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

Amy J. Saunders and Ian R. Crossley*

The group 14 chloropropargyls R₃C≡CH₃Cl (R = Bu, Sn, Ph, Sn₃, Me₃P₃Si, Ph₃Si, H, SiMe₂), obtained by a modified literature procedure, react with Li₃PMe₂ to afford the novel propargyl phosphanes Ph₃PCH₂C≡CER₂, in high yield, as viscous oils; (Me₃Si)₂PCH₂C≡CSiPhMe₃ is similarly obtained from Li₃P(SiMe₃)₂. In contrast, the reaction of Ph₃C≡CH₃Cl with CIP(NEt₃)₂ fails to produce a comparable propargyl phosphate, but generates preferentially (>70%) the novel phosphinoallene (Et₂N)₂PC(Ph)=C≡CH₃, 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, alkanyl 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-(α,β,π-C≡C) bridging mode has been described for [Cp₂Rh₂(CO)(μ-η²:η²:η₁-C¹:F¹:C¹:F¹:C¹)](PPh₃CH₂C≡CMes) and obtained by reaction of [Rh₂(CO)(μ-η²:η²:η₁-C¹:F¹:C¹:F¹:C¹)] with the diphosphane complex [Cp₂Rh₂(CO)(μ-η²:η²:η₁-C¹:F¹:C¹:F¹:C¹)](PPh₃CH₂C≡CMes). The remaining complexes described to date involve monodentate coordination of the phosphate, typically to metals of the mid transition series, with saturated coordination spheres. Thus, [M(CO)₃(PR₃)(η²-C≡C)] (M = Mo, R₃ = Ph₃, DBP; Cr, R₃ = Ph, SiMe₃), [Mo(CO)₃(η²-C≡C)] and [Mo(CO)₃(η²-C≡C)] and [Co₂(μ-η²:η²:η₁-C¹:F¹:C¹:F¹:C¹)](PPh₃CH₂C≡CMes) have been obtained directly from the respective phosphanes and suitable metal salts, as has the bimetallic complex [[(HC≡CC≡CH₃P₃)(η²-P₃P₃)CH₂C≡CMes] (P₃P₃)CH₂C≡CMes]. In contrast, [Co(NO)(CO)(PPh₃CH₂C≡C)] and the ruthenium phthalocyaninato (PC₂) complex [Ru(PC₂)(PPh₃CH₂C≡C)] are obtained from the respective diphenylphosphane complexes, via in situ deprotonation (BuLi) and quenching with the appropriate propargyl bromide; [CoMo(x²-O,P-P(O)Mes*(CH₂C≡CH))] is similarly prepared, but without need for base. Finally, [W(CO)₅(PPh₃OMe)(H)Me(C≡CSiPr₃)] was obtained upon methanolysis of the putative phosphaalkene [W(CO)₅(P(Ph)=C≡CMe(C≡CSiPr₃))]. Notably, no complexes of the group 10 metals have been described, though the formally related diaphane-bridged complexes [L₅M(μ-η¹-η₁-P₃P₃CH₂C≡C₃CH₂P₃P₃)] (L₅M = Cl₅Pt, Cl₅Pt, Cl₅Pt).
(OC)₂Ni) have been reported, alongside examples with other metals (L₄M = AuCl, CpCo₂(CO)₅, CpFe(CO)₅, C₆FeBr(CO), CpMn(NO)(CO), CpMo(CO)₅(COCH₃), Mo(CO)₅). The intriguing tetrameric complex [{(η⁵-C₅Me₅)Mo(CO)₄}{(η⁵-P-P-P-P-}
Ph₃CH₂C≡CH₂PPh₃]₂[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 ambiphilic systems and molecular conductive and/or optoelectronically active molecules. In continuing these works, we have had cause to access propargyl phosphanes of the type R₃P(Ph₃C≡CPh)₂ (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(Ph₃C≡CPh)₂ (E = Si, Sn), which we describe herein, along with attempts to obtain (Et₂N)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 co-ordinately unsaturated metal centres.

