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Synthesis of 3-stannyl and 3-silyl propargyl phosphanes and the formation of a phosphinoallene

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The group 14 chloropropargyls \( \text{R}_2\text{Cl} = \text{Bu}_2\text{Sn}, \text{Ph}_3\text{Sn}, \text{Me}_2\text{P}\text{Si}, \text{Pr}_3\text{Si}, \text{Bu}_3\text{Si} \), obtained by a modified literature procedure, react with \( \text{LiPPh} \) to afford the novel propargyl phosphanes \( \text{Ph}_2\text{PCH} = \text{CER} \), in high yield, as viscous oils; \( \text{Me}_2\text{Si} \cdot \text{PCH} = \text{C} = \text{S} \cdot \text{Mes} \text{Me}_2 \) is similarly obtained from \( \text{LiPMe}_2\text{SiMe}_2 \). In contrast, the reaction of \( \text{PhC} = \text{CMe}_2\text{MgCl} \) with \( \text{CIP(NEt}_2\text{)}_3 \) fails to produce a comparable propargyl phosphate, but generates preferentially (>70%) the novel phosphinoallene \( \text{Et}_2\text{N} \cdot \text{PC}(\text{Ph}) = \text{CCH} \), which is characterised spectroscopically, and through its reaction with \( \text{HCl} \). The coordination chemistry of representative phosphanes is explored with respect to platinum and palladium for the first time.

This lack of activity is surprising given continued interest in developing polyfunctional phosphorus-containing molecules, driven by their utility as ligands, optoelectronically active \( \pi \)-conjugates and, typically, frustrated Lewis pairs (FLPs).

In these contexts, propargylphosphanes should constitute ideal ‘building-block’ substrates, and allow for incorporation of further functionality (e.g. by cycloaddition, hydroboronation, hydrophosphination) akin to their more extensively utilised alkynyl, alkenyl and allyl counterparts. Moreover, they embody intrinsic potential to act as \( \sigma/\pi \)-chelating ligands.

Indeed, among very limited coordination chemistry reported to date, the \( \mu\text{-}\sigma(\text{P},\pi,\pi-C=\text{C}) \) bridging mode has been described for \( \text{[CP}_2\text{Rh}_2\text{(CO)}(\mu\text{-}\pi\cdot\pi \cdot \text{C}=\text{C})\text{CF}_2\text{CF}_2\text{]} \cdot \text{(PPPh}_2\text{CH}_2\text{CMe})\text{CO}_2\text{(CO)}_4 \), obtained by reaction of \( \text{[Co(CO)}_3\text{]} \) with the dithiodihem complex \( \text{[CP}_2\text{Rh}_2\text{(CO)}(\mu\cdot\pi\cdot\pi \cdot \text{C}=\text{C})\text{CF}_2\text{CF}_2\text{]} \cdot \text{(PPPh}_2\text{CH}_2\text{CMe})\text{CO}_2\text{(CO)}_4 \).

The remaining complexes described to date involve monodentate coordination of the phosphane, typically to metals of the mid transition series, with saturated coordination spheres. Thus, \( \{\text{M(CO)}_3\text{(PhR}_2\text{C}=\text{C})\} \) \( \{\text{M} = \text{Mo}, \text{R} = \text{Ph}, 1-3 \| \text{DBP}, \text{Cr}, 19 \) \( \text{R} = \text{Ph}, \text{SiMe}_2\} \), \( \{\text{Mo(CO)}_3\text{(Ph}_2\text{H}_2\text{C}=\text{C})\} \), \( \{\text{Mo(CO)}_3\text{(Ph}_3\text{Si} = \text{C})\} \) and \( \{\text{Cr}(\text{Me}_2\text{Si} = \text{C})\text{Me}_2\text{H}_2\text{C}=\text{C})\} \) have been obtained directly from the respective phosphanes and suitable metal salts, as has the bimetallic complex \( \{\text{H}(\text{C}=\text{C})\text{Ph}_2\text{P} \cdot \text{R} \cdot \text{Ph}_2\text{P}\{\text{Co(CO)}_3\} \cdot \text{(PPh}_2\text{)} \). In contrast, \( \{\text{Co(NO)}_3\text{(PPh}_2\text{CH}_2\text{C}=\text{C})\} \) and the ruthenium phthalocyaninato (Pc\(^2\)) complex \( \{\text{Ru}(\text{Pc})(\text{PPh}_2\text{CH}_2\text{C}=\text{C})\} \) are obtained from the respective diphenylphosphane complexes, via \emph{in situ} deprotonation (BuLi) and quenching with the appropriate propargyl bromide: \( \{\text{Co(MoX}_2\text{O-P-P} \cdot \text{P(O)M} \cdot \text{X}_2\text{C} = \text{C} \cdot \text{CH} = \text{C})\} \) is similarly prepared, but without need for base. Finally, \( \{\text{W(CO)}_3\text{(PPh}_2\text{O-Me} \cdot \text{C} \cdot \text{H} \cdot \text{C} \cdot \text{Me}(\text{C}=\text{S})\text{Pr}_3)\} \) was obtained upon methanalysis of the putative phosphaalkene \( \{\text{W(CO)}_3\text{(P(Ph) = \text{CMe} \cdot \text{C} \cdot \text{S} \cdot \text{Pr}_3))\} \).

