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Synthesis of 3-stanny1 and 3-silyl propargyl phosphanes and the formation of a phosphinoallene

Amy J. Saunders and Ian R. Crossley*

The group 14 chloropropargyls R₂E=CH₂SiMe₃ (R = Ph, SiMe₂), obtained by a modified literature procedure, react with LiPPh₂ to afford the novel propargyl phosphanes Ph₂PCH=CH₂SiMe₂, in high yield, as viscous oils; (Me₂Si)₂PCH₂C≡CSiMe₂ is similarly obtained from LiP(SiMe₂)₂. In contrast, the reaction of PhC=CH₂MgCl with CIP(NEt₂)₂ fails to produce a comparable propargyl phosphane, but generates preferentially (>70%) the novel phosphinoallene (Et₂N)₂PC(Ph)=C(CH₃)₂, which is characterised spectroscopically, and through its reaction with 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 π-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, hydroboration, hydrophosphination) akin to their more extensively utilised alkynyl, alkenyl and allyl counterparts. Moreover, they embody intrinsic potential to act as σ/π-chelating ligands. Indeed, among very limited coordination chemistry reported to date, the μ-(σ-R,π-C=C) bridging mode has been described for [Co₂P₂(C₂H₄)₂(PCPh₂C≡CMe₂)₂] (M = Mo, R = Ph, SiMe₂), [Mo(O)₂(PCPh₂C≡CMe₂)₂] and [Mo₂P₂(C₂H₄)₂] with the dirhodium complex [Co₂Rh₂(C₂H₄)₂(PCPh₂C≡CMe₂)₂] and the ruthenium phthalocyaninato (Pc²-) complex [Ru₂P₄(C₂H₄)₂], obtained by reaction of (Co₂(C₂H₄)₂) with the dirhodium complex [Co₂Rh₂(C₂H₄)₂(PCPh₂C≡CMe₂)₂] and the ruthenium phthalocyaninato (Pc²-) complex [Ru₂P₄(C₂H₄)₂].

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, [M(CO)₃(PCPh₂C≡CMe₂)] (M = Mo, R = Ph, SiMe₂), [Mo(O)₂(PCPh₂C≡CMe₂)₂], [Mo₂P₂(C₂H₄)₂] and [Mo₂P₂(C₂H₄)₂] with the dirhodium complex [Co₂Rh₂(C₂H₄)₂(PCPh₂C≡CMe₂)₂] and the ruthenium phthalocyaninato (Pc²-) complex [Ru₂P₄(C₂H₄)₂], obtained by reaction of (Co₂(C₂H₄)₂) with the dirhodium complex [Co₂Rh₂(C₂H₄)₂(PCPh₂C≡CMe₂)₂] and the ruthenium phthalocyaninato (Pc²-) complex [Ru₂P₄(C₂H₄)₂].

Notably, no complexes of the group 10 metals have been described, though the formally related diphenylphosphane-bridged complexes [L₃M(PPh₂C≡CMe₂)₂] (L₃M = Cp²Pt,
(OC)₃Ni) have been reported, along with examples with other metals (L₅M = AuCl₃, CpCo₂, CpFe(CO)₃, CpFeBr(CO), CpMn(NO)(CO), CpMo(CO)₅(COCH₃) and Mo(CO)₆). The intriguing tetrameric complex [(η⁵-C₅-Mo(CO)₅)(η₁-P,P-PPh₃CH₂C≡CH₂PPh₃)](Mo(CO)₅) has also been described.

We have recently been interested in the synthesis and study of reactive and functional phosphanes and organometallic phosphacarbons, with the goal of developing novel amphilic systems and molecular conductive and/or optoelectronically active molecules. In continuing these works, we have had cause to access propargyl phosphanes of the type R₂P(CH₂C≡CH₂) (E = Si, Sn) as intermediates, seeking to exploit their capacity for desilylative / destannylative functionalisation. In view of the limited range of propargyl phosphanes reported previously, we thus undertook to prepare a putative series of such materials; viz. Ph₃P(CH₂C≡CH₂) (E = Si, Sn), which we describe herein, along with attempts to obtain (Et₃N)₃P derivatives, leading to the generation of a novel, and very rare, phosphinoallene. We also outline the coordination chemistry of representative propargylphosphanes toward Pd and Pt, reporting the first such complexes from group 10, and the first to involve coordinately unsaturated metal centres.