Results and Discussion

Phosphane Synthesis

The silyl and stannyl chloropropargyl precursors R₃EC≡CH₂Cl were prepared following a modified literature procedure (Scheme 1), via the low-temperature (~78°C) lithiation of HC≡CH₂Cl, quenched with R₃SnCl (1 and 2) or R₃SiCl (3 – 7). The silanes were amenable to purification by reduced-pressure distillation, apart from the solid 7 (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 (δₛ = 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 methylenic resonances and respective group 14 centre in each case (¹H-X HMBHC, X = Sn; ²⁹Si); for the stannanes the ¹J(CH) coupling (~ 10 Hz) is also large enough to resolve tin satellites. The ¹⁳C(¹H)-NMR data are similarly consistent, while bulk purity was confirmed from microanalytical data. It is noted that ¹, ², ³⁰, ³² and ⁴³ 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 HPPPh₂ with ⁴BuLi) and the mixtures stirred overnight to afford the propargyl phosphanes Ph₃P(Ph₃C≡CPh)₂ (8 – 13, Scheme 1). Extraction with pentane afforded the phosphanes as viscous oils, the silyl derivatives 10 – 13 requiring no further purification. In contrast, stannanes formed in admixture with ⁴BuSn (4:1:4 of 8) or Ph₃BuSn (1:1 with 9), presumably due to metathesis of 1 and 2 with residual ⁴BuLi, as is 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 alkylic moieties exhibiting marginal change from those of the parent propargyls. Retention of the group 14 fragments is universally apparent (¹H-X HMBHC), with 8 and 9 also allowing for resolution of ¹²⁹Sn satellites (¹J(CH) ~ 14 Hz) in the ¹³C(¹H) spectra. The ¹³C(¹H) spectra of 8 and 9 indicate the presence of ⁴BuSn (δₛ = 119Sn ~ 120.0) and Ph₃BuSn (δₛ = 98.3) by-products respectively.

Attempts to vary the nature of the phosphanyl substituents met with limited success. Dicyclohexyl analogues failed to form, regenerating HC₆H₄, as the only phosphorus-containing product, which presumably reflects the greater basicity and steric bulk of ‘PC₆H₄’ (cf. ‘PPh₃’), favouring proton-abstraction from the chloropropargyls over Sn₂ 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, Me₂P(SiMe₃)₂(¹H)NMR data were consistent in admixture with P(SiMe₃)₂(4%) and a mono-silylphosphane (δₛ = 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 in generating ‘PhC=CH2MgCl’ under comparable conditions. However, our efforts to quench this reagent with (Et3N)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 (Et3N)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 (Et3N)2P moiety (δi 90.9; cf. PhP(NEt2)2 97.9,38 H2C=CH(C)(H)-P(NEt2)2 89.9%), the 1H NMR resonances integrating consistently against those for single equivalences of aromatic and methylenic fragments. However, the methylenic moiety is significantly deshielded (δi 4.72. δc 75.0) relative to both PhC=CH2Cl (δi 4.39, δc 31.2) and propargyl phosphines, and exhibits appreciably greater magnitude coupling to phosphorus (|JPh| = 7.1 Hz) than 8 – 14. The unsaturated carbon centres are also heavily deshielded (δi 137.4 (JPC 19.0 Hz) C12; 209.9 (JPC 11.3 Hz) C1), the latter in particular being more characteristic of an allenic, rather than alkynic centre; indeed, these data are in good agreement with those for the limited range of phosphinoallenes (Table 2) described previously.14,41 We thus confidently formulate 15 as (Et3N)2PCl(Ph)=C=CH2 (Scheme 2).

The reaction of propargyl Grignard reagents with R3PCl has been noted to afford mixtures that include alkenylphosphines, 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-allyl carbocation over its propargyl counterpart (localisation at a sp2, rather than sp3 centre) or be the result of conjugate addition, favoured by the relatively ‘soft’ CIP(NEt2)2 electrophile, 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 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 (Et3N)2Cl(Ph)=C=CH2 (16), as evidenced by the 1H NMR spectrum, which indicates loss of one diethy lamino moiety (Et3N 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 (δi 122; cf. PhCl(NEt2)PNET2 142.1%). Upon further treatment with HCl there is superficial evidence for removal of the remaining diethy lamino moiety, viz. loss of its 1H NMR resonances, and of diasterotopicity of the ‘=CH2’ protons (δi 8.9, JPhH 3 Hz). However, the 31P shift (δ3P 58.7, J31P 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 Propargylyphosphenes.**

