Alkynylbis(alkylidynyl)phosphines: $\{L_nM\equiv C\}_2PC\equiv CR$ Benjamin J. Frogley^a and Anthony F. Hill^{a†}

Sequential treatment of $[M(\equiv CBr)(CO)_2(Tp^*)]]$ ($M = Mo, W$; $Tp^* =$ hydrotris(dimethylpyrazolyl)borate) with nBuLi , $RPdCl_2$ and $LiC\equiv CSiMe_3$ affords $[M\{\equiv CPR(C\equiv CSiMe_3)\}(CO)_2(Tp^*)]]$ ($R = Ph, Cy$) which are readily desilylated (TBAF) to provide the parent ethynyl derivatives $[M\{\equiv CPR(C\equiv CH)\}(CO)_2(Tp^*)]]$. Alternatively, treating $[W(\equiv CBr)(CO)_2(Tp^*)]]$ with nBuLi , $\frac{1}{2} PCl_3$ and $LiC\equiv CR'$ affords the alkynylbis(alkylidynyl)phosphines $[R'C\equiv CP\{C\equiv W(CO)_2(Tp^*)\}_2]$ ($R' = C_6H_5, C_6H_4Me-4, CMe_3, SiMe_3$) and again the silyl derivative may be desilylated to the parent ($R' = H$) which is readily converted to an arsino derivative ($R' = AsPh_2$). These novel architectures present new linkages for bridge-assisted polymetallic assembly.

Alkynylphosphines, $[RR'PC\equiv CR'']$, are an intriguing subset of the ubiquitous phosphine ligands. A directly bonded alkynyl group bestows the phosphine with decreased basicity (due to the electronegativity of the sp -hybridised carbons bonded directly to P). There also arises the question as to what extent the phosphorus and alkynyl groups are π -conjugated. The alkynyl group provides the comparatively exposed phosphorus with a well-defined steric environment, with the majority of the steric bulk being directed away from the phosphorus centre and also conveniently tuneable through selection of the alkyne termini R'' . These features are epitomised by trialkynylphosphines, $[P(C\equiv CR)_3]$, which have recently been generating interest as potential ligands for metal complexes in a variety of catalytic systems.¹ Accordingly, an increasing number of metal complexes containing trialkynylphosphine ligands have now been prepared, some of which have been structurally characterised.^{1b,1d,2}

In contrast, examples of their organometallic analogues ($M\equiv C$ cf. $C\equiv C$) where even one transition-metal carbyne is bonded to a central phosphorus are scarce, and their properties are consequently far less studied. Phosphinocarbynes, $L_nM\equiv CPR_3^+$, are the largest of this small set and are most commonly observed on reaction of high-valent metal centres with phosphorus ylids.³ Phosphinocarbynes, $L_nM\equiv CPR_2$, are even rarer. Cummins reported the first examples, $[Mo(\equiv CPRCl)(N^tBuC_6H_3Me_2-3,5)_3]$ ($R = Cl, Ph$), *via* the reactions of $[Mo(\equiv CK)(N^tBuC_6H_3Me_2-3,5)_2]$ with Cl_2PR .⁴ We have enjoyed some success in employing lithiocarbyne intermediates, $[M(\equiv CLi)(CO)_2(Tp^*)]]$ ($M = Mo, W$; $Tp^* =$ hydrotris(3,5-dimethylpyrazol-1-yl)borate), which are conveniently generated on treatment of bromocarbynes $[M(\equiv CBr)(CO)_2(Tp^*)]]$ ($M = Mo$ **1a**; $M = W$ **1b**; Scheme 1) with nBuLi , in order to furnish phosphinocarbynes on reaction with

chlorophosphines.⁵ Extension of this method has recently allowed us to isolate the first examples of bis(alkylidynyl)phosphines, $[RP\{C\equiv M(CO)_2(Tp^*)\}_2]$ ($M = Mo, W$; $R = Ph, Cy, Me, ^nBu$), on reaction with dichlorophosphines.^{6a} Alternatively, palladium(0)-mediated P–C bond formation involving primary phosphines also provides access to secondary phosphinocarbynes^{5b} and bis(alkylidynyl)phosphines.^{6b}

