bond length of **6** (2.230(3) Å) is marginally (10 e.s.d.) shorter than observed in Nieger's compound (2.2628(15) Å), despite the excessive steric clutter around the core of **6**. The Mo–C–P angles at C1 (168.7(4)°) and C2 (158.8(3)°) deviate significantly from linearity, however such bending is commonplace amongst carbyne complexes of the form $[M\equiv CR](CO)_2(Tp^*)$,¹⁴ being due primarily to crystal packing and intermolecular non-bonded interactions.

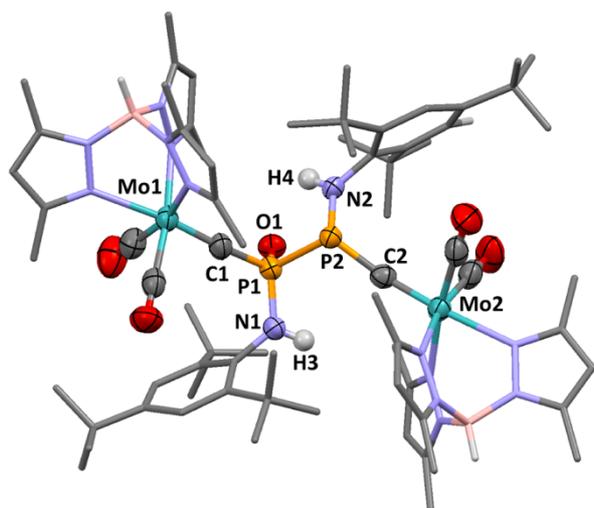
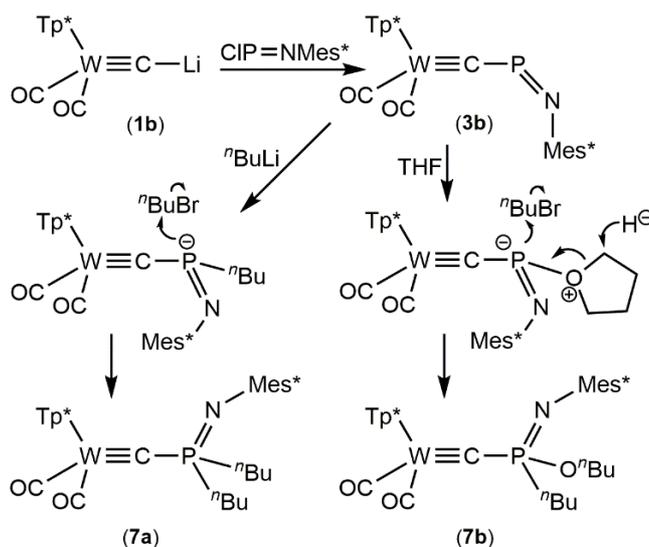


Figure 2. Molecular structure of **6** (60% displacement ellipsoids, pyrazolyl and aryl groups simplified and minor disorder components are not shown for clarity). Selected bond lengths (Å) and angles (°): Mo1–C1 1.796(6), Mo1–C11 2.026(7), Mo1–C12 2.004(8), Mo2–C2 1.816(6), P1–P2 2.230(3), P1–O1 1.486(5), P1–C1 1.801(6), P1–N1 1.667(5), P2–C2 1.831(6), P2–N2 1.680(5), P1–C1–Mo1 168.7(4), P2–C2–Mo2 158.8(3), P2–P1–O1 109.1(2), P2–P1–C1 97.5(2), P2–P1–N1 108.59(19), C1–P1–N1 111.1(3), P1–P2–C2 105.28(19), P1–P2–N2 91.34(18), C2–P2–N2 110.4(2), P1–C1–Mo1 168.7(4), P2–C2–Mo2 158.8(3).

Given the typically slower kinetics for 5d *cf* 4d metals, the corresponding reaction employing the tungsten analogue **1b** was investigated. As in the molybdenum case, an intense green solution was initially observed to form upon addition of **2** to the lithiocarbyne **1b**, and this empirically appeared to persist marginally longer (~30 min) but did ultimately discolour to orange even when maintained at $-78^\circ C$. The resulting mixture proved essentially intractable and no significant amount of a pure species could be isolated by either fractional crystallisation or cryostatic ($-30^\circ C$) column chromatography. However, when the volatiles were removed and the residue extracted with *n*-hexane, a small number of orange crystals formed which were found to be suitable for X-ray structural analysis and proved to be the mononuclear

complex with two *n*-butyl groups on a P^V centre, $[W\equiv CP(=NMe_s^*)^nBu_2](CO)_2(Tp^*)]$ (**7a**, Scheme 5). Additionally, a small amount of an impure product was collected as a small yellow band during an attempt at separation *via* silica gel column chromatography, which was found to be a second mononuclear carbyne complex, $[W\equiv CP(=NMe_s^*)(^nBu)(O^iBu)](CO)_2(Tp^*)]$ (**7b**), where one *n*-butyl and one *n*-butoxy group are bound to phosphorus.

The formation of both **7a** and **7b** are consistent with the intermediacy of the expected iminophosphanylcarbyne **3b**. To form the di-*n*-butyl complex **7a**, the intermediate **3b** could undergo nucleophilic attack at phosphorus to generate the anionic intermediate $[W\equiv CP(=NMe_s^*)^nBu](CO)_2(Tp^*)]Li$ which (*cf.* the molybdenum analogue) persists long enough to be alkylated by the nBuBr present as a side product from the initial lithium-halogen exchange process. The same anionic intermediate could alternatively be formed by initial formation of $^nBu-P=NMe_s^*$ which then undergoes nucleophilic attack at phosphorus by the lithiocarbyne. However, this pathway could be discounted by treating **2** with nBuLi in a separate reaction vessel and adding the resulting presumed solution of $^nBuP=NMe_s^*$ to the lithiocarbyne complex. In this case, the only species observed to form were $[W\equiv CH](CO)_2(Tp^*)]^{\ominus}$ and its decomposition product, the bimetallic vinylidene $[W_2(\mu-C=CH_2)(CO)_4(Tp^*)_2]$.¹⁵ Similar results were observed when **2** was first treated with methylolithium. In the case of **7b**, the reaction presumably proceeds by initial coordination of a molecule of THF to the highly electrophilic phosphorus of **3b**. This may then undergo a ring-opening reaction with hydride that is generated on decomposition of residual nBuLi as the mixture is warmed to room temperature (thermal decomposition of alkylolithium reagents in THF is known to generate lithium hydride and the corresponding vinyl species).¹⁶ The *n*-butyl group in **7b** is most likely also derived from the nBuBr present in the reaction mixture as a result of the initial lithium-halogen exchange.