As previously noted (vide supra) the coordination chemistry of propargylyphosphenes 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 propargylyphosphenes 8, 11 and 12 react with [PtCl2]2, as a suspension in CH2Cl2, to afford exclusively the complexes cis-[Pt(PhPCl(CH2C=CPh3)]2Cl2 (ER3 = ‘BuSn 17, ‘PrSi 18, ‘PbSi 19, Scheme 3) in excess of 75% isolated yield. For the silanes, palladium analogues (ER3 = ‘PrSi 20, ‘PbSi 21) are similarly obtained from [PdCl2]2, 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...
data, which verify the structural integrity of the ligands and coordination of the phosphorus centres ($\Delta \delta_\text{P} \sim +20$). For the platinum complexes 17 – 19, $|^{1}J_{\text{PP}}|$ values of ca 3600 Hz are wholly consistent with assignment of a cis geometry, while the palladium complexes exhibit virtual coupling in the $^{1}H$ and $^{13}C(\text{H})$-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 ($|^{1}J_{\text{PP}}|=2601$ Hz), consistent with trans-[Pt(PR$_2$)$_2$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 propargylyphosphinaphenes that feature tin and silicon termini on the alkyn moieties. Attempts to increase the range of phosphanyl termini used with palladium and platinum, adopting exclusively trans (Pd) or cis (Pt) geometries respectively, though the latter can be partially isomerised with propargyl Grignard reagents proved unsuccessful, but allowed for the generation of the novel allenylphosphine (Et$_3$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 phosphinophanes have been shown to form complexes [M(PPh$_3$CH$_2$CER$_2$Cl)$_2$] 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 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 HPPH$_2$ 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$_2$, PdCl$_4$) were obtained from STREM and used as supplied. HI(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 ($^{1}H$, 399.50 MHz; $^{13}C$, 100.46 MHz; $^{29}Si$, 79.37 MHz; $^{119}$Sn, 148.97 MHz; $^{195}$Pt, 85.53 MHz) or VNMRS 500 ($^{1}H$ 499.91 MHz; $^{13}C$, 125.72 MHz) spectrometer. All spectra were referenced to Me$_4$Si, 85% H$_2$PO$_4$, Me$_4$Sn or K$_2$PtCl$_6$ as appropriate. Carbon-13 NMR data were assigned with recourse to the 2D (HSQC, HMBC) spectra; detailed connectivity and $^{29}Si$ chemical shifts were assessed using $^{1}H$–X HMBC spectra ($X=^{29}Si$; $^{119}$Sn; $^{129}$P).

Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

Synthesis

$^6$Bu$_2$SnC=CCH$_3$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 $^6$BuLi (2.5 M, 6.0 cm$^3$, 1.5 x 10$^{-2}$ mol). The mixture was stirred for 30 min., after which time $^6$Bu$_2$SnCl (4.40 cm$^3$, 1.5 x 10$^{-2}$ mol) 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 HC≡CCH$_3$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 (CD$_2$Cl$_2$, 30°C): $^{1}H$-NMR: $\delta_{H}$ 0.91 (t, $^{3}J_{HH}$ 7.3 Hz, 9 H, C$_{3}$H$_{6}$), 0.97 (t, $^{3}J_{HH}$ 6 Hz, J$_{HH}$ 54 Hz, 6H, CH$_2$Sn), 1.34 (m, 6H, CH$_3$CH$_2$), 1.61 (m, 6H, CH$_3$CH$_2$Sn), 3.70 (s, $^{2}J_{HH}$ 58 Hz, 6H, C$_3$H$_7$). $^{13}C$($^1H$)-NMR: $\delta_{C}$ 11.3 (s, C$_2$H$_5$Sn), 1.14 (s, C$_{3}$H$_7$Sn), 365 Hz, $^{119}$Sn(C$_{3}$H$_7$Sn) 382 Hz, 13.9 (s, C$_2$H$_5$), 27.3 (s, C$_{3}$H$_7$Sn), 44 (s, C$_{3}$H$_7$Sn) 58 Hz, $^{129}$Sn(C$_{3}$H$_7$Sn) 60 Hz, 29.3 (s, CH$_2$CH$_2$), 32.1 (s, CH$_2$CH$_2$), 3.67 (s, $^{1}J_{HH}$ 10.5 Hz, 2H, CH$_2$Cl), 91.1 (s, C$_{3}$C=CH$_2$Cl), 105 (s, C$_{3}$C=CH$_2$Cl). $^{119}$Sn($^{1}H$)-NMR: $\delta_{Sn}$ = −65.1. Anal. Found: C, 49.44; H, 7.86. Calcd. for C$_6$H$_{22}$SnCl$_3$: C, 49.56; H, 8.04.