Herein we address the confluence of these two classes of compound with the synthesis of the first examples of alkynylbis(alkylidynyl)phosphines, $[RC\equiv CP\{C\equiv W(CO)_2(Tp^*)\}_2]$. As for simple alkynylphosphines, the phosphorus remains available for coordination to metal centres and the organic alkyne substituent can be derivatised. These results hold promise for their incorporation as building blocks in extended frameworks, with particularly interesting consequences for intermetallic electronic communication and whether heteroatomic junctions might act as modulators or ‘switches’ in such structures.

From the out-set, it is clear that neither of the above strategies are attractive for the preparation of $[RC\equiv CP\{C\equiv W(CO)_2(Tp^*)\}_2]$ complexes as they call for either primary or dichloroalkynylphosphines ($RC\equiv CPX_2$, $X = H, Cl$), neither of which are conveniently accessible substrates. Rather, we sought a general protocol that involved diverse alkynyl installation at a late, common synthetic intermediate.

We have previously found that chlorophosphinocarbyne complexes serve as versatile intermediates to a range of substituted derivatives *via* treatment with appropriate nucleophiles. In one such example, reaction of $[W(\equiv CPClPh)(CO)_2(Tp^*)]]$ and $LiC\equiv CPh$ gave an alkynylphosphinocarbyne, $[W\{\equiv CPPh(C\equiv CPh)\}(CO)_2(Tp^*)]]$.^{5d} This procedure can be extended to give the trimethylsilyl analogues. Thus, sequential treatment of the bromocarbynes $[M(\equiv CBr)(CO)_2(Tp^*)]]$ ($M = Mo$ **1a**; $M = W$ **1b**) with nBuLi , Cl_2PR ($R = Ph, Cy$) and finally $LiC\equiv CSiMe_3$ gives (trimethylsilylethynyl)phosphinocarbynes, $[M\{\equiv CPR(C\equiv CSiMe_3)\}(CO)_2(Tp^*)]]$ ($M = Mo, R = Ph$ **2a**, $R = Cy$ **3a**; $M = W, R = Ph$ **2b**, $R = Cy$ **3b**) in low (non-optimised) yields as bright orange microcrystalline solids (Scheme 1, See ESI).

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CCDC 1851868-1851878 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Scheme 1. Synthesis of alkynyl(alkylidynyl)phosphine complexes.

Subsequent treatment of these complexes with one equivalent of (moist) tetrabutylammonium fluoride (TBAF) cleaves this protecting group and furnishes the parent ethynylphosphinocarbynes, $[M\{\equiv CPR(C\equiv CH)\}(CO)_2(Tp^*)]$ ($M = Mo, R = Ph$ **4a**, $R = Cy$ **5a**; $M = W, R = Ph$ **4b**, $R = Cy$ **5b**), as yellow to orange microcrystalline solids. The spectral data for **2–5** are reassuringly similar to the few other reported phosphinocarbynes,^{5a-c,5e,7} including a single example of an alkynyl(alkylidynyl)phosphine, $[W\{\equiv CPh(C\equiv CPh)\}(CO)_2(Tp^*)]$.^{5d} In the case of **2a**, **2b**, **3a** and **5b**, the formulations are also supported by single crystal X-ray structure determinations (see ESI, Figures S1–S4), which call for little comment.

We recently observed that the tungsten bromocarbene **1b** could be sequentially treated with n -BuLi and half an equivalent of PCl_3 to furnish a chlorobis(alkylidynyl)phosphine, $[ClP\{C\equiv W(CO)_2(Tp^*)\}_2]$ (see Scheme 2).^{6a} Although this species was found to be too sensitive to isolate as a pure compound, it could be used as an intermediate *en route* to a variety of bis(alkylidynyl)phosphine derivatives *via* nucleophilic halide substitution at phosphorus with organolithium reagents including $PhLi$, $MeLi$ and n -BuLi.^{6b} In light of our results with the carbynes **2–5**, we reasoned that this intermediate might also be susceptible to halide substitution with alkynylmetal reagents.