Scheme 5. Synthesis of iminophosphanylcarbynes.

The single crystal X-ray structures of both **7a** and **7b** have been determined, the results of which are summarised in Figures 3 and 4, respectively. The W–C–P spines are slightly bent ($167.7(4)^\circ$ and $176.7(3)^\circ$, respectively) whilst the $W\equiv C$ (1.801(11),

1.842(5) Å) and C1–P (1.840(12), 1.788(6) Å) bond lengths are comparable to those previously reported for the chalcophosphorylcarbynes $[W\{\equiv CP(=A)Ph_2\}(CO)_2(Tp^*)]$ (A = S: 160.5(3)°, 1.829(4), 1.785(4) Å; A = Se: 164.6(2)°, 1.823(4), 1.784(4) Å).^{11b} The P–N bond distances (1.551(9) and 1.517(4) Å, respectively) are significantly shorter than those found in **5** (1.691(3) Å), consistent with the double bond character.

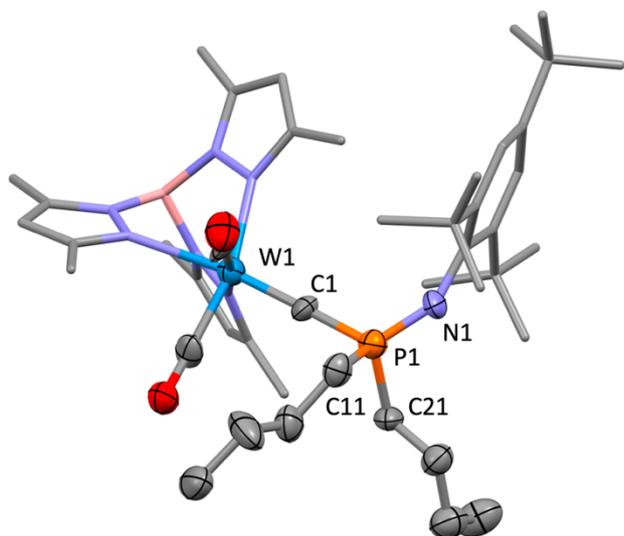


Figure 3. Molecular structure of **7a** (50% displacement ellipsoids, mesityl and pyrazolyl groups simplified and H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): C1–W1 1.801(11), C1–P1 1.840(12), N1–P1 1.551(9), C11–P1 1.831(13), C21–P1 1.815(12), W1–C1–P1 167.8(7), C31–N1–P1 149.1(8), C1–P1–C11 102.8(5), C1–P1–C21 106.2(5), C11–P1–C21 102.2(6), C1–P1–N1 116.9(5)

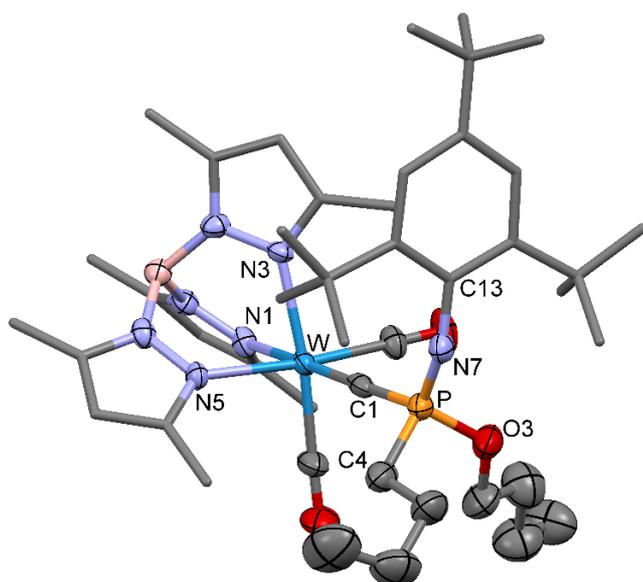


Figure 4. Molecular structure of **7b** (50% displacement ellipsoids, mesityl and pyrazolyl groups simplified and H-atoms omitted for clarity). Selected bond lengths (Å) and angles (°): W–C1 1.842(5), C1–P 1.778(5), P–C4 1.788(6), P–O3 1.605(4), P–N7 1.517(4), W–N1 2.312(4), W–N3 2.201(3), W–N5 2.207(3), W–C1–P 176.7(3), C1–P–C4 106.0(2), C1–P–O3 107.1(2), C1–P–N7 116.6(2), N7–P–C4 111.5(3), N7–P–O3 111.7(2), O3–P–C4 103.0(3).

Given the interference of ⁿBuLi and/or ⁿBuBr manifest in the formation of **4**, **6** and **7**, we turned to Seebach's lithium-halogen exchange protocol¹⁷ which employs two equivalents of ^tBuLi, such

that the side-produced ^tBuBr is rapidly quenched in an *E*₂ reaction with the second equivalent of ^tBuLi. Treating **1b** with two equivalents of ^tBuLi at –78 °C followed by **2** resulted again in a complex mixture of products, only one of which could be isolated in trace amounts by fractional crystallisation. This complex was structurally characterised (Scheme 6, Figure 6) and identified as a bimetallic bis(carbyne) complex bridged by an aminophosphino group, $[W_2(\mu_2-C_2PNHMe^*)(CO)_4(Tp^*)_2]$ (**8b**). The same product was obtained, without any improvement in yield, when **1b** was generated with slightly less than one equivalent of ⁿBuLi (to suppress formation of the *n*-butyl substituted derivatives) and subsequently treated with ²/₃ an equivalent of ClP=NMe^{*}. Similar results were observed when this latter procedure was attempted with the molybdenum analogue **1a**, where only an impure trace amount of the related complex $[Mo_2(\mu_2-C_2PNHMe^*)(CO)_4(Tp^*)_2]$ (**8a**) could be obtained, structurally characterised (Figure 5), and limited spectroscopic data acquired.