Ph$_5$SnC≡CCH$_3$Cl (2). As for 1, using propargyl chloride (2.03 g, 2.7 x 10$^{-2}$ mol), $^6$BuLi (2.5 M, 5.4 cm$^3$, 1.3 x 10$^{-2}$ mol) and Ph$_5$SnCl (5.25 g, 1.3 x 10$^{-2}$ mol). Isolated as yellow oil. Yield: 3.96 g, 72%. NMR (CD$_2$Cl$_2$, 30°C): $^{1}H$-NMR: $\delta_{H}$ 3.67 (s, $^{2}J_{HH}$ 10.5 Hz, 2H, CH$_2$Cl), 7.10 – 7.20 (m, 9H, mp-$^5$C$_{5}$H$_{11}$), 7.60 – 7.65 (m, $^{1}J_{HH}$ 55 Hz, 6H, o-$^5$C$_{6}$H$_{5}$). $^{13}C$($^1H$)-NMR: $\delta_{C}$ 30.8 (s, $^{3}J_{HH}$ 10 Hz, CH$_2$Cl), 88.5 (s, C$_{3}$=CCH$_2$Cl), 106.8 (s, C$_{3}$=CCH$_2$Cl), 128.8 (s, p-$^5$C$_{5}$H$_{11}$), 129.5 (s, m-$^5$C$_{5}$H$_{11}$), 130.1 (s, i-$^5$C$_{5}$H$_{11}$), 136.7 (s, o-$^5$C$_{6}$H$_{5}$). $^{119}$Sn($^{1}H$)-NMR: $\delta_{Sn}$ = −169.5. Anal. Found: C, 59.63; H, 4.12. Calcd. for C$_{20}$H$_{25}$SnCl$_3$: C, 59.55; H, 4.05.

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MePPhSiC=CCH₂Cl (3). As for 1, using propargyl chloride (3.73 g, 5.0 x 10⁻² mol), BuLi (2.5 M, 10.0 cm³, 2.5 x 10⁻² mol) and MePPhSiCl₂ (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 (CD₂Cl₂, 30°C): ¹H-NMR: δ = 3.21 (s, J = 7.2 Hz, 6 H, SiC₃H₃), 7.14 – 7.16 (m, 9 H, m-p-C₆H₄), 7.73 – 7.78 (m, 6 H, o-C₆H₄). ¹³C(CH₃)-NMR: δ = 133.3 (s, C₆H₄), 138.1 (s, C₆H₄), 143.4 (s, C₆H₄), 140.9 (s, C₆H₄), 138.4 (s, C₆H₄), 130.4 (s, C₆H₄), 133.4 (s, C₆H₄), 136.0 (s, C₆H₄). ²⁵Si(CH₃)-NMR: δ = -28.8. Anal. Found: C, 75.68; H, 5.11. Calcd. for C₂₃H₂⁺Cl₂Si: C, 75.77; H, 5.15.

Bu₅SnC≡CPh₂PPh₃ (8). To an ether solution (ca 20 cm³) of HPPPh₂ (0.375 g, 2.02 x 10⁻³ mol) held at -78 °C was added drop-wise BuLi (2.5 M, 0.808 cm³, 2.02 x 10⁻³ mol); the mixture was stirred for 30 min. A solution of (0.733 g, 2.02 x 10⁻³ mol) in ether (ca 10 cm³) 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: 800.0 g (4.188 SnBu₅). NMR (CD₂Cl₂, 30°C): ¹H-NMR: δ = 0.93 (m, CH₃), 1.36 (m, 12 H, 2 × CH₂), 1.58 (m, 6 H, CH₂), 2.87 (d, J = 1.6 Hz, J = 11.75 Hz, 8.7 Hz, J = 11.75 Hz, 12.4 Hz, 2H, CH₃P), 7.02 – 7.13 (m, 6 H, m-p-C₆H₄), 7.43 – 7.51 (m, 4 H, o-C₆H₄). ¹³C(CH₃)-NMR: δ = 11.3 (s, C₆H₅₂Ph), 136.6 Hz, 298 Hz, 383 Hz, 139.3 (s, CH₃), 20.4 (d, J = 18 Hz, CH₃PPh₂), 27.4 (s, CH₂C₆H₅), J = 853 Hz, 850.0 (d, J = 6 Hz, C₆H₅C₆H₄), 106.8 (d, J = 5 Hz, C₆H₅C₆H₄), 128.6 (d, J = 6 Hz, C₆H₅C₆H₄), 128.9 (s, p-C₆H₄), 133.2 (d, J = 19 Hz, o-C₆H₄), 138.8 (d, J = 17 Hz, i-C₆H₄). ³¹P(CH₃)-NMR: δ = -13.4 (s, J = 14.5 Hz). ¹¹Sn(CH₃)-NMR: δ = -68.5 (d, J = 14.5 Hz, 45.0), 120.0 (s, 15SnBu₅).