Results and Discussion

Phosphone Synthesis

The silyl and stannyl chloropropargyl precursors R₂EC≡CCH₂Cl (E = Si, Sn) were prepared following a modified literature procedure (Scheme 1), via the low-temperature (−78°C) lithiation of HC≡CCH₂Cl, quenched with R₂SnCl (1 and 2) or R₂SiCl (3 – 7). The silanes were amenable to purification by reduced-pressure distillation, apart from the solid (R = 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 1H NMR spectra, which exhibit resonances associated with the group 14 fragment, integrating consistently against that of the propargyl methylene moiety (δ₁H 3.5 – 3.7), 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 (1H-X HMBCl; X = 119Sn, ²⁹Si); for the stannanes the Jₖ,iH coupling (~ 10 Hz) is also large enough to resolve tin satellites. The 13C(¹H)-NMR data are similarly consistent, while bulk purity was confirmed from microanalytical data. It is noted that 1, 2, 3, 4 and 5 have been previously obtained via alternate methodology.

Ethereal solutions of 1 to 6 were added (−78°C) to LiPPH₂ in ether (formed by in situ lithiation of HPPH₂ with ⁶Li) and the mixtures stirred overnight to afford the propargyl phosphanes Ph₃P(CH₂C≡CH₂) (8 – 13, Scheme 1). Extraction with pentane afforded the phosphases as viscous oils, the silyl derivatives 10 – 13 requiring no further purification. In contrast, stannanes formed in admixture with ⁸BuSn (1:4 of 8) or Ph₃BuSn (1:1 with 9), presumably due to metathesis of 1 and 2 with residual Ph₃P(CH₂C≡CH₂)Cl.

Table 1

<table>
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<th>Compounds</th>
<th>δ₁H(C₁H)</th>
<th>δ₁H(C₂)</th>
<th>δ₁H(C₃)</th>
<th>δ₁H(E)</th>
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<td>13</td>
<td>−13.5</td>
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<td>85.5</td>
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<tr>
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<td>−158.9</td>
<td>2.43</td>
<td>83.3</td>
<td>109.3</td>
</tr>
</tbody>
</table>

*As Cd₂O solutions; †couplings in Hz

BuLi, as common among Sn(IV) organyls. 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 (¹H-X HMBCl), with 8 and 9 also allowing for resolution of 119Sn satellites (Jₖ,iH ~ 14 Hz) in the 31P(¹H) spectra. The ¹¹³Sn spectra of 8 and 9 indicate the presence of ⁶BuSn (δ₁H ~12.0) and Ph₃BuSn (δ₁H ~98.3) by-products respectively.

Attempts to vary the nature of the phosphanyl substituents met with limited success. Dicyclohexyl analogues failed to form, regenerating HPCy₂, as the only phosphorus-containing product, which presumably reflects the greater basicity and steric bulk of ‘PCy₃’ (cf. ‘PPH₃’), favouring proton-abstraction from the chloropropargyls over Si₂ substitution. In contrast, reactions with LiP(SiMe₃)₂ did afford species consistent with the desired propargylphosphanes, though in admixture with several significant contaminants, which defied separation or characterisation. Nonetheless, Me₂PSSiC≡C(CH₂P(SiMe₃)) (14) was obtained as the primary product (92%) by ¹H-NMR in admixture with P(SiMe₃)₂ (4%) and a mono-silylphosphane (δ₁H ~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...
less favoured than their bromide analogues, propargyl chlorides have been shown to form Grignard reagents, and we encountered no difficulty is generating ‘PhC=CH₂MgCl’ under comparable conditions. However, our efforts to quench this reagent with (Et₃N)₂P(Cl) 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 (Et₃N)₂P(Cl) 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 (Et₃N)₂P(PO₂) moity (δH 90.9; cf. PhP(NET₃)₂ 97.9,⁵⁸ H₂C=CH(PO₂)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 (δH 4.72. δC 75.0) relative to both PhC=CH₂Cl (δH 4.39, δC 31.2) and propargyl phosphines, and exhibits appreciably greater magnitude coupling to phosphorus (/JPH₂ = 7.1 Hz) than 8 – 14. The unsaturated carbon centres are also heavily deshielded (δH 137.4 (JEC 19.0 Hz) C₂; 209.9 (JEC 11.3 Hz) C₁), the latter in particular being more characteristic of an allenic,⁴⁰ rather than alkynic centre; indeed, these data are in good agreement with those for the limited range of phosphinoallenes (Table 2) described previously.¹⁴¹⁴ We thus confidently formulate 15 as (Et₃N)₂P(Cl)=CH₂ (Scheme 2).