Scheme 6. Synthesis of aminobis(alkylidynyl)phosphines.

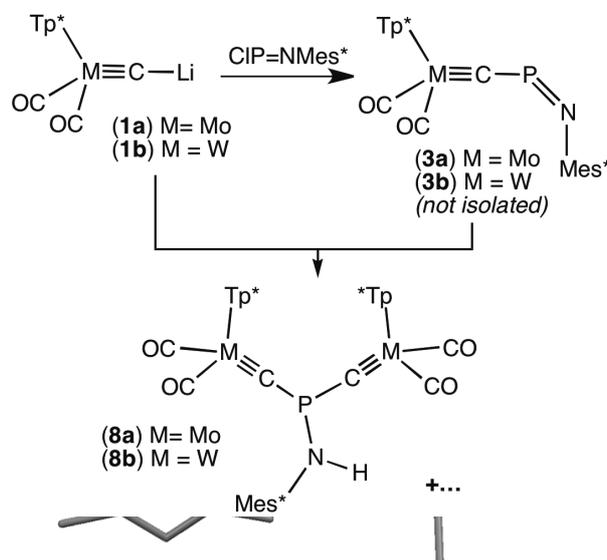


Figure 5. Molecular structure of **8a** (50% displacement ellipsoids, mesityl and pyrazolyl groups simplified for clarity). Selected bond lengths (Å) and angles (°): Mo1–C1 1.808(4), C1–P 1.795(4), P–C2 1.779(4), C2–Mo2 1.813(4), P–N13 1.724(3), N13–C7 1.421(5), Mo1–N1 2.333(3), Mo1–N3 2.219(3), Mo1–N5 2.210(3), Mo2–N7 2.326(3), Mo2–N9 2.231(3), Mo2–N11 2.231(3), Mo1–C1–P 164.3(2), P–C2–Mo2 171.1(2), C1–P–C2 97.88(16), C1–P–N13 107.40(16), C2–P–N13 102.49(16).

We have previously described the synthesis of bis(alkylidynyl)phosphines $[W_2(\mu_2-C_2PR)(CO)_4(Tp^*)_2]$ (R = Cl, Ph, Cy)^{10e-g} via the reactions of the bromocarbyne **1b** with ⁿBuLi and a dichlorophosphine (Cl₂PR, Scheme 3) or alternatively via the palladium catalysed reaction of the **1b** with a primary phosphine (H₂PR). Primary aminophosphines (R = amino) are generally unstable with respect to amine elimination and formation of cyclopolyposphanes, such that **8a** and **8b** are not available via this route.

Structural features associated with the (MC)₂PN core in **8a** and **8b** are in general accord with those observed for other bis(alkylidynyl)phosphines,¹⁰ other than to note that (i) the geometry at the amino N is somewhat flattened ($\Sigma^\circ\text{N} = 350.2$ and 350.5° , respectively) which might reflect a combination of steric congestion and N π -P π overlap and (ii) the angles at P more closely approach orthogonality ($\Sigma^\circ\text{P} = 307.8$ and 308.5° , respectively) and may be compared with those for the organoalkynylamine ^tBuC \equiv CP(NPh₂)C₆H₂Me₃-2,4,6 for which a similar angle sum is observed ($\Sigma^\circ\text{P} = 308.9^\circ$).¹⁸

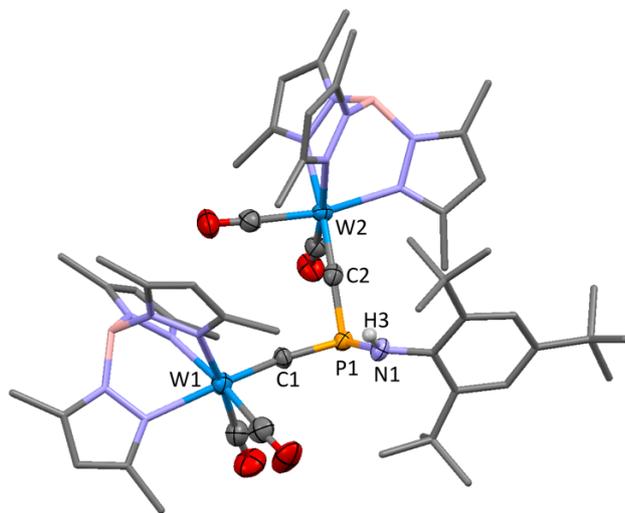


Figure 6. Molecular structure of **8b** (50% displacement ellipsoids, mesityl and pyrazolyl groups simplified for clarity). Selected bond lengths (Å) and angles ($^\circ$): W1–C1 1.823(5), W2–C2 1.826(6), P1–C1 1.775(5), P1–C2 1.804(6), P1–N1 1.722(4), N1–C31 1.425(6), W1–N111 2.313(5), W1–N121 2.213(5), W1–N131 2.220(5), W2–N211 2.321(4), W2–N221 2.205(4), W2–N231 2.209(4), N1–P1–C1 102.5(2), N1–P1–C2 107.5(2), C1–P1–C2 98.5(2), P1–N1–C31 121.2(3), P1–C1–W1 171.2(3), P1–C2–W2 164.7(3).