Notably, no complexes of the group 10 metals have been described, though the formally related diphenylphosphane-bridged complexes \( \{\text{L}_2\text{M}[(\mu\cdot\pi\cdot\pi \cdot \text{C}=\text{C})\text{CH} \cdot \text{C} \cdot \text{H} \cdot \text{C} \cdot \text{Me}] \} \) \( \{\text{L}_2\text{M} = \text{Cl} \cdot \text{Pt}, \text{Cl} \cdot \text{Ir} \cdot \text{Os}\} \), and a metallophthalocyaninato (Pc\(^2\)) complex \( \{\text{Ru}(\text{Pc})(\text{PPh}_2\text{CH}_2\text{C}=\text{C})\} \) have been developed.
(OC)\textsubscript{2}Ni) have been reported,\textsuperscript{26} alongside examples with other metals \((\text{L}_\text{M} = \text{AuCl}, \text{CpCoCl}, \text{CpFe(CO)}\textsuperscript{n}, \text{CpFeBr(CO)}, \text{CpMn(NO)(CO)}, \text{CpMo(CO)}\textsubscript{2}(\text{COCH})\textsubscript{3},\textsuperscript{26} \text{Mo(CO)}\textsuperscript{4}). The intriguing tetrameric complex \([(\text{C} \equiv \text{C-Mo}=\text{CO})(\text{C} \equiv \text{P-P-}

We have recently been interested in the synthesis and study of reactive and functional phosphanes\textsuperscript{26} and organometallic phosphacarbons,\textsuperscript{26} with the goal of developing novel amphiphilic systems\textsuperscript{28c} and molecular conductive and/or optoelectronically active molecules.\textsuperscript{29b} In continuing these works, we have had cause to access propargyl phosphanes of the type \(\text{R}_n\text{P}((\text{CH}_2=\text{C} \equiv \text{C})\textsubscript{n})\) \((E = \text{Si, Sn})\) as intermediates, seeking to exploit their capacity for desilylative / destannyllative functionalisation. In view of the limited range of propargyl phosphanes reported previously, we thus undertook to prepare a putative series of such materials; viz. \(\text{Ph}_3\text{P}((\text{CH}_2=\text{C} \equiv \text{C})\textsubscript{2})\) \((E = \text{Si, Sn})\), which we describe herein, along with attempts to obtain \('(\text{Et}_n\text{N})\text{P}’\) derivatives, leading to the generation of a novel, and very rare, phosphinoallene. We also outline the coordination chemistry of representative propargylphosphanes toward \(\text{Pd}\) and \(\text{Pt}\), reporting the first such complexes from group 10, and the first to involve co-ordinately unsaturated metal centres.

Results and Discussion

Phosphane Synthesis

The silyl and stannyl chloropropargyl precursors \(\text{R}_n\text{EC} \equiv \text{CCH}_2\text{Cl}\) were prepared following a modified literature procedure (Scheme 1),\textsuperscript{30} via the low-temperature (\(-78^\circ\text{C}\)) lithiation of \(\text{HC} \equiv \text{CCH}_2\text{Cl}\), quenched with \(\text{R}_n\text{SnCl} (1 \text{ and } 2)\) or \(\text{R}_n\text{SiCl} (3 \text{ – } 7)\). The silanes were amenable to purification by reduced-pressure distillation, apart from the solid \(7 (R = \text{Ph})\), which was sublimed. However, both silanes and stannanes are typically obtained in adequate purity for further reaction (>95%) upon extraction with pentane. In each compound, compound identity was apparent from the \(^1\text{H} \text{NMR} \) spectra, which exhibit resonances associated with the group 14 fragment, integrating consistently against that of the propargyl methylene moiety \((\delta = 3.5 \text{ – } 3.7,\text{ Hz})\), which is shifted by ca 0.3 ppm to lower frequency compared with propargyl chloride. Moreover, correlations are observed between the methylene resonances and respective group 14 centre in each case \((^1\text{H}-\text{X} \text{HMBC}; \text{X} = \text{Sn, } \text{Si})\); for the stannanes the \(^3\text{J}_{\text{CH}} \text{ coupling } (\sim 10 \text{ Hz})\) is also large enough to resolve tin satellites. The \(^{13}\text{C}(^1\text{H})-\text{NMR} \) data are similarly consistent, while bulk purity was confirmed from microanalytical data. It is noted that \(^1\text{H},\text{2,3,31} \text{ and } \text{4,33}\) have been previously obtained via alternate methodology.