The reaction of propargyl Grignard reagents with R₃PCl has been noted to afford mixtures that include allenylphosphines, their proportion being dependent on the nature of ‘R’:⁴² 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 carbanion 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 cation, as compared, for instance, with the notionally ‘harder’ PCl₅, with which we encountered significantly greater complexity, yielding a largely intractable mixture.

In order to confirm or dismiss the presence of Cl₂P(Cl)=CH₂ within this mixture, we sought to prepare an authentic sample, treating 15 with HCl (2 equiv.). This effected quantitative conversion to (Et₃N)₂[C(Cl)=CH₂] (16), as evidenced by the ¹H NMR spectrum, which indicates loss of one diethylamino moiety (Et₂N vs Ph resonances) and emergence of diasterotopicity for the methylenic ‘=CH₂’. The phosphorus resonance of 16 is appreciably deshielded from that of 15, consistent with replacement of NEt₂ by Cl (δH 122; cf. PhP(Cl)PNEt₂ 142.1). Upon further treatment with HCl there is superficial evidence for removal of the remaining diethylamino moiety, viz. loss of its ¹H NMR resonances, and diasterotopicity of the ‘=CH₂’ protons (δH 4.63, δJ₂,3 3 Hz). However, the ³¹P shift (δP 58.7, t, δJ₃,4 3 Hz) seems inconsistent with a species of the type RPCl₃; 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 Proparglyphosphines. As previously noted (vide supra) the coordination chemistry of proparglyphosphines 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 proparglyphosphines 8, 11 and 12 react with [PtCl₂], as a suspension in CH₂Cl₂, to afford exclusively the complexes cis-[Pb₂(H₂C=CH(CER₃)]₂Cl] (ER₃ = ‘Bu₃Sn 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 [PdCl₂]ₓ, 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

Table 2 Selected ¹H and ¹³C(¹H)-NMR data for precedent phosphinoallenes ¹⁴

<table>
<thead>
<tr>
<th>Compound</th>
<th>δH (CH₂)</th>
<th>δC (CH₂)</th>
<th>δC (CH₂)</th>
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<tr>
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<td>72.26</td>
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<tr>
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<tr>
<td>R₃P(Cl)=CH₂</td>
<td>209.6</td>
<td></td>
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</tbody>
</table>

¹chemical shifts in ppm. ²data sourced from references 14 and 41.

Scheme 2. Reagents and conditions: i) Et₃O, HgCl₂ (5 mol%), Mg, Δ, 4h; ii) (Et₃N)₂P(Cl), −78°C, 30 min; iii) r.t. 18 h; iv) Me/Cl₂; v) 2 equiv. HCl/Et₃O.