Because **8a** and **8b** are formed in such low yield, detailed mechanistic conjecture would be inappropriate. It is nevertheless noteworthy that its formation may be rationalised by once again invoking the intermediacy of the desired but elusive complexes **3a** and **3b**. In the absence of extraneous ^tBuLi, a corollary of the Seebach protocol, the only potential nucleophile available is a further equivalent of unreacted **1b** which undergoes nucleophilic attack at phosphorus followed by protonation at nitrogen on work-up (Scheme 6). Thus a common feature of the mechanistic proposals in Schemes 4, 5 and 6 is the electrophilicity of the phosphorus in **3a** and **3b**.

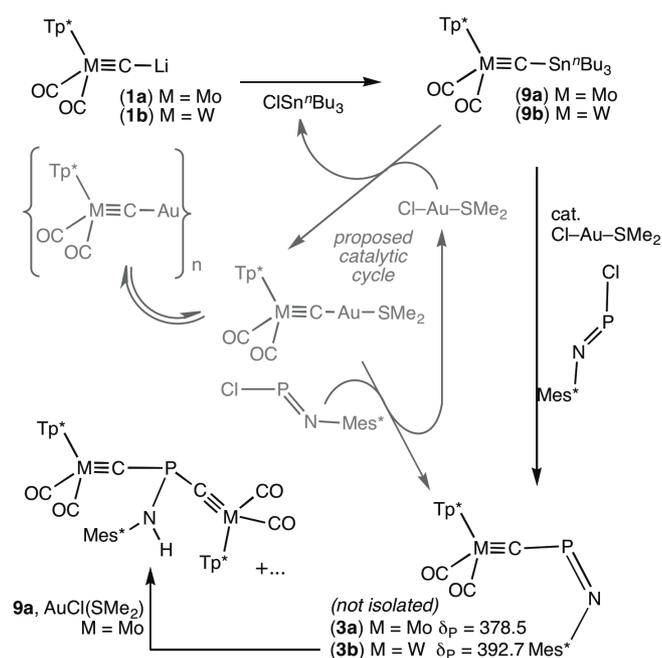
During these ongoing and consistently frustrating studies, in separate work we have recently discovered that the stannylcarbyne [W(\equiv CsnⁿBu₃)(CO)₂(Tp*)] (**9b**)²² can undergo transmetallation from tin to gold(I) to afford an unusual octametallic gold carbido species [W₄Au₄(μ -C)₄(CO)₈(Tp*)₄]. This in turn is capable of transmetallating the 'C \equiv W(CO)₂(Tp*)' fragment to palladium(II) making it a viable partner in a range of Pd/Au catalysed cross-coupling reactions with carbon-halogen bonds.²³ It was thought that a similar gold(I)-mediated reaction might be possible between the stannylcarbynes and reactive main-group halides, specifically CIP=NMes* to furnish **3a** or **3b** by a different route which obviates many of the extraneous reagents (ⁿBuLi, BrⁿBu *etc.*), which were proving troublesome in the earlier reactions.

The requisite molybdenum stannyl carbyne [Mo(\equiv CsnⁿBu₃)(CO)₂(Tp*)] (**9a**) is unknown but could be prepared in manner similar to that described for **9b**, and [Mo(\equiv CsnR₃)(CO)₂(Tp*)] (R = Me,^{9b} Ph²²). The complex forms in good yield and is not only thermally stable but is also resistant to hydrolysis under column chromatography conditions on silica gel. In contrast, the corresponding tungsten complex [W(\equiv CsnⁿBu₃)(CO)₂(Tp*)] (**9b**) is readily and cleanly hydrolysed to the parent methylidyne [W(\equiv CH)(CO)₂(Tp*)]^[8] during chromatography, indeed this proves to be the most convenient means of generating the thermally unstable methylidyne as required from a storable precursor.

In an NMR-tube the reaction between [Mo(\equiv CsnⁿBu₃)(CO)₂(Tp*)] and CIP=NMes* was investigated at ambient temperature and found not to proceed in the absence of any further additives. When a catalytic amount of [AuCl(SMe₂)] (ca 5 mol%) was however introduced the colour of the solution changed rapidly to dark green and this colour persisted long enough for limited spectroscopic data to be obtained. The ³¹P{¹H} NMR spectrum is comprised of two major resonances in an approximate 72:28 ratio. The predominant resonance is located significantly down-field, at $\delta_P = 378.5$, and falls within the region expected for especially deshielded, two-coordinate phosphorus nuclei as in the desired iminophosphanlycarbyne **3a** (Scheme 7).

The first step in the catalytic process, i.e., transmetallation of the carbido unit from tin to gold is well-understood and in the absence of strong ligands, the dimethylsulfide is lost with reversible formation of oligomeric "[M(CAu)(CO)₂(Tp*)]_n". In the case of tungsten in the solid state a tetrameric cyclic structure (n = 4) is adopted although subsequent addition of strong ligands e.g., PEt₃ results in cleavage with formation of monomeric [W(\equiv CAuPEt₃)(CO)₂(Tp*)]. We might therefore assume that transient coordination of the gold to the phosphorus of **2** helps to co-locate the Au–C and P–Cl bonds for transfer of the carbido from gold to phosphorus.

We are uncertain of the identity of the second major component, which resonates at $\delta_P = 104.7$, although we note that while it is similar to that of **8a** ($\delta_P = 106.8$) the bimetallic complex appears to be absent by ¹H NMR spectroscopy. The magnitude of the resonance at 378.5 ppm is rapidly diminished after a few hours and even in a sealed vessel a "forest" of new phosphorus resonances arise between –20 and 150 ppm. While it might be thought that the slower kinetics associated with 5d *cf* 4d metals might mean that **3b** could be isolated more easily by this route, this was not found to be the case. Sample preparation in the same manner did give the initial green solution, although this still rapidly decolourised to orange-brown. NMR spectroscopy did, however, allow a small resonance at $\delta_P = 392.7$ to be identified although unfortunately ¹J_{CW} couplings could not be observed. This, again, is where the phosphorus nuclei in the iminophosphanlycarbyne **3b** might be expected to resonate. The dominant resonance in this spectrum is $\delta_P = 114.7$ (²J_{PW} = 71 Hz) which is also fairly similar but not identical to that of an aminobis(alkylidynyl)phosphine such as **10** ($\delta_P = 128.6$, ²J_{PW} = 76 Hz, *vide infra*) and possibly corresponds to a gold or stannyl amide, hydrolysis of which would afford **8b**.