Ethereal solutions of 1 to 6 were added (\(-78^\circ\text{C}\)) to \(\text{LiPPH}_2\) in ether (formed by \textit{in situ} lithiation of \(\text{HPPH}_2\) with \(^8\text{BuLi}\)) and the mixtures stirred overnight to afford the propargyl phosphanes \(\text{Ph}_3\text{P}((\text{CH}_2=\text{C} \equiv \text{C})\textsubscript{n}) (8 \text{ – } 13, \text{Scheme 1})\). Extraction with pentane afforded the phosphanes as viscous oils, the silyl derivatives \(10 \text{ – } 13\) requiring no further purification. In contrast, stannanes formed in admixture with \(^8\text{BuSn}\) \((1:4 \text{ of } 8)\) or \(\text{Ph}_3\text{BuSn} (1.1 \text{ with } 9)\), presumably due to metathesis of 1 and 2 with residual

\(^6\text{BuLi},\text{ as common among Sn(IV) organyls.} \textsuperscript{34}\) Both 8 and 9 are unstable toward distillation and were thus only characterised spectroscopically, though for 8, further data were obtained by coordination to platinum (vide infra), which proceeds cleanly. In contrast, 9 forms in a complex, inseparable mixture that includes unidentified by-products; it has not been studied further.

Compounds 8 to 13 are identified from characteristic spectroscopic data (Table 1), the alkynic moieties exhibiting marginal change from those of the parent propargyls. Retention of the group 14 fragments is universally apparent \((^1\text{H}-\text{X} \text{HMBC})\), with 8 and 9 also allowing for resolution of \(^{119}\text{Sn} \) satellites \((^3\text{J}_{\text{SnP}} \sim 14 \text{ Hz})\) in the \(^{31}\text{P}(^1\text{H})\) spectra. The \(^{119}\text{Sn} \) spectra of 8 and 9 indicate the presence of \(\text{Bu}_4\text{Sn} (\delta_{\text{Sn}} = -12.0)\textsuperscript{25}\) and \(\text{Ph}_3\text{SnBu} (\delta_{\text{Sn}} = -98.3)\textsuperscript{26}\)-by-products respectively.

Attempts to vary the nature of the phosphinyl substituents met with limited success. Dicyclohexyl analogues failed to form, regenerating \(\text{HPCy}_2\), as the only phosphorus-containing product, which presumably reflects the greater basicity and steric bulk of ‘PCy\((\text{Cy})\)’, favouring proton-abstraction from the chloropropargyls over \(\text{Sn}_2\) substitution. In contrast, reactions with \(\text{LiP(SiMe}_3\text{)}\) did afford species consistent with the desired propargylphosphanes, though in admixture with several significant contaminants, which defied separation or characterisation. Nonetheless, \(\text{Me}_3\text{P(SiMe}_3\text{)}\text{P(\text{Bu})}_2\) \((14)\) was obtained as the primary product (92%) by \(^{31}\text{P}(^1\text{H})-\text{NMR}\) in admixture with \(\text{P(SiMe}_3\text{)}\text{P(\text{Bu})}_2\) \((4\%)\) and a mono-silylphosphane \((\delta_{\text{P}} = -84.4; 4\%\), which presumably result from disproportionation; indeed, the bulk composition is consistent with that of 14.

Given these difficulties, the generation of propargyl Grignard reagents from 1 to 7 was considered as an alternative approach; however, these reactions proved unreliable, presumably reflecting diminished reactivity of the halide in comparison to organo-propargyl derivatives. Indeed, though

\[\begin{align*}
\text{R}_n\text{P}((\text{CH}_2=\text{C} \equiv \text{C})\textsubscript{n}) & \text{ (8 \text{ – } 13, \text{Scheme 1})} \\
\text{Ph}_3\text{P}((\text{CH}_2=\text{C} \equiv \text{C})\textsubscript{n}) & \text{ (8 \text{ – } 13, \text{Scheme 1})}
\end{align*}\]
less favoured than their bromide analogues, propargylphosphines have been shown to form Grignard reagents, and we encountered no difficulty in generating ‘PhC=CH₂MgCl’ under comparable conditions. However, our efforts to quench this reagent with (Et₅N)₂PCl led to an unexpected outcome.

**Formation of a phosphino-allene.** The addition of freshly prepared ‘PhC=CH₂MgCl’ to a cooled (−78 °C) THF solution of (Et₅N)₂PCl affords, after work-up, a deep red oil comprising one predominant phosphorus-containing product (15; 75%). The spectroscopic features of 15 confirm the presence of a (Et₅N)₂P moiety (δPH 90.9; cf. PhP(NET₃)₂ 97.9, 38 H₂C=C(Ph)P(NET₃)₂ 89.9), the ¹H NMR resonances integrating consistently against those for single equivalents of aromatic and methylenic fragments. However, the methylenic moiety is significantly deshielded (δ_C 4.72. δC 75.0) relative to both PhC=CH₂Cl (δ_C 4.39, δC 31.2) and propargyl phosphines, and exhibits appreciably greater magnitude coupling to phosphorus (Jₘₚₘ 7.1 Hz) than 8 – 14. The unsaturated carbon centres are also heavily deshielded (δ_C 137.4 (J 19.0 Hz) C₁; 209.9 (J 11.3 Hz) C₂), the latter in particular being more characteristic of an allenic, rather than alkynic; indeed, these data are in good agreement with those for the limited range of phosphinoallenes (Table 2) described previously. We thus confidently formulate 15 as (Et₅N)₂PCl(Ph)=C=CH₂ (Scheme 2).

