Alkynylphosphines, \([\text{RR}’\text{PC}≡\text{CR}’]\), 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, \([\text{P}(≡\text{CR})_3]\), 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 trialkynylphosphinyl ligands have now been prepared, some of which have been structurally characterised.\(^1b,1d,2\)

In contrast, examples of their organometallic analogues (\(\text{M}≡\text{C}≡\text{C}\)) where even one transition-metal carbonyl is bonded to a central phosphorus are scarce, and their properties are consequently far less studied. Phosphinocarbynes, \(\text{L}_3\text{M}≡\text{CPR}^+\), are the largest of this small set and are most commonly observed on reaction of high-valent metal centres with phosphorus ylids.\(^3\) Phosphinocarbynes, \(\text{L}_3\text{M}≡\text{CPR}^+\), are even rarer. Cummins reported the first examples, \([\text{Mo}≡\text{CPR}](\text{N}’\text{Bu}3\text{H}5\text{Me}2-3,5)_2\) \((R = \text{Cl}, \text{Ph})\), via the reactions of \([\text{Mo}≡\text{CK}](\text{N}’\text{Bu}3\text{H}5\text{Me}2-3,5)_2\) with \(\text{Cl}_3\text{PR}\).\(^4\) We have enjoyed some success in employing thiocarbonyl intermediates, \([\text{M}(≡\text{C}\text{Li})(\text{CO})_2(Tp^+)]\) \((\text{M} = \text{Mo}, \text{W}; \text{Tp}^+ = \text{hydrotris}(3,5\text{-dimethylpyrazol-1-yl})\text{borate})\), which are conveniently generated on treatment of bromocarbynes \([\text{M}(≡\text{CB}(\text{CO})_2(Tp^+)]\) \((\text{M} = \text{Mo} 1a; \text{M} = \text{W} 1b; \text{Scheme 1})\) with \(\text{BuLi}\), 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, \([\text{RP}(≡\text{M}(\text{CO})_2(Tp^+))]_2\) \((\text{M} = \text{Mo}, \text{W}; R = \text{Ph, Cy}, \text{Me}, \text{Bu}^+\text{Li})\), on reaction with dichlorophosphines.\(^6a\)

Alternatively, palladium(0)-mediated P–C bond formation involving primary phosphines also provides access to secondary phosphinocarbynes\(^6b\) 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, \([\text{RC}≡\text{CP}(≡\text{W}(\text{CO})_2(Tp^+))]_2\). 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 \([\text{RC}≡\text{CP}(≡\text{W}(\text{CO})_2(Tp^+))]_2\) complexes as they call for either primary or dichloroalkynylphosphines \((\text{RC}≡\text{CPX}_2; X = \text{H, Cl})\), neither of which are conveniently accessible substrates. Rather, we sought a general protocol that involved diverse alkynyl in installation at a late, common synthetic intermediate. We have previously found that chlorophosphinocarbonyl complexes serve as versatile intermediates to a range of substituted derivatives \(via\) treatment with appropriate nucleophiles. In one such example, reaction of \([\text{W}≡\text{CP}≡\text{Ph}](\text{CO})_2(Tp^+)]\) and \(\text{LiC}≡\text{Ph}\) gave an alkynylphosphino-carbonyl, \([\text{W}≡\text{CP}≡\text{Ph}](\text{CO})_2(Tp^+)]\).\(^6d\) This procedure can be extended to give the trimethylsilyl analogues. Thus, sequential treatment of the bromocarbynes \([\text{M}(≡\text{CB}(\text{CO})_2(Tp^+)]\) \((\text{M} = \text{Mo} 1a; \text{M} = \text{W} 1b)\) with \(\text{BuLi}, \text{Cl}_3\text{PR}\) \((R = \text{Ph, Cy})\) and finally \(\text{LiC}≡\text{SiMe}_3\) gives \((\text{trimethylsilylthienyl})\text{phosphinocarbynes, \([\text{M}(≡\text{C}≡\text{SiMe}_3)(\text{CO})_2(Tp^+)]\) \((\text{M} = \text{Mo}, \text{R} = \text{Ph} 2a, \text{R} = \text{Cy} 3a); \text{M} = \text{W}, \text{R} = \text{Ph} 2b, \text{R} = \text{Cy} 3b)\)} 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.