Sequential treatment of the tungsten bromocarbene **1b** with n -BuLi, half an equivalent of PCl_3 and finally a separately prepared solution of $LiC\equiv CR$ (from $HC\equiv CR$ and n -BuLi in THF) gives dark red-brown solutions. From these mixtures the desired alkynylbis(alkynylidynyl)phosphines, $[RC\equiv CP\{C\equiv W(CO)_2(Tp^*)\}_2]$ ($R = Ph$ **6**; p -tolyl **7**; t -Bu **8**; TMS **9**), were isolated as dark red solids in moderate yields following chromatographic purification (Scheme 2). Desilylation of **9** with one equivalent of TBAF furnishes the parent ethynylbis(alkylidynyl)phosphine, $[HC\equiv CP\{C\equiv W(CO)_2(Tp^*)\}_2]$ (**10**), also as red microcrystals. The yields of complexes **6–9** vary rather significantly, the major side product being the n -butyl derivative, $[nBuP\{C\equiv W(CO)_2(Tp^*)\}_2]$, which rapidly forms

Scheme 2. Synthesis of alkynylbis(alkylidynyl)phosphines of tungsten.

on reaction with any residual n -BuLi present. This was routinely isolated in 10% or greater yield even when a slight deficiency of n -BuLi was employed. The chloro- intermediate is also known to undergo spontaneous rearrangement into a reactive *P*-chloro-phospha-acyl,^{6a} which is presumed to be a source of some of the other unidentified side products. Nonetheless, with careful manipulation over 50% yields could be obtained for **6**, **7** and **9**. Once formed, these complexes are remarkably stable and persist for weeks in air in the solid state and for several days in a $CDCl_3$ solution. An exception is the *tert*-butyl derivative, **8**, which was obtained in a disappointing 20% yield. This complex was found to be moderately air-sensitive, decomposing in solution within a few hours into mixtures of unidentified products. X-ray crystallography (*vide infra*) indicates that $H\cdots H$ distances between pyrazolyl and *t*-butyl groups may be as small as 2.4 Å, and so unfavourable steric interactions may contribute to both the instability of **8** and the poor yield obtained, which may however simply reflect the lower selectivity of the reaction and difficulties attending purification.

Selected spectroscopic and structural data for complexes **6–10** are given in Table 1. The phosphorus nuclei in these complexes give rise to chemical shifts between 33.8 and 36.1 ppm in the $^{31}P\{^1H\}$ spectra, downfield of the monometallic complexes **2–5** (–5.5 to 10.0 ppm) but to higher frequency of alkyl- or aryl-bis(alkylidynyl)phosphines (50 – 90 ppm).⁶ The carbene carbon nuclei in **6–10** resonate within the narrow range 272.9 – 277.9 ppm in their respective $^{13}C\{^1H\}$ NMR spectra, which is not significantly distinct from the related nuclei in **2–5** (280.8 – 302.5 ppm) and alkyl- or arylbis(alkylidynyl)-phosphines (290–300 ppm).⁶

Figure 1. Molecular structure of **9** in a crystal of **9**·CHCl₃ (50% thermal probability ellipsoids, pyrazolyl groups are simplified and hydrogen atoms, solvent molecules and disorder components omitted). Only half of the molecule is crystallographically unique. Selected distances [Å] and angles [°]: W1–C1 1.827(5), W1–N1 2.274(4), W1–N3 2.204(4), W1–N5 2.219(4), C1–P 1.769(6), P–C7 1.590(9), C7–C8 1.232(13), C8–Si 1.826(13), W1–C1–P 171.3(4), C1–P–C1 103.8(4), C1–P–C7 109.2(4), P–C7–C8 165.2(9). Inset: Space-filling representation.