The reaction of propargyl Grignard reagents with R₂PCl has been noted to afford mixtures that include allenylphosphines, their proportion being dependent on the nature of ‘R’. However, this is to our knowledge the first example of an allenylphosphine being obtained as the major product (> 70%) in such a reaction, with minimal levels (< 2%) of the propargyl tautomer. While we have not further studied this reaction, the noted outcome might reasonably be considered to reflect either enhanced stability of the α-phenyl-allenyl carbocation over its propargylic counterpart (localisation at an sp², rather than sp³ centre) or be the result of conjugate addition, favoured by the relatively ‘soft’ CIP(NET₃)₂ electrophil, as compared, for instance, with the notionally ‘harder’ PhPCl₂, with which we encountered significantly greater complexity, yielding a largely intractable mixture.

In order to confirm or dismiss the presence of Cl₂PCl(Ph)=C=CH₂ within this mixture, we sought to prepare an authentic sample, treating 15 with HCl (2 equiv.). This effected quantitative conversion to (Et₅N)(Cl)PCl(Ph)=C=CH₂ (16), as evidenced by the ¹H NMR spectrum, which indicates loss of one diethylenediamino moiety (Et₂N vs Ph resonances) and emergence of diastereotopy for the methylenic ‘=CH₂’. The phosphorus resonance of 16 is appreciably deshielded from that of 15, consistent with replacement of NET₃ by Cl (δPH 122; cf. Ph(PrCl)CNET₃ 142.1). Upon further treatment with HCl there is superficial evidence for removal of the remaining diethylenediamino moiety, viz. loss of its ¹H NMR resonances, and of diastereotopy of the ‘=CH₂’ protons (δH 4.63, J = 3 Hz). However, the ³¹P shift (δ 58.7, 7. J = 3 Hz) seems inconsistent with a species of the type RPCl₂; moreover, several other unidentified species are apparent in both the ¹H and ³¹P-NMR spectra, precluding confident assignment of the bulk product.

**Coordination Chemistry of Propargylphosphines.**

As previously noted (vide supra) the coordination chemistry of propargylphosphines is significantly underdeveloped and focussed exclusively on co-ordinately saturated, mid-transition metals. We thus sought to prepare representative complexes featuring the unsaturated group 10 metals Pd and Pt.

The propargylphosphines 8, 11 and 12 react with [PtCl₃]₃, as a suspension in CH₂Cl₂, to afford exclusively the complexes cis-[Pt(PPh₃)(CH₂C=CHR)]Cl₂ (ER₃ = BuSn 17, Pr₃Si 18, Pr₃Si 19, Scheme 3) in excess of 75% isolated yield. For the silanes, palladium analogues (ER₃ = Pr₃Si 20, Pr₃Si 21) are similarly obtained from [PdCl₃]₃, forming exclusively as the trans isomers.

Complexes 17 – 21 have, thus far, not yielded X-ray quality single crystals, in common with most of the limited range of precedent examples. Nonetheless, their identities are unequivocally established from characteristic spectroscopic

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**Table 2** Selected ¹H and ¹³C(¹H)-NMR data for precedent phosphinoallenes.¹²

<table>
<thead>
<tr>
<th>Compound</th>
<th>δH(¹H)</th>
<th>δC(¹H)</th>
<th>δC(¹³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhC=CH₂Cl</td>
<td>71.12</td>
<td>204.9</td>
<td></td>
</tr>
<tr>
<td>(Et₅N)₂PCl(Ph)=C=CH₂</td>
<td>72.35</td>
<td>206.4</td>
<td></td>
</tr>
<tr>
<td>Cl₂PCl(Ph)=C=CH₂</td>
<td>71.7</td>
<td>213.2</td>
<td></td>
</tr>
</tbody>
</table>

¹²chemical shifts in ppm. ¹data sourced from references 14 and 41.
data, which verify the structural integrity of the ligands and coordination of the phosphorus centres (ΔδP ≈ +20). For the platinum complexes 17 – 19, 1′–1′′{1} values of ca 3600 Hz are wholly consistent with assignment of a cis geometry, while the palladium complexes exhibit virtual coupling in the 1H and 13C{1H}-NMR resonances associated with the CH2P moiety, consistent with a trans ligand arrangement. Notably, despite coordinative unsaturation of the metals, there is no evidence for either intra or intermolecular association of the pendant alkynyl moieties, the spectroscopic features of these units being little perturbed from the free ligands.

All of the complexes appear robust, both in solution and the solid state, universally resisting attempts to thermally induce cis/trans isomerisation. However, the UV irradiation (broad spectrum) of the platinum complex cis-19 over a period of 30 minutes did result in partial isomerisation, affording a mixture of cis-19 (42%) and trans-19 (58%). The identity of trans-19 was established on the basis of i) reduced magnitude Pt-P coupling (1′{1} = 2601 Hz), consistent with trans-[Pt(PR3)2X2], and ii) manifestation of virtual coupling for the CH2P centres, as in the palladium systems. However, attempts to effect complete conversion to trans-19 through extended irradiation proved unsuccessful, no further perturbation of the isomeric distribution being achieved.