Scheme 7. Synthesis of iminophosphanycarbynes via gold mediated transmetalation of stannyl carbynes (proposed catalytic cycle shown in grey).

When **9a** was treated with half an equivalent of $\text{ClP}=\text{NMe}_s^*$ under the same conditions, a mixture ensued over time from which it was possible to isolate small amounts (ca 10%) of the dinuclear complex **8a** following chromatography. It would therefore appear that **9a** (or more likely “ $\{\text{AuCW}(\text{CO})_2(\text{Tp}^*)\}_n$ ”^[24]) is sufficiently nucleophilic to slowly attack **3a**, again attesting to the electrophilic nature of phosphorus in the latter.

The above results together substantiate the viability of iminophosphanycarbynes, notwithstanding what appears to be a high phosphorus-centred reactivity that has precluded their isolation. We have therefore computationally interrogated the simpler hypothetical model complexes $[\text{Mo}(\text{CANMe})(\text{CO})_2(\text{Tp}^*)]$ ($\text{A} = \text{N}$ **10N**, $\text{A} = \text{P}$ **10P**). Beginning in both cases with a least favourable linear MoCANMe spine, geometry optimisation resulted in bending at *both* the terminal nitrogen and the carbyne-bound nitrogen (**10N**) or phosphorus (**10P**) resulting in the geometries depicted in Figure 7. The frontier orbitals of interest are also depicted and their topology helps to explain the synthetic results described above, all of which point towards the phosphorus on **3** displaying electrophilic character. As is found for other carbynes of the $[\text{M}(\text{CR})(\text{CO})_2(\text{L})]$ ($\text{L} = \text{Cp}, \text{Tp}, \text{Tp}^* \text{ etc.}$,) with a facial ligand ‘L’, the (d_{xy}) HOMO is orthogonal to the MCR spine and primarily associated with retrodative binding of the two carbonyls. As such, it is of little interest with respect to reactivity, other than redox processes. The HOMO-1 in both cases includes lone pair character at the terminal nitrogen as well as the carbyne bound phosphorus or nitrogen, being marginally higher in energy for the latter (**10N**). For both **10N** and **10P**, the LUMO of π -symmetry is delocalised along the MoCNN or MoCPN spine, is Mo–C and N=N/P=N antibonding in nature and has CN/CP π -bonding character. Although this is marginally higher in energy for **10P** than **10N**, the contribution from phosphorus orbitals is increased, accounting for the *P*-regioselectivity of nucleophilic attack. The LUMO+1 also includes some, albeit modest, contribution from phosphorus which is σ -symmetry but ca 1 eV

higher, i.e., in a frontier-orbital controlled reaction, the nucleophile is likely to approach orthogonal to the MoCPNC plane.

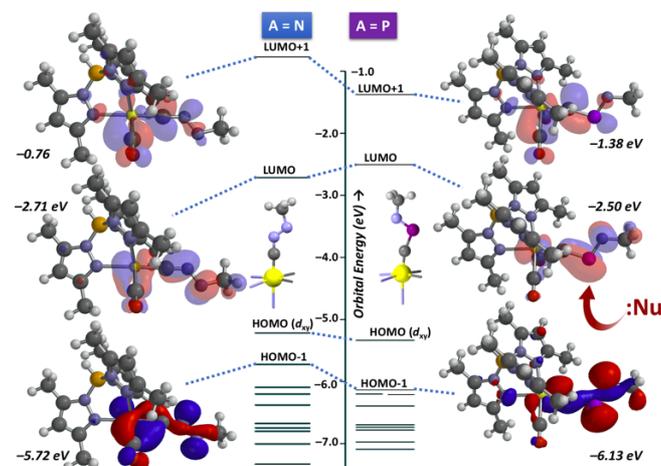
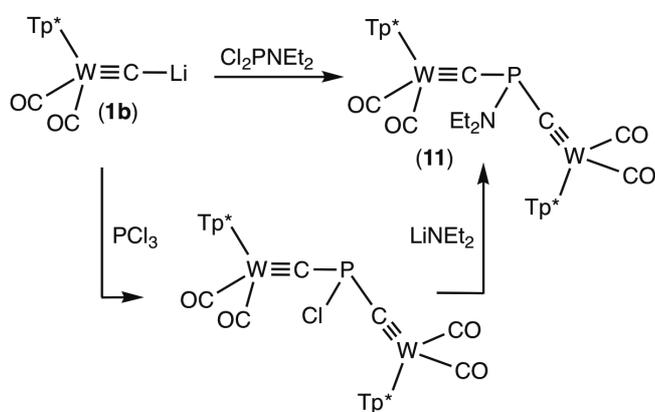


Figure 7. Geometries optimised at the DFT: B3LYP-6-31G*(LANL2DZ) level of theory for the hypothetical complexes $[\text{Mo}(\text{CANMe})(\text{CO})_2(\text{Tp}^*)]$ ($\text{A} = \text{N}$ **10N**, $\text{A} = \text{P}$ **10P**) with the respective frontier orbitals of interest (Isovalue = 0.032).