Ph₅PPh₅C≡CPh₂PPh₃ (9). As for 8, using HPPPh₂ (0.309 g, 1.66 x 10⁻³ mol), BuLi (2.1 M, 0.80 cm³, 1.66 x 10⁻³ mol) and 2 (0.876 g, 1.66 x 10⁻³ mol). Isolated as yellow oil. NMR (CD₂Cl₂, 30°C): ¹H-NMR: δ = 2.84 (d, J = 3.0 Hz, J = 14.8 Hz, 2H, CH₃P), 6.89 – 7.20 (m, m-p-C₆H₄), 7.37 – 7.70 (m, Ar, m-p-C₆H₄), ¹³C(CH₃)-NMR: δ = 20.2 (d, J = 21 Hz, J = 11.75 Hz, 19 Hz, CH₃P), 82.8 (d, J = 6 Hz, 3J = 4.3 Hz, C₆H₅C₆H₄), 109.3 (d, J = 3.4 Hz, C₆H₅C₆H₄), 133.2 (d, 13C, 19 Hz, o-C₆H₄), 138.8 (d, J = 17 Hz, i-C₆H₄). ³¹P(CH₃)-NMR: δ = -13.2 (s, J = 14.5 Hz). ¹¹Sn(CH₃)-NMR: δ = -168.4 (J = 14.5 Hz, 15n), -98.3 (s, Bu₅SnPh₅, 15n).

MePPhSiC≡CCH₂Cl (10). As for 8, using HPPPh₂ (0.780 g, 4.2 x 10⁻³ mol), BuLi (2.5 M, 1.7 cm³, 4.24 x 10⁻³ mol) and 3 (0.884 g, 4.24 x 10⁻³ mol). Isolated as brown oil. Yield: 1.19 g, 78%. NMR (CD₂Cl₂, 30°C): ¹H-NMR: δ = 0.30 (m, 6 H, SiC₃H₃), 2.75 (d, J = 2.9 Hz, 2H, CH₂P), 7.01 – 7.09 (m, m-p-C₆H₄), 7.17 – 7.22 (m, 4 H, o-p-C₆H₄), 7.39 – 7.46 (m, 3 H, m-p-C₆H₄), 7.52 – 7.58 (m, 2 H, o-SiC₃H₃). ¹³C(CH₃)-NMR: δ = -0.6 (s, Si(CH₃)₂), 18.9 (d, J = 21 Hz, CH₃P), 85.7 (d, J = 5 Hz, C₆H₅C₆H₄), 104.9 (d, J = 4 H, C₆H₅C₆H₄), 128.7 (d, J = 6.5 Hz, m-C₆H₄), 129.0 (s, p-C₆H₄), 129.5 (s, p-C₆H₄), 133.2 (d, J = 19.5 Hz, o-C₆H₄), 134.2 (s, o-C₆H₄), 137.7 (s, i-C₆H₄), 138.1 (d, J = 16 Hz, i-C₆H₄). ³¹P(CH₃)-NMR: δ = -13.5 (s). ¹¹Sn(CH₃)-NMR: δ = -22.9. Anal. Found: C, 76.89; H, 6.34. Calcd. for C₂₃H₂⁺Cl₂Si: C, 77.06; H, 6.47.