Scheme 3. Reagents and conditions: i) CH₂Cl₂, 12 h.; ii) C₆D₆, h r, 30 min.
data, which verify the structural integrity of the ligands and coordination of the phosphorus centres ($\Delta \delta_P \sim +20$). For the platinum complexes $17 - 19$, $|J_{PH}|$ 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 $^{113}C(\text{H})$-NMR resonances associated with the CH$_2$P 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 ($|J_{PH}| = 2601$ Hz), consistent with trans-[Pt(PR$_3$)$_2$X$_2$], and ii) manifestation of virtual coupling for the CH$_2$P 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 propargylphosphines that feature tin and silicon termini on the alkyn moiety. Attempts to increase the range of phosphanyl termini used via the reaction of R$_3$PCI with propargyl Grignard reagents proved unsuccessful, but allowed for the generation of the novel allenylphosphines (Et$_2$N)$_2$PC(Ph)=C=CH$_2$, 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 \[ [\text{M}(\text{Ph})_2\text{C} \equiv \text{C}(\text{R})_2\text{Cl}] \] 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 phosphane 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 (M Braun) 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 HPH$_2$ 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 (PdCl$_2$, PtCl$_2$) were obtained from STREM and used as supplied. HPi(SiMe$_3$)$_2$ was prepared by literature procedure. Deuterated solvents were supplied by Goss Scientific and purified by refluxing with potassium (hydrocarbon) or CaH$_2$ (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; $^{13}C$, 100.46 MHz; $^{31}P$, 161.71 MHz; $^{29}Si$, 79.37 MHz; $^{119}Sn$, 148.97 MHz; $^{195}Pt$, 85.53 MHz) or VNMRS 500 ($^1H$ 499.91 MHz; $^{13}C$, 125.72 MHz) spectrometer. All spectra were referenced to Me$_4$Si, 85% H$_2$PO$_4$, Me$_3$Sn or K$_2$PtCl$_4$ as appropriate. Carbon-13 NMR data were assigned with recourse to the 2D (HSQC, HMBC) spectra; detailed connectivities and $^{29}Si$ chemical shifts were assessed using $^1H$-X HMBC spectra ($X = ^{29}Si$; $^{119}Sn$; $^3P$). Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

Synthesis

$^8$Bu$_3$SnC=CH$_2$Cl (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 cm$^3$) was cooled to –78°C before the drop-wise addition of $^8$BuLi (2.5 M, 6.0 cm$^3$, 1.5 x 10$^{-2}$ mol). The mixture was stirred for 30 min., after which time $^8$Bu$_3$SnCl (4.40 cm$^3$, 1.5 x 10$^{-2}$ mol) was added as solution in THF (ca 10 cm$^3$) 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 HCl/C6H$_5$Cl 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 ($C_D_6$, 30°C): $^1H$-NMR: $\delta$ 0.91 (t, $^3J_{HH}$ 7.3 Hz, 9 H, $CH_3$), 0.97 (t, $^3J_{HH}$ 6 Hz, $J_{HH}$ 54 Hz, 6H, $CH_2$Sn), 1.34 (m, 6H, $CH_2$CH$_2$), 1.61 (m, 6H, $CH_2$CH$_2$Cl), 3.70 (s, $J_{HH}$ 6 Hz, 2H, $CH_2$Cl). $^{13}$C(\text{H})$-NMR: $\delta$ 11.3 (s, $CH_2$Sn), $^{119}$Sn(\text{H})$-NMR: $\delta_6$ 117.5 ppm. Anal. Found: C, 49.44; H, 7.86. Calcld. for C$_8$H$_{17}$SnC: C, 49.56; H, 8.04.

$^8$Ph$_3$SnC=CH$_2$Cl (2). As for 1, using propargyl chloride (2.03 g, 2.7 x 10$^{-2}$ mol), $^8$BuLi (2.5 M, 5.4 cm$^3$, 1.3 x 10$^{-2}$ mol) and Ph$_3$SnCl (5.25 g, 1.3 x 10$^{-2}$ mol). Isolated as yellow oil. Yield: 3.96 g, 72%. NMR ($C_D_6$, 30°C): $^1H$-NMR: $\delta$ 3.67 (s, $J_{HH}$ 10.5 Hz, 2H, $CH_2$Cl), 7.10 – 7.20 (m, 9H, $m$/p-$C_8$H$_{17}$), 7.60 – 7.65 (m, $J_{HH}$ 55 Hz, 6H, o-$C_6$H$_4$). $^{13}$C(\text{H})$-NMR: $\delta$ 30.8 (s, $J_{HH}$ 10 Hz, $CH_2$Cl), 88.5 (s, $CH_2$C=CH$_2$Cl), 106.8 (s, $C_6$H$_{15}$C$\equiv$CH), 128.8 (s, p-$C_6$H$_4$), 129.5 (m, o-$C_6$H$_4$), 130.1 (s, i-$C_6$H$_4$), 136.7 (s, o-$C_6$H$_4$). $^{119}$Sn(\text{H})$-NMR: $\delta_6$ –169.5 ppm. Anal. Found: C, 59.63; H, 4.12. Calcld. for C$_{20}$H$_{31}$SnCl: C, 59.55; H, 4.05.
As 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^{-1} mol) and Me_{3}SiCl (4.26 g, 2.5 x 10^{-2} mol). The crude product was distilled at 66 °C, 8.1 x 10^{-2} mbar to afford colourless oil. Yield: 4.98 g, 96%. NMR (CD_{2}Cl_{2}, 30°C): 1^H-NMR: δ_{H} 0.32 (s, J_{SH} 8 Hz, 6 H, SiCH_{3}), 3.21 (s, 2H, CH_{2}Cl), 7.14 – 7.18 (m, 3H, m-p-C_{6}H_{4}), 7.55 – 7.59 (m, 2H, o-C_{6}H_{4}). 1^3C_{(H)}-NMR: δ_{C} – 1.2 (s, SiCH_{3}, J_{SC} 58 Hz), 30.5 (s, CH_{2}Cl), 102.0 (s, C=C(=SiC)). 25Si(N)-NMR: δ_{Si} – 21.6. Anal. Found: C, 63.18; H, 6.14. Calcld. for C_{7}H_{3}SiC: C, 63.29; H, 6.28.  