Under the conditions employed experimentally above, there were no opportunities for attack at **3** by electrophiles, however a consideration of the shape of the HOMO-1 for **10P**¹⁹ suggests that the molecule is an ambident nucleophile with the possibility of electrophilic attack occurring at nitrogen, phosphorus or the Mo≡C bond. The isolobal analogy with Weber’s alkylidenephosphanycarbynes would appear to support this prediction given that whilst $[\text{W}(\equiv\text{CP}=\text{C}(\text{NEt}_2)_2)(\text{CO})_2(\text{Tp}^*)]$ is alkylated (MeOTf) at phosphorus, the kinetic product of protonation at phosphorus slowly rearranges to the thermodynamic isomer involving protonation at the carbyne carbon.^{5b}

Whilst the structural studies of **8a** and **8b** confirm the viability of bis(alkylidynyl)aminophosphines, the low yields obtained precluded the satisfactory acquisition of useful spectroscopic data. Accordingly, an alternative synthetic strategy was developed to access substantive amounts of such a complex. Recently it was shown that sequential treatment of $[\text{M}(\equiv\text{CLi})(\text{CO})_2(\text{Tp}^*)]$ with $2/3$ an equivalent of PCl_2R afforded reasonable yields of the bis(alkylidyne)phosphines $[\text{M}_2(\mu_2\text{-C}_2\text{PR})(\text{CO})_4(\text{Tp}^*)_2]$ ($\text{M} = \text{Mo}, \text{W}; \text{R} = \text{Me}, \text{Ph}, \text{Cy}$)^{10e,10g} or alternatively treatment with $2/3$ equivalents of PCl_3 followed by an alkynyllithium furnishes alkynylbis(alkylidynyl)phosphines, $[\text{W}_2(\mu_2\text{-C}_2\text{PC}(\text{R})(\text{CO})_4(\text{Tp}^*)_2)]$ ($\text{R} = \text{Ph}, p\text{-tolyl}, \text{tBu}, \text{SiMe}_3$).^{10f} We therefore resolved to determine whether these approaches could be extended to give bis(alkylidynyl)aminophosphines. This was indeed found to be the case and treatment of **1b** with $2/3$ equivalents of PCl_2NEt_2 furnishes the expected bimetallic complex, $[\text{W}_2(\mu_2\text{-C}_2\text{PNEt}_2)(\text{CO})_4(\text{Tp}^*)_2]$ (**11**), directly as an orange solid following chromatographic purification in 65% yield (Scheme 8). The alternative method, whereby **1b** was treated initially with PCl_3 to furnish the $[\text{W}_2(\mu_2\text{-C}_2\text{PCl})(\text{CO})_4(\text{Tp}^*)_2]$ intermediate followed by LiNEt_2 (prepared from HNEt_2 and $^t\text{BuLi}$) also gave **11** but in a much poorer 22% yield.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum comprises a singlet resonance at $\delta_{\text{P}} = 128.6$ ($^2J_{\text{PW}} = 76$ Hz), a downfield shift compared to previously known bis(alkylidynyl)phosphines (ca 30–90 ppm),^{10e-g} all of which have possessed hydrocarbyl substituents, consistent with the amino substituent on phosphorus. The carbyne carbon gives rise to a doublet at $\delta_{\text{C}} = 298.2$ ($^1J_{\text{CP}} = 81$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. Characterisation of **11** also included an X-ray structural determination and the molecular structure is shown in Figure 8. The structural features very closely match those of **8a** and **8b**, e.g., the nitrogen is essentially trigonal ($\Sigma^{\circ}\text{N} = 353.5^{\circ}$) whilst the phosphorus has pyramidal geometry ($\Sigma^{\circ}\text{P} = 317.7^{\circ}$) with the smallest angle being between the carbyne substituents (C1–P–C2 $99.9(2)^{\circ}$). Despite the trigonal nitrogen geometry in the solid state, only a single set of resonances is observed for the ethyl substituents in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra indicating that free rotation occurs on these NMR timescales.



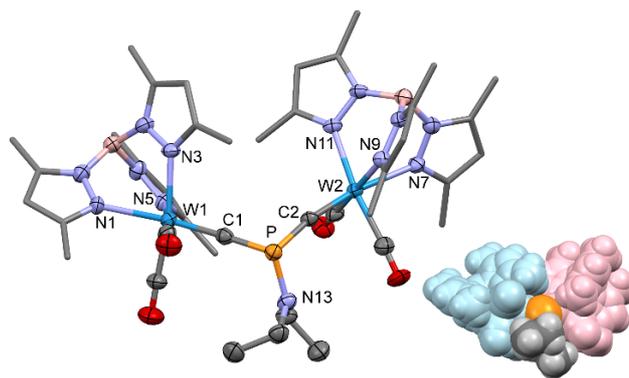
Scheme 8. Synthesis of a bis(alkylidynyl)aminophosphine.

Conclusions

Having first suggested that iminophosphanylcarbynes might be viable species akin to the simple and isolobal fulminate ligand, our efforts to isolate actual examples were consistently confounded. These failures notwithstanding, each of the novel products obtained was consistent with the actual formation of the desired species, but in the presence of extraneous reagents capable of further reactions ($^n\text{BuBr}$, $^n\text{BuLi}$, THF or further lithiocarbyne). These results point to considerable electrophilic character at the phosphorus of the putative ligand, a supposition that could be computationally substantiated.

To circumvent these various interferences an alternative synthetic approach involving gold mediated transmetalation from a stannyl carbyne successfully allowed the spectroscopic identification of the desired iminophosphanylcarbynes. The synthetic utility of lithiocarbynes **1** has been amply demonstrated^[7-10] however there are attendant caveats, not least that they are not isolable and can only be generated at low temperature and only (so far) in THF. Their synthesis via lithium-

Figure 8. Molecular structure of **10** in a crystal of **10**.CHCl₃ (50% displacement ellipsoids, mesityl and pyrazolyl groups simplified for clarity). Selected bond lengths (Å) and angles ($^{\circ}$): W1–C1 1.840(5), C1–P 1.783(5), P–C2 1.763(5), C2–W2 1.843(5), P–N13 1.686(5), N13–C7 1.461(7), N13–C9 1.460(7), W1–N1 2.290(4), W1–N3 2.211(4), W1–N5 2.222(4), W2–N7 2.296(4), W2–N9