Conclusions

We have described the synthesis and characterisation of a series of novel propargylyphosphines that feature tin and silicon termini on the alkynyl moiety. Attempts to increase the range of phosphanyl termini used via the reaction of R3PCI with propargyl Grignard reagents proved unsuccessful, but allowed for the generation of the novel allenylphosphine (Et3N)2PC(Ph)=C≡CH2, the first time a species of this type has been obtained as the primary product (>70%) of such a reaction.

Representative phosphines have been shown to form complexes [M(PPh3)2C6H4Cl2] with palladium and platinum, adopting exclusively trans (Pd) or cis (Pt) geometries respectively, though the latter can be partially isomerised under UV irradiation. These are the first examples of propargyl phosphine complexes incorporating group 10, or indeed any unsaturated, metals and are among a very limited number (<25) of coordination compounds known for any such ligands.

Experimental

General Methods

All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under at atmosphere of dry argon or dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å for DCM and THF) or potassium mirrors. Propargyl chloride, group 14 triorganohalides and HPPH2 were obtained from Sigma-Aldrich, purified by appropriate methods and degassed (freeze-thaw) before use. ‘BuLi’ (2.5 M in hexanes) was obtained from Sigma-Aldrich and titrated to establish concentration. Precious metal salts (PtCl4, PdCl2) were obtained from STREM and used as supplied. HPI(SiMe4)2 was prepared by literature procedure. Deuterated solvents were supplied by Goss Scientific and purified by refluxing with potassium (hydrocarbon) or CaH2 (chlorinated) for 3 days prior to use, being vacuum transferred and stored under inert atmosphere. Unless otherwise stated, NMR spectra were recorded on a Varian VNMRS 400 (1H, 399.50 MHz; 13C, 100.46 MHz; 19F, 161.71 MHz; 29Si, 79.37 MHz; 119Sn, 148.97 MHz; 195Pt, 85.53 MHz) or VNMRS 500 (1H 499.91 MHz; 13C, 125.72 MHz) spectrometer. All spectra were referenced to Me4Si, 85% H3PO4, Me6Sn or K2PtCl6 as appropriate. Carbon-13 NMR data were assigned with recourse to the 2D (HSQC, HMBC) spectra; detailed connectivity and distribution being achieved.

Synthesis

8Bu2SnCCH2Cl (1). In a modification of literature procedure, a solution of propargyl chloride (2.24 g, 3.0 x 10−2 mol) in THF (ca 20 cm3) was cooled to −78°C before the drop-wise addition of 8BuLi (2.5 M, 6.0 cm3, 1.5 x 10−2 mol). The mixture was stirred for 30 min, after which time 8Bu2SnCl (4.40 cm3, 1.5 x 10−2 mol) as solution in THF (ca 10 cm3) was added drop-wise, resulting in formation of a yellow solution. The mixture was held at −78°C for a further 30 min. with continued stirring before being allowed to warm to ambient temperature overnight. Solvent and excess HClCCH2Cl were removed under reduced pressure and the product extracted with pentane, stripped of volatiles and dried in vacuo as yellow oil.

Yield: 5.09 g, 94%. NMR (CD2Cl2, 30°C): 1H-NMR: δ H, 0.91 (t, J8s 7.3 Hz, 9 H, CH9), 0.97 (t, J8s 6.7 Hz, J8h 54 Hz, 6H, CH6Sn), 1.34 (m, 6H, CH3CH2), 1.61 (m, 6H, CH2CH2Sn), 3.70 (s, J8h 9.6 Hz, 2H, CH2Cl). 13C{H}-NMR: δ C, 11.3 (s, CH2Sn), 24 Hz), 31.2 (s, J8h 8 Hz, CH2Sn), 91.1 (s, C=CCCH2Cl), 105 (s, C=CCCH2Cl). 119Sn{H}-NMR: δSn ~0.5. Anal. Found: C, 49.44; H, 7.86. Calcd. for C10H10ClSnS: C, 49.56; H, 8.04.

Ph3SnCCH2Cl (2). As for 1, using propargyl chloride (2.03 g, 2.7 x 10−2 mol), 8BuLi (2.5 M, 5.4 cm3, 1.3 x 10−2 mol) and Ph3SnCl (5.25 g, 1.3 x 10−2 mol). Isolated as yellow oil. Yield: 3.96 g, 72%. NMR (CD2Cl2, 30°C): 1H-NMR: δ H, 0.37 (s, J8h 10.5 Hz, 2H, CH2), 1.10 – 1.30 (m, 9H, m-C6H4H), 2.50 – 2.70 (m, 6H, m-C6H4H), 7.50 – 7.60 (m, 5H, 6H, o-C6H4H). 13C{H}-NMR: δ C, 36.7 (s, J8h 10.5 Hz, 2H, CH2), 7.10 – 7.20 (m, 9H, m-C6H4H), 7.00 – 7.10 (m, 5H, 6H, o-C6H4H). 119Sn{H}-NMR: δSn ~169.5. Anal. Found: C, 59.63; H, 4.12. Calcd. for C18H19ClSn: C, 59.55; H, 4.05.
For 1, using propargyl chloride (3.73 g, 5.0 x 10^2 mol), BuLi (2.5 M, 10.0 cm^3, 2.5 x 10^2 mol) and Me₂PhSiCl (4.26 g, 2.5 x 10^2 mol). The crude product was distilled at 65 °C, 8.1 x 10^3 mbar to afford colourless oil. Yield: 4.98 g, 96%. NMR (C₆D₆, 30°C): 1H-NMR: δH = 0.32 (s, JHH 8 Hz, 6 H, SiCH₃), 3.21 (s, 2H, CH₂Cl), 7.14 – 7.18 (m, 4H, m-p-C₆H₄), 7.53 – 7.55 (m, 2H, o-C₆H₄). 13C(C₆H₄)-NMR: δC = –1.2 (s, SiCH₂, JSC 58 Hz), 30.5 (s, 2H, CH₂Cl), 102.0 (s, C=CH₂Cl). 29Si(C₆H₄)-NMR: δSi = –21.6. Anal. Found: C, 63.18; H, 6.14. Calcd. for C₂₁H₁₃ClSi: C, 63.29; H, 6.28.