For 1, using propargyl chloride (6.24 g, 8.4 x 10^{-2} mol), BuLi (2.5 M, 16.8 cm^{3}, 4.2 x 10^{-2} mol) and PH_{3}SiCl (8.06 g, 4.2 x 10^{-1} mol). The crude product was distilled at 52 °C, 3.0 x 10^{-2} mbar to afford colourless oil. Yield: 5.76 g, 60%. NMR (CD_{2}Cl_{2}, 30°C): 1^H-NMR: δ_{H} 1.03 (m, 2H, SiCH), 1.11 (d, J_{SH} 6.5 Hz, 18H, CH_{3}Si), 1.53 (s, 2H, CH_{2}Cl). 1^3C_{(H)}-NMR: δ_{C} 11.5 (s, SiCH, J_{SC} 57 Hz), 18.8 (s, CH_{2}Cl), 30.6 (s, CH_{3}Si), 88.4 (s, C=C(=SiC)). 29Si(N)-NMR: δ_{Si} – 16.8. Anal. Found: C, 62.38; H, 9.85. Calcld. for C_{12}H_{25}SiCl: 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 cm^{3}, 1.1 x 10^{-1} mol) and PH_{3}SiCl (2.09 g, 1.1 x 10^{-1} mol). Obtained as orange oil. Yield: 2.33 g, 93%. NMR (CD_{2}Cl_{2}, 30°C): 1^H-NMR: δ_{H} 0.60 (m, 6 H, SiCH_{2}), 0.99 (t, J_{SH} 7.2 Hz, 9H, CH_{3}), 1.47 (m, 6H, CH_{2}CH_{3}), 3.55 (s, 2H, CH_{2}Cl). 1^3C_{(H)}-NMR: δ_{C} 16.2 (s, CH_{2}Si, J_{SC} 52.6 Hz), 17.9 (s, CH_{3}), 18.4 (s, CH_{2}CH_{2}Si, J_{SC} 6 Hz), 30.7 (s, CH_{2}Si), 90.2 (s, C=C(=SiC)). 29Si(N)-NMR: δ_{Si} – 13.0. Anal. Found: C, 62.87; H, 9.79. Calcld. for C_{12}H_{25}SiCl: C, 62.43; H, 10.04.  

As for 1, using propargyl chloride (1.92 g, 2.5 x 10^{-2} mol), BuLi (2.5 M, 5.2 cm^{3}, 1.3 x 10^{-1} mol) and PH_{3}SiCl (3.02 g, 1.29 x 10^{-1} mol). Obtained as orange oil. Yield: 3.08 g, 88%. NMR (CD_{2}Cl_{2}, 30°C): 1^H-NMR: δ_{H} 0.67 (m, 6H, SiCH_{2}), 0.92 (t, J_{SH} 7.3 Hz, 9H, CH_{3}), 1.38 (m, 6H, CH_{2}CH_{3}), 1.46 (m, 6H, CH_{2}CH_{3}Si), 3.56 (s, 2H, CH_{2}Cl). 1^3C_{(H)}-NMR: δ_{C} 13.3 (s, CH_{2}Si, J_{SC} 57 Hz), 14.0 (s, CH_{3}), 26.5 (s, CH_{2}CH_{3}), 26.8 (s, CH_{2}CH_{2}Si, J_{SC} 6 Hz), 30.7 (s, CH_{3}Si), 90.3 (s, C=C(=SiC)). 29Sn(N)-NMR: δ_{Sn} – 11.3. Anal. Found: C, 66.39; H, 10.02. Calcld. for C_{12}H_{25}SnCl: C, 66.01; H, 10.71.  