Pr₅SiC≡CPh₂PPh₃ (11). As for 8, using HPPPh₂ (0.870 g, 4.24 x 10⁻³ mol), BuLi (2.5 M, 1.7 cm³, 4.24 x 10⁻³ mol) and 4 (0.976 g, 4.24 x 10⁻³ mol). Isolated as orange oil. Yield: 1.45 g, 90%. NMR (CD₂Cl₂, 30°C): ¹H-NMR: δ = 1.01 (m, 3H, SiCH₃), 1.09 (d, J = 6.8 Hz, 18H, CH₃), 1.75 (d, J = 2.3 Hz, 2H, CH₂P), 7.02 – 7.12 (m, 6 H, m-p-C₆H₄), 7.39 – 7.47 (m, 4 H, o-p-C₆H₄). ¹³C(CH₃)-NMR: δ = 11.7 (s, Si(CH₃)₂), 1.89 (s, J = 15.9 Hz, CH₃), 19.9 (d, J = 15.5 Hz, CH₃P), 83.3 (d, J = 5 Hz, C₆H₅C₆H₄), 104.7 (d, J = 4 Hz, m-C₆H₄), 128.7 (d, J = 6.5 Hz, m-C₆H₄), 129.0 (s, p-C₆H₄), 133.1 (d, J = 19 Hz, o-C₆H₄), 138.3 (d, J = 16 Hz, i-C₆H₄). ³¹P(CH₃)-NMR: δ = -13.5 (s, J = 20 Hz). ¹¹Sn(CH₃)-NMR: δ = -3.03. Anal. Found: C, 75.77; H, 8.64. Calcd. for C₂₃H₂⁺Cl₂Si: C, 75.74; H, 8.74.
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 (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 0.89 (d, $^1$J$_{HH}$ 7.0 Hz, 12H, CH$_3$), 3.05 (q, $^1$J$_{HH}$ 7.0 Hz, 8H, CH$_2$), 4.69 (d, $^1$J$_{HH}$ 7.0 Hz, =CH$_2$), 7.11 – 7.15 (m, 3H, m-Pr$_2$C$_6$H$_4$), 7.63 – 7.59 (m, 2H, o-C$_6$H$_4$). $^{13}$C($^1$H)-NMR: $\delta_2$ 14.8 (d, $^1$J$_{CH}$ 3.2 Hz, CH$_3$), 43.4 (d, $^1$J$_{CH}$ 17.4 Hz, NCH$_2$), 75.0 (s, =CH$_2$), 105.9 (d, $^1$J$_{CH}$ 13.5 Hz, i-C$_6$H$_3$), 137.4 (d, $^3$J$_{CH}$ 19 Hz, PhC$_6$(N$_2$)$_2$=C=), 127.8 (s, o-C$_6$H$_4$), 127.9 (overlapped m-|p-|C$_6$H$_4$), 209.9 (d, $^3$J$_{CP}$ 11.4 Hz, =Ce). $^{31}$P($^1$H)-NMR: $\delta_3$ 140.0 (d, $^3$J$_{CP}$ 5 Hz, CH$_3$), 19.8 (m, CH$_2$), 42.8 (d, $^3$J$_{CP}$ 17 Hz, NCH$_2$), 81.5 (s, C$_3$C$_2$C$_6$H$_4$), 87.6 (s, C$_6$C$_2$C$_6$H$_4$). $^{31}$P($^1$P)-NMR: $\delta_5$ 83.2 (s, br, 5%).  

$^{1}$(Et$_3$N)$_4$CIP$_2$(Ph)=C(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, $^1$J$_{HH}$ 6.9 Hz, 6H, CH$_3$), 2.94 (q, $^1$J$_{HH}$ 4.7 Hz, 4H, CH$_2$) 4.89 (dd, $^1$J$_{HH}$ 13.0 Hz, 5.7 Hz, 1H, =CH$_2$), 4.93 (dd, $^1$J$_{HH}$ 13.0 Hz, 5.7 Hz, 1H, =CH$_2$) 6.94 – 7.02 (m, 1H, p-|C$_6$H$_4$), 7.11 (7, $^1$J$_{HH}$ 7.8 Hz, 2H, m- C$_6$H$_4$), 7.50 (d, $^1$J$_{HH}$ 7.8 Hz, 2H, o-C$_6$H$_4$). $^{13}$C($^1$H)-NMR: $\delta_2$ 13.9 (d, $^1$J$_{HH}$ 6.2 Hz, CH$_3$), 43.9 (d, $^1$J$_{HH}$ 13 Hz, NCH$_2$), 77.6 (s, =CH$_2$), 105.3 (d, $^3$J$_{CP}$ 40 Hz, PhC$_6$(N$_2$)$_2$=C=), 135.4 (d, $^3$J$_{CP}$ 24 Hz, i-C$_6$H$_3$), 127.6 (d, $^3$J$_{CP}$ 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$_{CP}$ 8.4 Hz, =Ce). $^{31}$P($^1$P)-NMR: $\delta_3$ 13.0 (s, br, 77%).