Structural data for each of the complexes **6–10** have been obtained by X-ray crystallography (see Figure 1 and Figures S5–S9 in the ESI). For each compound, the geometry about phosphorus is pyramidal ($\Sigma^\circ(\text{P}) = 303.4\text{--}322.2^\circ$), comparable to that of triethynylphosphine itself (303°).⁸ Slight differences might be attributed to steric forces which vary with the alkyne substituent. The $\text{W}\equiv\text{C}$ distances are equal (within 6 e.s.d.) and comparable to other reported tungsten carbynes.⁹ The $\text{W}\equiv\text{C}\text{--P}$ angles (*ca.* 170°) deviate slightly from linearity but are consistent with other reported phosphinocarbynes. Non-linearity in these complexes typically arises from solid-state packing effects.^{5,7} The $\text{P}\text{--C}\equiv\text{C}$ angles also differ slightly from linearity ($165\text{--}175^\circ$) although again this is comparable to triethynylphosphine itself ($169\text{--}172^\circ$)⁸ and other reported trialkynylphosphines.^{1b,1d,10}

Table 1. Selected NMR and structural data for complexes **6–13**.

	δ_{P}^a	δ_{C}^a	$^2J_{\text{PW}}^b$	$^1J_{\text{CP}}^b$	$r_{\text{W}\equiv\text{C}}^c$
6	34.5	274.6	82	77	1.831(7)
7	34.8	275.1	83	75	1.813(5)
8	36.0	277.9	80	74	1.823(3)
9	36.1	274.1	83	76	1.827(5)
10	33.8	272.9	84	76	1.827(5)
11	9.7	255.2	159	20	
12	9.7	254.1	158	20	1.819(17)
13	37.0	273.5	84	77	1.831(6)

^a(ppm), measured in CDCl₃. ^b(Hz), measured in CDCl₃. ^c(Å).

As one might expect, the complexes **6–10** possess a number of sites which are available for further reactivity. The lone pair on phosphorus remains available for coordination and treatment of **7** or **9** with one equivalent of AuCl(THT) (THT = tetrahydrothiophene), furnishes the coordination complexes $[\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_2\text{P}(\text{C}\equiv\text{CR})(\text{AuCl})]$ ($\text{R} = p\text{-tolyl}$ **11**; $\text{R} = \text{SiMe}_3$ **12**)

in good yield by phosphine displacement of the labile THT ligand (Scheme 3).

Scheme 3. Two reactions of alkynylbis(alkylidynyl)phosphines; phosphine coordination to gold(I) and alkyne derivatisation to give a (diphenylarsinoethynyl)bis-(alkylidynyl)phosphine complex.

Coordination causes an appreciable up-field shift of *ca* 25 ppm for the phosphorus nuclei in the $^{31}\text{P}\{^1\text{H}\}$ spectra of **11** and **12**, as well as a *ca* 20 ppm up-field shift for the carbyne carbon in the respective $^{13}\text{C}\{^1\text{H}\}$ spectra. This is attended by a dramatically increased phosphorus-tungsten ($^2J_{\text{PW}}$) coupling, and a decreased carbon-phosphorus ($^1J_{\text{CP}}$) coupling, which is consistent with a four-coordinate phosphorus centre. Similar observations were made for the diphenylphosphinocarbyne adducts $[(\text{Tp}^*)(\text{CO})_2\text{W}(\equiv\text{CP}(\text{E})\text{PPh}_2)]$ ($\text{E} = \text{BH}_3, \text{O}, \text{S}, \text{Se}$)^{5c} or coordination complexes ($\text{E} = \text{RhCl}_2(\text{Cp}^*), \text{AuCl}$).^{5e} A crystal structure of **12** has also been determined (see ESI, Figure S10), although the bond precision is too poor to allow conclusions on structural changes to be drawn and thus it is included primarily as evidence of connectivity.