For 1, using propargyl chloride (1.00 g, 1.3 x 10^{-2} mol), BuLi (2.5 M, 2.7 cm^{3}, 6.7 x 10^{-2} mol) and PH_{3}SiCl (3.83 g, 1.3 x 10^{-1} mol). The crude product was sublimed under reduced pressure (23.0 x 10^{-2} mbar) to afford colourless solid. Yield: 3.04 g, 89%. NMR (CD_{2}Cl_{2}, 30°C): 1^H-NMR: δ_{H} 3.49 (s, 2H, CH_{2}Cl), 7.14 – 7.16 (m, 9H, m-p-C_{6}H_{4}), 7.73 – 7.78 (m, 6H, o-C_{6}H_{4}). 1^3C_{(H)}-NMR: δ_{C} 30.4 (s, CH_{2}Cl), 87.6 (s, C=C(=SiC)), 104.9 (s, C=C(=SiC)), 128.4 (s, p-C_{6}H_{4}), 130.4 (s, m-C_{6}H_{4}), 133.4 (s, i-C_{6}H_{4}), 136.0 (s, C=C(=SiC)). 25Si(N)-NMR: δ_{Si} = – 28.8. Anal. Found: C, 75.68; H, 5.11. Calcld. for C_{22}H_{37}ClSi: C, 75.77; H, 5.15.  

As for 1, using propargyl chloride (0.375 g, 2.0 x 10^{-3} mol) held at –78 °C was added drop-wise BuLi (2.5 M, 0.808 cm^{3}, 2.02 x 10^{-3} mol). The mixture was stirred for 30 min. A solution of HCl (0.733 g, 2.0 x 10^{-3} mol) in ether (ca 10 cm^{3}) was then added drop-wise and the mixture maintained at –78 °C while stirring for 30 min. The mixture was allowed to warm to ambient temperature while stirring overnight. Volatiles were removed under reduced pressure and the product extracted with pentane; the solvent was removed and the product dried in vacuo to afford yellow oil. Yield: 8.000 g (4.18 S:BuN). NMR (CD_{2}Cl_{2}, 30°C): 1^H-NMR: δ_{H} 0.93 (m, CH_{3}), 1.36 (m, 12H, 2 x CH_{2}H), 1.58 (m, 6H, CH_{2}Cl), 2.87 (d, J_{SH} 1.6 Hz, J_{175Si} 8.7 Hz, J_{195P} 12.4 Hz, 2H, CH_{2}P), 7.02 – 7.13 (m, 6H, m-p-C_{6}H_{4}), 7.43 – 7.51 (m, 4H, o-C_{6}H_{4}). 1^3C_{(H)}-NMR: δ_{C} 11.3 (s, SiCH_{2}, J_{175Si} 366 Hz, J_{195P} 383 Hz), 13.9 (s, CH_{3}), 20.4 (d, J_{195P} 18Hz, CH_{2}PPh_{3}), 27.4 (s, CH_{2}CH_{2}N, J_{195P} 850 Hz) 85.0 (d, J_{195P} 6 Hz, C=C(=SiP)), 106.8 (d, J_{195P} 5 Hz, C=C(=SiP)), 128.6 (d, J_{195P} 6 Hz, m-C_{6}P), 128.9 (s, p-C_{6}P), 133.2 (d, J_{195P} 19 Hz, o-C_{6}P), 138.8 (d, J_{195P} 17 Hz, i-C_{6}P). 3^1P_{(H)}-NMR: δ_{P} = – 13.4 (s, J_{195P} 14.5 Hz). 119Sn(N)-NMR: δ_{Sn} = –68.5 (d, J_{195P} 14.5 Hz, 45 Hz).
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%. (174 %): NMR (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 0.89 (t, $^3$J$_{HH}$ 7.0 Hz, 12H, CH$_3$), 3.05 (q, $^3$J$_{HH}$ 7.0 Hz, 8H, CH$_2$), 4.69 (d, $^3$J$_{HH}$ 7.0 Hz, 2H, =CH$_2$), 7.11 – 7.15 (m, 3H, m-p-C$_6$H$_4$), 7.63 – 7.59 (m, 2H, o-C$_6$H$_4$). $^{13}$C(1$^H$)-NMR: $\delta_1$ 14.8 (d, $^3$J$_{HC}$ 3.2 Hz, CH$_3$), 43.4 (d, $^3$J$_{CC}$ 17.4 Hz, NCH$_3$), 75.0 (s, =CH$_2$), 105.9 (d, $^3$J$_{CC}$ 13.5 Hz, i-C$_6$H$_4$), 137.4 (d, $^3$J$_{CC}$ 19 Hz, PhC$_6$P(_NET$_3$)$_2$=C), 127.8 (s, o-C$_6$H$_4$), 127.9 (overlapped m-p-C$_6$H$_4$), 209.9 (d, $^3$J$_{CC}$ 11.4 Hz, =Ce). $^3$P(1$^H$)-NMR: $\delta_1$ 91.0 (s, br, 74%). Propargyl tautomer (55%): NMR (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 1.02 (t, $^3$J$_{HH}$ 7.2 Hz, 12H, CH$_3$), 2.71 (d, $^3$J$_{HH}$ 5.8 Hz, 2H, CH$_2$), 2.87 (m, 8H, NCH$_3$). $^{13}$C(1$^H$)-NMR: $\delta_1$ 14.0 (d, $^3$J$_{HC}$ 5 Hz, CH$_3$), 19.8 (m, CH$_2$), 42.8 (d, $^3$J$_{HC}$ 17 Hz, NCH$_3$), 81.5 (s, C=C=CH$_2$), 87.6 (s, =C=C=CH$_2$). $^3$P(1$^H$)-NMR: $\delta_1$ 83.2 (s, br, 5%).