2.214(4), W2–N11 2.198(4), W1–C1–P 161.7(3), C1–P–C2 99.9(2), P–C2–W2 169.0(3), C1–P–N13 112.0(2), C2–P–N13 105.9(2), P–N13–C7 115.1(4), P–N13–C9 121.1(4), C7–N13–C9 117.3(5).

halogen exchange generates an equivalent of alkyl halide (typically $^n\text{BuBr}$) which may compete with the intended electrophile to provide either $[\text{M}(\equiv\text{C}^n\text{Bu})(\text{CO})_2(\text{Tp}^*)]$ (S_{N}) or $[\text{M}(\equiv\text{CH})(\text{CO})_2(\text{Tp}^*)]$ (E_2). Furthermore, the highly reducing nature of the lithiocarbynes means that reactions may alternatively proceed via single electron transfer to afford the ethane-diyldynes $[\text{M}_2(\mu\text{-C}_2)(\text{CO})_4(\text{Tp}^*)_2]$.^[7b,9a,28] Each of these problems is likely to be precluded by the use of the new gold-mediated process. We are currently exploring the considerable scope this offers for the synthesis of new types of main-group element functionalised carbynes.

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Keywords: carbyne • alkylidyne • binuclear • iminophosphane • fulminate

- [1] (a) F. Kurzer, *J. Chem. Educ.*, **2000**, *77*, 851-857; (b) W. Beck, *Eur. J. Inorg. Chem.*, **2003**, 4275-4288; (c) W. Beck, J. Evers, M. Göbel, G. Oehlinger and T. M. Klapötke, *Z. Anorg. Allg. Chem.*, **2007**, *633*, 1417-1422.
- [2] (a) W. Beck and E. Schuierer, *Chem. Ber.*, **1962**, *95*, 3048-3055; (b) W. Beck and K. Feldl, *Z. Anorg. Allg. Chem.*, **1965**, *341*, 113-123; (c) W. Beck and E. Schuierer, *Chem. Ber.*, **1965**, *98*, 298-306; (d) D. Britton and J. D. Dunitz, *Acta Crystallogr.*, **1965**, *19*, 662-668; (e) W. Beck and E. Schuierer, *Z. Anorg. Allg. Chem.*, **1966**, *347*, 304-309; (f) W. Beck and K. Feldl, *Z. Naturforsch.*, **1966**, *21B*, 588; (g) W. Beck, C.-J. Oetker and P. Swoboda, *Z. Anorg. Allg. Chem.*, **1973**, *28*, 229; (h) U. Nagel, K. Peters, H. G. v. Schnering and W. Beck, *J. Organomet. Chem.*, **1980**, *185*, 427-432; (i) W. Weigand, U. Nagel and W. Beck, *J. Organomet. Chem.*, **1986**, *314*, C55-C58; (j) W. P. Bosman, W. Bos, J. M. M. Smits, P. T. Beurskens, J. J. Bour and J. J. Steggerda, *Inorg. Chem.*, **1986**, *25*, 2093-2096; (k) Ponikwar, Walter, E. Schuierer and W. Beck, *Z. Anorg. Allg. Chem.*, **2000**, *626*, 1282-1284; (l) P. Mayer, W. Ponikwar, K. Feldl, P. Swoboda and W. Beck, *Z. Anorg. Allg. Chem.*, **2000**, *626*, 2038-2039; (m) W. Ponikwar, P. Mayer, H. Piotrowski, P. Swoboda, C.-J. Oetker and W. Beck, *Z. Anorg. Allg. Chem.*, **2002**, *628*, 15-19.
- [3] (a) B. Weinberger and W. P. Fehlhammer, *Angew. Chem., Int. Ed. Engl.*, **1980**, *19*, 480-481; (b) Wolf P. Fehlhammer, F. Schoder, B. Weinberger, H. Stolzenberg and W. Beck, *Z. Anorg. Allg. Chem.*, **2009**, *635*, 1367-1373.