For 1, using propargyl chloride (6.24 g, 8.4 x 10^3 mol), BuLi (2.5 M, 16.8 cm³, 4.2 x 10^2 mol) and Ph₂SiCl₂ (8.06 g, 4.2 x 10^3 mol). The crude product was distilled at 52 °C, 3.0 x 10^3 mbar to afford colourless oil. Yield: 5.76 g, 60%. NMR (C₆D₆, 30°C): 1H-NMR: δH = 1.03 (m, JHH 6 Hz, 6 H, SiCH₃), 1.11 (d, JHH 6.5 Hz, 18H, CH₃), 3.53 (s, 2H, CH₂Cl). 13C(C₆H₄)-NMR: δC = 11.5 (s, SiCH₂, JSC 57 Hz), 18.8 (s, 2H, CH₂Cl), 30.6 (s, CH₂Cl), 88.4 (s, C=CH₂Cl), 102.7 (s, C=CH₂Cl). 29Si(C₆H₄)-NMR: δSi = –16.8. Anal. Found: C, 62.38; H, 9.85. Calcd. for C₂₁H₁₃ClSi: C, 62.43; H, 10.04.

For 1, using propargyl chloride (1.62 g, 2.2 x 10^2 mol), BuLi (2.5 M, 4.35 cm³, 1.1 x 10^2 mol) and Ph₂SiCl₂ (2.09 g, 1.1 x 10^2 mol). Obtained as orange oil. Yield: 2.33 g, 93%. NMR (C₆D₆, 30°C): 1H-NMR: δH = 0.60 (m, JHH 6 Hz, 6 H, SiCH₃), 0.99 (t, JHH 7.2 Hz, 9H, CH₃), 1.47 (m, 6H, CH₂CH₂), 3.55 (s, 2H, CH₂Cl). 13C(C₆H₄)-NMR: δC = 16.2 (s, CH₃Si, JSC 56 Hz), 17.9 (s, CH₃), 18.4 (s, CH₂CH₂Si, JSC 6 Hz), 30.7 (s, CH₂Cl), 90.2 (s, C=CH₂Cl), 101.8 (s, C=C=CH₂Cl). 29Si(C₆H₄)-NMR: δSi = –13.0. Anal. Found: C, 58.27; H, 9.79. Calcd. for C₂₁H₁₃ClSi: C, 62.43; H, 10.04.

For 1, using propargyl chloride (1.92 g, 2.5 x 10^2 mol), BuLi (2.5 M, 5.2 cm³, 1.3 x 10^2 mol) and Ph₂SiCl₂ (3.02 g, 1.29 x 10^2 mol). Obtained as orange oil. Yield: 3.08 g, 88%. NMR (C₆D₆, 30°C): 1H-NMR: δH = 0.67 (m, JHH 6 Hz, 6 H, SiCH₃), 0.92 (t, JHH 7.3 Hz, 9H, CH₃), 1.38 (m, 6H, CH₂CH₂), 1.46 (m, 6H, CH₂CH₂), 3.56 (s, 2H, CH₂Cl). 13C(C₆H₄)-NMR: δC = 13.3 (s, CH₃Si, JSC 57 Hz), 14.0 (s, CH₃), 26.5 (s, CH₂CH₂CH₂), 26.8 (s, CH₂CH₂Si, JSC 6 Hz), 30.7 (s, CH₂Cl), 90.3 (s, C=CH₂Cl), 101.8 (s, C=C=CH₂Cl). 29Si(C₆H₄)-NMR: δSi = –11.3. Anal. Found: C, 66.39; H, 10.02. Calcd. for C₂₁H₁₃ClSi: C, 66.01; H, 10.71.