(En$_5$Tol)(Cl)(PhMe)=C$_6$H$_4$ (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 (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 0.81 (t, $^3$J$_{HH}$ 6.9 Hz, 6H, CH$_3$), 2.94 (q, $^3$J$_{HH}$ 7.4 Hz, 4H, CH$_2$) 4.89 (dd, $^3$J$_{HH}$ 13.0 Hz, 1H, 5.7 Hz, 1H, =CH$_2$), 4.93 (dd, $^3$J$_{HH}$ 13.0 Hz, 1H, 5.7 Hz, 1H, =CH$_2$) 7.11 (7, $^3$J$_{HH}$ 7.8 Hz, 2H, m - C$_6$H$_4$), 7.50 (d, $^3$J$_{HH}$ 7.8 Hz, 2H, o-C$_6$H$_4$). $^{13}$C(1$^H$)-NMR: $\delta_1$ 13.9 (d, $^3$J$_{HC}$ 6.2 Hz, CH$_3$), 43.9 (d, $^3$J$_{HC}$ 13 Hz, NCH$_3$), 77.6 (s, =CH$_2$), 105.3 (d, $^3$J$_{HC}$ 40 Hz, PhC$_6$P(_NET$_3$)$_2$=C), 153.4 (d, $^3$J$_{HC}$ 24 Hz, i-C$_6$H$_4$), 127.6 (d, $^3$J$_{HC}$ 1.5 Hz, o-C$_6$H$_4$), 127.98 (s, p-C$_6$H$_4$) 128.9 (s, m-C$_6$H$_4$), 210.6 (d, $^3$J$_{HC}$ 8.4 Hz, =Ce). $^3$P(1$^H$)-NMR: $\delta_1$ 122.0 (s, br, 77%).