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Subsequent treatment of these complexes with one equivalent of (moist) tetrabutylammonium fluoride (TBAF) cleaves this protecting group and furnishes the parent ethynylbis(alkylidynyl)phosphine, $[\text{M}\{\text{C}═\text{P}═\text{C}≡\text{n(H)}\}(\text{CO})_2\{\text{Tp}^+\}]$ (M = Mo, $R = \text{Ph}$, $1\text{a}$, $M = W$, $R = \text{Ph}$, $1\text{b}$). The yield of complexes $1\text{a}$–$1\text{b}$ was found to be moderately air-sensitive (vide infra), which could be obtained for $1\text{a}$–$1\text{b}$, as yellow to orange microcrystalline solids. The spectral data for $2$–$5$ are reassuringly similar to those reported for other phosphinocarbynes, including those of the parent ethynylbis(alkylidynyl)phosphine derivatives. In the case of $2\text{a}$, $2\text{b}$, $3\text{a}$ and $5\text{b}$, 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 bromocarbyne $1\text{b}$ could be sequentially treated with $^\text{tBuLi}$ and half an equivalent of PCl$_3$ to furnish a chlorobis(alkylidynyl)phosphine, $[\text{ClP}═\text{C}≡\text{n(H)}\{(\text{CO})_2\{\text{Tp}^+\}]$ (Scheme 2). Although this species was found to be too sensitive to isolate as a pure compound, it could be used as an intermediate to provide a variety of bis(alkylidynyl)phosphine derivatives via nucleophilic halide substitution at phosphorus with organolithium reagents including PhLi, MeLi and $^\text{tBuLi}$. 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 bromocarbyne $1\text{b}$ with $^\text{tBuLi}$, half an equivalent of PCl$_3$ and finally a separately prepared solution of LiC═SiMe$_3$ (from HSiC═SiMe$_3$ and $^\text{tBuLi}$ in THF) gives dark red-brown solutions. From these mixtures the desired alkynylbis(alkylidynyl)phosphines, $[\text{HC}═\text{C}═\text{P}═\text{C}≡\text{n(H)}\{(\text{CO})_2\{\text{Tp}^+\}]$ (R = Ph $2\text{a}$, p-tolyl $2\text{b}$, $^\text{tBu}$, TMS $2\text{c}$), were isolated as dark red solids in moderate yields following chromatographic purification (Scheme 2). Desilylation of $9$ with a single equivalent of TBAF furnishes the parent alkynylbis(alkylidynyl)phosphine, $[\text{H}═\text{C}═\text{C}═\text{P}═\text{C}≡\text{n(H)}\{(\text{CO})_2\{\text{Tp}^+\}]$ (10), also as red microcrystals. The yields of complexes $6$–$9$ vary rather significantly, the major side product being the $n$-butyl derivative, $[\text{BuP}═\text{C}═\text{C}≡\text{n(H)}\{(\text{CO})_2\{\text{Tp}^+\}]$, which rapidly forms on reaction with any residual $^\text{tBuLi}$ present. This was routinely isolated in 10% or greater yield even when a slight deficiency of $^\text{tBuLi}$ was employed. The chloro-intermediate is also known to undergo spontaneous rearrangement into a reactive P-chlorophospha-acyl, 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...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 $^3\text{P}$(H) spectra, downfield of the monometallic complexes $2$–$5$ ($\sim 5.5$ to $10.0$ ppm) but to higher frequency of alkyl- or aryl-bis(alkylidynyl)phosphines ($30$ – $90$ ppm). The carbonyl carbon nuclei in $6$–$10$ resonate within the narrow range $272.9 – 277.9$ ppm in their respective $^1\text{C}$(H) 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).
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 (Σ°(P) = 303.4–322.2°), comparable to that of triethylphosphine itself (303°).8 Slight differences might be attributed to steric forces which vary with the alkyne substituent. The W≡C distances are equal (within 6 e.s.d.) and comparable to other reported tungsten carbynes.9 The W≡C–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 P–C≡C angles also differ slightly from linearity (165–175°) although again this is comparable to triethylphosphine itself (169–172°)8 and other reported trialkylphosphines.10

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 \([(Tp^*)_2W\equivCP(C\equivCR)(AuCl)]\) (R = p-tolyl 11; R = SiMe₃ 12) in good yield by phosphine displacement of the labile THT ligand (Scheme 3).

Coordination causes an appreciable up-field shift of ca 25 ppm for the phosphorus nuclei in the 31P{1H} spectra of 11 and 12, as well as a ca 20 ppm up-field shift for the carbony carbene in the respective 13C{1H} spectra. This is attended by a dramatically increased phosphorus-tungsten (J_{P-W}) coupling, and a decreased carbon-phosphorus (J_{C-P}) coupling, which is consistent with a four-coordinate phosphorus centre. Similar observations were made for the diphenylphosphinocarbene adducts \([(Tp^*)_2W\equivCP(E)PPh_2)]\) (E = BH₃, O, S, Se)10 or coordination complexes (E = RhCl₃(Cp*), 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 PC≡CH unit may be deprotonated and derivatives can be accessed via reactions of the (unisolated) alkynyllithium intermediate. Thus, treatment of 10 with °BuLi followed by BrAsPh₂ furnishes the diphenylarsinoethynyl derivative, \([(Tp^*)(CO)_2W\equivCP(C\equivCSiMe_3)AsPh_2)]\) (13) as an orange solid in good yield (Scheme 3). This species contains the rather unusual R₃P–C≡C–As−R₂ fragment (only one example of which, Ph₃P≡CCAsPh₂ has been previously reported11), with the phosphorus flanked by two tungsten carbony 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 (Σ°(P) = 305.1°, Σ°(As) = 298.8°). The P–C≡C and C≡C–As angles (170.0(6)° and 174.6°, respectively) deviate only slightly from linearity. Structural data were not previously available in the CCDC for the P–C≡C–C≡As connectivity, although a number of crystallographically characterized examples of a P–C≡C–P unit are known and the associated angles are in the range of 170–180°.12
In conclusion, we have demonstrated that alkylnylbis(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- or three-dimensional structure. Heteromet-al-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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Notes and references