For 1, using propargyl chloride (1.00 g, 1.3 x 10² mol), BuLi (2.5 M, 2.7 cm³, 6.7 x 10¹ mol) and Ph₂SiCl₂ (3.83 g, 1.3 x 10³ mol). The crude product was sublimed under reduced pressure (23.0 x 10³ mbar) to afford colourless solid. Yield: 3.04 g, 89%. NMR (C₆D₆, 30°C): 1H-NMR: δH = 3.49 (s, 2H, CH₂Cl), 7.14 – 7.16 (m, 9H, m-p-C₆H₄), 7.73 – 7.78 (m, 6H, o-C₆H₄). 13C(C₆H₄)-NMR: δC = 30.4 (s, CH₂Cl), 87.6 (s, C=CH₂Cl), 104.9 (s, C=CH₂Cl), 128.4 (s, p-C₆H₄), 130.4 (s, m-C₆H₄), 133.4 (s, i-C₆H₅), 136.0 (s, C=CH₂). 29Si(C₆H₄)-NMR: δSi = –28.8. Anal. Found: C, 75.68; H, 5.11. Calcd. for C₂₁H₁₃ClSi: C, 75.77; H, 5.15.

For 1, using propargyl chloride (0.375 g, 2.02 x 10³ mol) held at –78 °C was added
of volatiles under reduced pressure then extracted with pentane; this fraction was taken to dryness and dried in vacuo to afford the product as dark red oil. Yield: 1.46 g, 76%. 15 (74%): NMR (C<sub>D6</sub>, 30°C): 1<sup>1</sup>H-NMR: δ<sub>H</sub> 0.89 (t, 3<sub>J</sub>H = 7.0 Hz, 1H, CH₂), 2.05 (q, 3<sub>J</sub>H = 7.0 Hz, 2H, CH₂P), 3.79 – 3.82 (m, 2H, o-PC<sub>6</sub>H₅)), 7.45 – 7.49 (m, 4H, o-PC<sub>6</sub>H₅)). 13<sup>C</sup>(H)-NMR: δ<sub>C</sub> 14.8 (d, 3<sub>J</sub>C = 3.2 Hz, CH₂), 43.4 (d, 3<sub>J</sub>C = 17.4 Hz, NCH₃), 75.0 (s, CH₃), 105.9 (d, 3<sub>J</sub>C = 13.5 Hz, i-CH₃), 137.4 (d, 3<sub>J</sub>C = 19 Hz, Ph), 127.8 (s, o-CH₃), 127.9 (overlapped m- or p-CH₃), 209.9 (d, 3<sub>J</sub>C = 11.4 Hz, =C=). 31<sup>P</sup>(H)-NMR: δ<sub>P</sub> 91.0 (s, br, 74%). Propargyl tautomer (5%): NMR (C<sub>D6</sub>, 30°C): 1<sup>1</sup>H-NMR: δ<sub>H</sub> 1.02 (t, 3<sub>J</sub>H = 7.2 Hz, 2H, CH₂), 2.71 (d, 3<sub>J</sub>H = 5.8 Hz, 2H, CH₂P), 2.87 (m, 8H, NCH₃), 13<sup>C</sup>(H)-NMR: δ<sub>C</sub> 14.0 (d, 3<sub>J</sub>C = 5 Hz, CH₂), 19.8 (m, CH₂P), 42.8 (d, 3<sub>J</sub>C = 17 Hz, NCH₃), 81.5 (s, C≡CCH₃P), 87.6 (s, C≡CCH₃P). 31<sup>P</sup>(H)-NMR: δ<sub>P</sub> 83.2 (s, br, 5%).

(Et<sub>3</sub>N<sub>2</sub>Cl)PCl(CH₂C≡CCH₃) (16). To an ethereal solution of 15 held at −78 °C was added drop-wise two equivalent of HCl (1M in ether). The mixture was held at −78 °C while stirring for 20 min, before being allowed to warm to ambient temperature and stir overnight. The resulting suspension was filtered and stripped of volatiles under reduced pressure, the resulting orange oil was dried in vacuo. NMR (C<sub>D6</sub>, 30°C): 1<sup>1</sup>H-NMR: δ<sub>H</sub> 0.81 (t, 3<sub>J</sub>H = 6.9 Hz, 6H, CH₃), 2.94 (q, 3<sub>J</sub>H = 7.4 Hz, 4H, CH₂), 4.89 (dd, 3<sub>J</sub>H = 13.0 Hz, 3<sub>J</sub>H = 5.7 Hz, 1H, =CH₂), 4.93 (dd, 3<sub>J</sub>H = 13.0 Hz, 3<sub>J</sub>H = 5.7 Hz, 1H, =CH₂), 3.55 – 2.70 (m, 8H, NCH₃), 7.11 (7, 3J = 7.8 Hz, 2H, m-CH₃), 7.50 (d, 3<sub>J</sub>C = 7.8 Hz, 2H, o-CH₃), 13<sup>C</sup>(H)-NMR: δ<sub>C</sub> 13.9 (d, 3<sub>J</sub>C = 6.2 Hz, CH₂), 43.9 (d, 3<sub>J</sub>C = 13 Hz, NCH₃), 77.6 (s, CH₃), 105.3 (d, 3<sub>J</sub>C = 40 Hz, Ph), 127.6 (d, 3<sub>J</sub>C = 15 Hz, o-CH₃), 127.5 (s, p-CH₃), 129.5 (s, m-CH₃), 210.6 (d, 3<sub>J</sub>C = 8.4 Hz, =C=). 31<sup>P</sup>(H)-NMR: δ<sub>P</sub> 122.0 (s, br, 77%).