Platinum and palladium complexes. In a typical procedure, to a suspension of the [MCl$_2$]$_2$ (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(Ph)$_2$C$_6$H$_4$C$_6$H$_4$SiMe$_3$]$Cl$_2$ (17). Yield: 78%. NMR (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 0.81 (m, 12H, SnC$_2$H$_6$), 0.88 (m, 18H, CH$_3$), 1.27 (m, 12H, CH$_2$), 1.44 (m, 12H, CH$_2$), 3.78 (m, J$_{HH}$ ~ 5Hz, 4H, CH$_2$), 6.90 – 7.01 (m, 12H, m-p-C$_6$H$_4$), 7.63 – 7.77 (m, 8H, o-C$_6$H$_4$). $^{13}$C(1$^H$)-NMR: $\delta_1$ 11.1 (s, CH$_2$Cl, $^3$J$_{HC}$ $^{17}$O 365 Hz, $^{13}$J$_{HC}$ 381 Hz), 13.9 (s, CH$_3$), 23.8 (d, $^3$J$_{HC}$ 27 Hz, CH$_2$PPh$_3$), 27.4 (s, CH$_2$SnC$_6$H$_4$C$_6$H$_4$SiMe$_3$), 58.8, J$^{13}$PC $^{17}$O 60.7 Hz, 29.2 (s, p-C$_6$H$_4$ 10 Hz, CH$_2$), 88.7 (m, C=C=CH$_2$PPh$_3$), 104.0 (m, C=C=CH$_2$PPh$_3$), 127.9 (br, m- p- (C$_6$H$_4$Cl), 129.9 (br, p- (C$_6$H$_4$Cl), 131.1 (s, p- (C$_6$H$_4$Cl)), 134.4 (m, o- (C$_6$H$_4$Cl)). $^3$P(1$^H$)-NMR: $\delta_1$ 6.0 (s, J$_{HP}$ 3618 Hz). $^{13}$Sn(1$^H$)-NMR: $\delta_1$ –68.2 (m, $^{193}$Pt(1$^H$)-NMR: $\delta_1$ –4407 (t, J$_{HP}$ 3618 Hz). Anal. Found: C, 50.23; H, 5.95. Calcd. for C$_{27}$H$_{35}$P$_2$SnSi$_2$: C, 50.18; H, 6.08.

cis-[Pt(Ph)$_2$C$_6$H$_4$C$_6$H$_4$SiMe$_3$]$Cl$_2$ (18). Yield: 86%. NMR (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 0.84 (sept, $^3$J$_{HH}$ 7.1 Hz, 6H, SiCH$_3$), 0.93 (d,
cis-[Pt(PPh₃)₂(CpSiPr)]₂Cl₂ (19). Yield: 78%. NMR (CD₂Cl₂, 30°C): 1H-NMR: δ₀ = 0.41 (m, 12H, SiCH₃), 0.93 (t, J₉= 7.2 Hz, CH₂), 1.23 (m, 12H, CH₂CH₂Si), 3.81 (d, J₉ = 10 Hz, 4H, CH₂), 6.86 – 6.93 (m, 8H, m-P(C₆H₄)₂), 6.94 – 7.00 (m, 4H, o-P(C₆H₄)₂), 7.54 – 7.62 (m, 8H, o-P(C₆H₄)₂). 13C¹(H)-NMR: δ₁ = 16.3 (s, CH₃), 12.5 (s, CH₃), 18.5 (s, CH₃), 55.3 Hz), 17.8 (s, CH₃), 18.5 (s, CH₃), 55.7 Hz). 19F-NMR: δ₂ = -11.5 (s, J₉= 2601 Hz). 31P¹(H)-NMR: δ₃ = -33.3 (t, J₉= 2601 Hz).

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Notes and references

† DBP = dibenzophosphophenate.
§ 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.


2 For a recent review see: E. Bernoud, R. Veillard, C. Alayrac, A.-C. Gaumont, Molecules, 2012, 17, 14573-14587.


Synopsis – for table of contents use only

The propargyl phosphanes Ph$_2$PCH$_2$C≡CER$_3$ (R$_3$E = $^n$Bu$_3$Sn, Ph$_3$Sn, Me$_2$PhSi, Pr$_3$Si, $^n$Bu$_3$Si) and (Me$_3$Si)$_2$PCH$_2$C≡CSiPhMe$_2$ are obtained in high yield, while quenching PhC≡CCH$_2$MgX with ClP(NEt$_2$)$_2$ preferentially affords (>70%) the novel phosphinoallene (Et$_2$N)$_2$PC(Ph)=C=CH$_2$. 