In the terminal ethynyl derivative **10**, the $\text{P}\text{C}\equiv\text{CH}$ unit may be deprotonated and derivatives can be accessed *via* reactions of the (unisolated) alkynyllithium intermediate. Thus, treatment of **10** with $n\text{BuLi}$ followed by BrAsPh_2 furnishes the diphenylarsinoethynyl derivative, $[\{(\text{Tp}^*)(\text{CO})_2\text{W}\equiv\text{C}\}_2\text{P}\text{--C}\equiv\text{CAsPh}_2]$ (**13**) as an orange solid in good yield (Scheme 3). This species contains the rather unusual $\text{R}_2\text{P}\text{--C}\equiv\text{C}\text{--AsR}_2$ fragment (only one example of which, $\text{Ph}_2\text{PC}\equiv\text{CAsPh}_2$ has been previously reported¹¹), with the phosphorus flanked by two tungsten carbyne moieties.

The spectral (see Table 1 and the ESI) and structural (Figure 2) data for **13** do not differ appreciably from the simpler analogues, **6–10**. The geometry about both the phosphorus and arsenic atoms is pyramidalised ($\Sigma^\circ(\text{P}) = 305.1^\circ$, $\Sigma^\circ(\text{As}) = 298.8^\circ$). The $\text{P}\text{--C}\equiv\text{C}$ and $\text{C}\equiv\text{C}\text{--As}$ angles ($170.0(6)^\circ$ and 174.6° , respectively) deviate only slightly from linearity. Structural data were not previously available in the CCDC for the $\text{P}\cdots\text{C}^2\cdots\text{C}^2\cdots\text{As}$ connectivity, although a number of crystallographically characterized examples of a $\text{P}\text{--C}\equiv\text{C}\text{--P}$ unit are known and the associated angles are in the range of $170\text{--}180^\circ$.¹²

Figure 2. Molecular structure of **13** (50% thermal probability ellipsoids, pyrazolyl and phenyl groups simplified and hydrogen atoms omitted). Selected distances [Å] and angles [°]: W1–C1 1.831(6), C1–P 1.783(6), P–C2 1.779(7), C2–W2 1.830(7), W1–N1 2.295(5), W1–N3 2.206(5), W1–N5 2.208(5), W2–N7 2.294(5), W2–N9 2.205(5), W2–N11 2.209(6), P–C7 1.770(7), C7–C8 1.188(10), C8–As 1.919(7), As–C9 1.972(7), As–C15 1.969(9), W1–C1–P 167.2(4), W2–C2–P 170.8(4), C1–P–C2 101.7(3), C1–P–C7 104.8(3), C2–P–C7 98.6(3), P–C7–C8 170.0(6), C7–C8–As 174.6(6), C8–As–C9 96.7(3), C8–As–C15 99.3(4), C9–As–C15 102.8(3). Inset: space-filling representation and view along the As1–P1 vector.

In conclusion, we have demonstrated that alkynylbis(alkylidynyl)phosphines of tungsten can be prepared via nucleophilic halide substitution of a chlorobis(alkylidynyl)phosphine intermediate. Two reactions of these unusual compounds have been demonstrated, namely coordination of phosphorus to a gold(I) centre and a two-step lithiation and nucleophilic halide substitution of the terminal ethynylbis(alkylidynyl)phosphine **10** to give an unusual derivative containing a PC≡CAs unit. We anticipate that, by exploiting the reactivity of the $W\equiv C$, $C\equiv C$ or (in the case of **10**) C–H bonds, as well as the capacity for $W\equiv C$, phosphine or arsine coordination to metal substrates, these complexes will find utility as precursors to extended two- or three-dimensional structures. Heteroatom-interrupted π -conjugated metal-carbon frameworks of this type could be expected to exhibit a variety of interesting and potentially useful properties — a matter we are presently exploring.

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