Platinum and palladium complexes. In a typical procedure, to a suspension of the [MC≡CH] (M = Pt, Pd) in DCM was added a cooled DCM solution of the respective ligand (8, 11 or 12). The mixture was stirred overnight then stripped of volatiles under reduced pressure to afford the complexes as yellow solids, which were recrystallised from DCM/ether.

cis-[Pt(Ph₂CP(NEt₂)CH₂C≡C(CH₃)Ph)Cl₂] (17). Yield: 78%. NMR (C<sub>D6</sub>, 30°C): 1<sup>1</sup>H-NMR: δ<sub>H</sub> 0.81 (m, 12H, SnCH₃), 0.88 (m, 18H, CH₃), 1.27 (m, 12H, CH₂), 1.44 (m, 12H, CH₂), 3.78 (m, J<sub>HH</sub> = 5Hz, 4H, CH₂P), 6.90 – 7.01 (m, 12H, m-PC₆H₅), 7.63 – 7.77 (m, 8H, o-PC₆H₅). 13<sup>C</sup>(H)-NMR: δ<sub>C</sub> 11.1 (s, CH₃Sn, J<sub>HH</sub> = 365 Hz, 195<sup>P</sup>C₆H₅), 13.9 (s, CH₃), 23.8 (d, 3<sub>J</sub>C = 27 Hz, CH₂PPh₂), 27.4 (s, CH₂SnCH₃), 131.3 (d, 3<sub>J</sub>C = 27 Hz, CH₂PPh₂), 88.7 (m, C≡CCH₂PPh₂), 104.0 (m, C≡CCH₃PPh₂), 127.9 (br, m-PC₆H₅), 129.0 (br, m-PC₆H₅), 31<sup>P</sup>(H)-NMR: δ<sub>P</sub> 68.2 (m, 195<sup>P</sup>C₆H₅), 137.2 (d, 3<sub>J</sub>C = 5.6 Hz, 195<sup>P</sup>C₆H₅). Anal. Found: C, 50.23; H, 5.95. Calc. for C₇₂H₄₃P₃Sn₂Si: C, 50.18; H, 6.08.

cis-[Pt(Ph₂CP(NEt₂)CH₂C≡C(CH₃)Ph)Cl₂] (18). Yield: 86%. NMR (C<sub>D6</sub>, 30°C): 1<sup>1</sup>H-NMR: δ<sub>H</sub> 0.84 (sept, 3<sub>J</sub>H = 7.1 Hz, 6H, SiCH₃), 0.93 (d,
cis-[Pt(PPh₃CH₂C≡SiPr)₂]Cl₂ (19). Yield: 78%. NMR (CD₂Cl₂, 30°C): δH-NMR: δH-NMR: 7.03 – 7.12 (m, 12H, C—H), 18.8 (s, CH₃), 23.9 (t, JCH₃ = 40 Hz, CH₃P), 85.8 (m, C—C(CH₃)P), 101.9 (m, C=C(CH₂)P), 127.9 (m, C—C, 131.1 (m, C—C), 134.2 (m, C—C), 134.6 (m, i-C₃H₇), 31P{¹H}-NMR: δP = 5.83 (s, JPP = 3614 Hz).

cis/trans-isomerisation of [Pt(PPh₃CH₂C≡SiPr)₂]Cl₂ (19). In a borosilicate NMR tube was placed cis-19 as solution in CD₂Cl₂. The sample was irradiated for 20 min. with a 500 mW full spectrum mercury lamp, resulting in precipitation of an orange solid, which redissolved upon agitation. Yield of trans-19 (by ¹H NMR): 58%. NMR (CD₂Cl₂, 30°C): δH-NMR: 7.06 (m, 12H, CH₂C(3H), 1.35 (t, JCH = 4 Hz, CH₂P), 7.03 – 7.13 (m, 12H, m/P(C₃H₃)), 7.98 – 7.98 (m, 8H, o-P(C₃H₃)), 13C{¹H}-NMR: δC = 11.6 (s, CH₂Si), 18.8 (s, CH₃), 18.9 (s, C—C(CH₃)P), 101.7 (m, C=C(CH₂)P), 127.6 (m, C—C, 131.3 (m, C—C), 134.7 (m, C—C), 134.7 (m, C—C), 134.8 (m, i-C₃H₇), 31P{¹H}-NMR: δP = 5.83 (s, JPP = 3614 Hz).

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Notes and references
1. DBP = dibenzophosphole
2. We note that allenylphosphonates have been more heavily studied; indeed, several of the limited allenylphosphines reported previously have been obtained through reduction of the respective phosphonates.
Synopsis – for table of contents use only

The propargyl phosphanes Ph₂PCH₂C≡CER₃ (R₃E = "Bu₃Sn, Ph₃Sn, Me₂PhSi, Pr₃Si, "Bu₂Si) and (Me₃Si)₂PCH₂C≡CSiPhMe₂ are obtained in high yield, while quenching PhC≡CCH₂MgX with ClP(NEt₂)₂ preferentially affords (>70%) the novel phosphinoallene (Et₂N)₂PC(Ph)=C=CH₂.