- [4] (a) H. Fischer, F. Seitz and J. Riede, *J. Chem. Soc., Chem. Commun.*, **1985**, 537-539; (b) H. Fischer, F. Seitz, J. Riede and J. Vogel, *Angew. Chem., Int. Ed. Engl.*, **1985**, *24*, 121-123; (c) H. Fischer, F. Seitz and J. Riede, *Chem. Ber.*, **1986**, *119*, 2080-2093; (d) F. Seitz, H. Fischer, J. Riede and J. Vogel, *Organometallics*, **1986**, *5*, 2187-2192; (e) F. Seitz, H. Fischer, J. Riede, T. Schöttle and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, **1986**, *25*, 744-746; (f) M. Tamm, T. Bannenber, A. Grzegorzewski and R. Fröhlich, *J. Organomet. Chem.*, **2001**, *617-618*, 640-646.
- [5] (a) L. Weber, G. Dembeck, R. Boese and D. Bläser, *Chem. Ber.*, **1997**, *130*, 1305-1308; (b) L. Weber, G. Dembeck, H.-G. Stammler, B. Neumann, M. Schmidtman and A. Müller, *Organometallics*, **1998**, *17*, 5254-5259; (c) L. Weber, G. Dembeck, H.-G. Stammler and B. Neumann, *Eur. J. Inorg. Chem.*, **1998**, 579-582; (d) L. Weber, G. Dembeck, P. Lönneke, H.-G. Stammler and B. Neumann, *Organometallics*, **2001**, *20*, 2288-2293.
- [6] L. Weber, G. Dembeck, R. Boese and D. Bläser, *Organometallics*, **1999**, *18*, 4603-4607.
- [7] (a) R. L. Cordiner, A. F. Hill and J. Wagler, *Organometallics*, **2008**, *27*, 5177-5179; (b) A. L. Colebatch, A. F. Hill, R. Shang and A. C. Willis, *Organometallics*, **2010**, *29*, 6482-6487.
- [8] The complex **1b** was first reported by Templeton and accessed via a multi-step synthesis: (a) G. M. Jamison, A. E. Bruce, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, **1991**, *113*, 5057 – 5059. (b) A. E. Enriquez, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, **2001**, *123*, 4992 – 5002.
- [9] (a) A. L. Colebatch, R. L. Cordiner, A. F. Hill, K. T. H. D. Nguyen, R. Shang and A. C. Willis, *Organometallics*, **2009**, *28*, 4394-4399; (b) R. L. Cordiner, A. F. Hill, R. Shang and A. C. Willis, *Organometallics*, **2011**, *30*, 139-144.
- [10] (a) R. L. Cordiner, P. A. Gugger, A. F. Hill and A. C. Willis, *Organometallics*, **2009**, *28*, 6632-6635; (b) A. L. Colebatch and A. F. Hill, *J. Am. Chem. Soc.*, **2014**, *136*, 17442-17445; (c) A. L. Colebatch, A. F. Hill and M. Sharma, *Organometallics*, **2015**, *34*, 2165-2182; (d) A. L. Colebatch and A. F. Hill, *Organometallics*, **2016**, *35*, 2249-2255; (e) A. L. Colebatch, Y.-S. Han, A. F. Hill, M. Sharma, R. Shang and J. S. Ward, *Chem. Commun.*, **2017**, *53*, 1832-1835; (f) B. J. Frogley and A. F. Hill, *Chem. Commun.*, **2018**, *54*, 12373-12376; (g) B. J. Frogley and A. F. Hill, *Chem. Commun.*, **2018**, *54*, 7649-7652.
- [11] N. Edgar, N. Martin and R. Franz, *Angew. Chem., Int. Ed. Engl.*, **1988**, *27*, 1715-1716.
- [12] R. Keat, D. S. Rycroft and D. G. Thompson, *J. Chem. Soc., Dalton Trans.*, **1979**, 1224-1230.
- [13] M. Nieger, H. Hupfer, E. Niecke and H.-M. Schiffer, private communication to the Cambridge Crystallographic Data Centre (CCDC114927, HIHGUA)
- [14] L. M. Caldwell, *Adv. Organomet. Chem.*, **2008**, *56*, 1-94.
- [15] G. M. Jamison, A. E. Bruce, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, **1991**, *113*, 5057-5059.
- [16] K. Ziegler and H.-G. Gellert, *Justus Liebigs Annal. Chem.*, **1950**, *567*, 179-184.
- [17] D. Seebach and H. Neumann, *Chem. Ber.*, **1974**, *107*, 847-853.
- [18] H. Klöcker, M. Layh, A. Hepp and W. Uhl, *Dalton Trans.*, **2016**, *45*, 2031-2043.
- [19] The HOMOs of both **10N** and **10P** are primarily metal-based d_{xy} in nature and associated with CO binding.
- [20] B. J. Frogley and A. F. Hill, *Chem. Commun.*, **2018**, *54*, 2126-2129.
- [21] *Spartan 18*® (2018) Wavefunction, Inc., 18401 Von Karman Ave., Suite 370 Irvine, CA 92612 U.S.A.
- [22] (a) E. S. Borren, A. F. Hill, R. Shang, M. Sharma and A. C. Willis, *J. Am. Chem. Soc.*, **2013**, *135*, 4942-4945; (b) A. Reinholdt, J. Bendix, A. F. Hill and R. A. Manzano, *Dalton Trans.*, **2018**, *47*, 14893-14896.
- [23] (a) B. J. Frogley and A. F. Hill, *Chem. Commun.*, **2019**, *55*, 15077-15080. (b) B. J. Frogley and A. F. Hill, *Dalton Trans.*, **2020**, *49*, 3272-3283. (c) B. J. Frogley, A. F. Hill and A. Seitz, *Chem. Commun.*, **2020**, *56*, 3265-3268.
- [24] In the case of M = W, the gold carbide intermediate was structurally characterised as a tetramer (n = 4).^[22a] For the molybdenum intermediate this is most likely also a labile tetramer, however this has not been isolated.
- [25] (a) A. F. Hill, R. Shang and A. C. Willis, *Organometallics*, **2011**, *30*, 3237-3241. (b) A. F. Hill and R. Shang, *Organometallics*, **2012**, *31*, 4635-4638.
- [26] (a) F. J. Lalor, G. Ferguson and M. Parvez, *J. Chem. Soc., Chem. Commun.*, **1984**, 75-76. (b) W. A. Herrmann (Ed.) *Synthetic Methods of Organometallic and Inorganic Chemistry*, Georg Thieme Verlag, New York, **1997**, *7*, 189.
- [27] (a) B. J. Frogley and A. F. Hill, *Chem. Commun.*, **2019**, *55*, 12400-12403. (b) B. J. Frogley, A. F. Hill, C. S. Onn and L. J. Watson, *Angew. Chem., Int. Ed.*, **2019**, *58*, 15349-15353. (c) I. A. Cade, A. F. Hill and C. M. A. McQueen, *Dalton Trans.*, **2019**, *48*, 2000-2012. (d) B. J. Frogley, A. F. Hill, R. A. Manzano and M. Sharma, *Chem. Commun.*, **2018**, *54*, 1702-1705. (e) A. L. Colebatch and A. F. Hill, *Dalton Trans.*, **2017**, *46*, 4355-4365. (f) A. F. Hill, M. Sharma and A. C. Willis, *Organometallics*, **2012**, *31*, 2538-2542. (g) A. F. Hill, A. L. Colebatch, R. L. Cordiner, R. D. Dewhurst, C. M. A. McQueen, K. T. H. D. Nguyen, R. Shang and A. C. Willis, *Comments Inorg. Chem.*, **2010**, *31*, 121-129.
- [28] (a) B. E. Woodworth, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, **1998**, *120*, 9028-9033. (b) B. J. Frogley and A. F. Hill, *Angew. Chem., Int. Ed.*, **2019**, *58*, 8044-8048.