**Platinum and palladium complexes.** In a typical procedure, to a suspension of the [MCl$_3$]$_4$ (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(PPh$_3$)$_2$C$_6$H$_4$]Cl$_2$ (17). Yield: 78%. NMR (CD$_2$Cl$_2$, 30°C): $^1$H-NMR: $\delta_1$ 0.81 (m, 12H, SnC$_6$H$_4$), 0.88 (m, 18H, CH$_2$), 1.27 (m, 12H, CH$_2$), 1.44 (m, 12H, CH$_2$), 3.78 (m, $^3$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: $\delta_2$ 11.1 (s, C$_3$Sn, $^1$J$^1$$_{HH}$ 365 Hz, $^1$J$^2$$_{HH}$ 381 Hz, 13.9 (s), CH$_2$, 23.8 (d, $^3$J$_{HH}$ 27 Hz, CH$_2$P$_3$H$_4$), 27.4 (s, C$_3$SnC$_6$H$_4$, $^1$J$^1$$_{HH}$ 588, $^1$J$^2$$_{HH}$ 60.7 Hz, 29.2 (s, $^3$J$_{HH}$ 10 Hz, CH$_2$), 6.87 (m, C$_3$C$_2$C$_6$H$_4$P$_3$H$_4$), 104.0 (m, C$_3$C$_6$C$_2$H$_4$P$_3$H$_4$), 127.9 (br, m- |p-|C$_6$H$_4$), 129.9 (s, m-|p-|C$_6$H$_4$), 131.1 (s, m-|p-|C$_6$H$_4$), 134.4 (m, o- |p-|C$_6$H$_4$). $^{31}$P($^1$H)-NMR: $\delta_3$ 6.0 (s, $^3$J$_{CP}$ 3618 Hz). $^{119}$Sn($^1$H)-NMR: $\delta_4$ = -68.2 (m). $^{195}$Pt($^1$H)-NMR: $\delta_8$ = -4407 (t, $^3$J$_{CP}$ 3618 Hz). Anal. Found: C, 50.23; H, 5.95. Calcd. for C$_2$H$_9$Cl$_2$Pt$_2$Sn$_2$: C, 50.18; H, 6.08.

$cis$-[Pt(PPh$_3$)$_2$C$_6$H$_4$CSi$_3$(C$_6$H$_4$)$_2$] (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, SiC$_6$H$_4$), 0.93 (d,
cis-[Pt(PPh3)2Cl2CSiPr3]2Cl (19). Yield: 78%. NMR (C6D6, 30°C): 1H-NMR: δi 0.41 (m, 12H, SiCH3), 0.93 (t, JHe 7.2 Hz, 18H, CH3), 1.23 (m, 12H, CH2SiCH3), 3.81 (d, JHe 10.8 Hz, 4H, CH2P), 6.86 – 6.93 (m, 8H, m-P(C6H4)3), 6.94 – 7.00 (m, 4H, o-P(C6H4)3), 7.54 – 7.62 (m, 8H, o-P(C6H4)3). 13C{1H}-NMR: δs 16.3 (s, CH2Si, JHe 55 Hz), 17.8 (s, CH3), 18.5 (s, CH2SiCH3, JHe 7.4 Hz), 23.9 (d, JHe 46 Hz, CH2P), 88.0 (m, C6CCH2Cl), 101.4 (m, C6CCH2P), 128.2 (m, m-C6H4), 129.0 (m, p-C6H4), 131.1 (s, o-C6H4), 134.3 (m, i-C6H4). 31P{1H}-NMR: δp 5.83 (s, JHeP 3614 Hz).

trans-[Pt(PPh3)2Cl2CSiPr3]2Cl (20). Yield: 88%. NMR (C6D6, 30°C): 1H-NMR: δi 0.90 (m, 6H, SiCH3), 0.97 (d, JHe 6.7 Hz, 36H, CH3), 3.74 (t, JHe 3.9 Hz, 2H, CH2P), 7.05 – 7.11 (m, 12H, m-P(C6H4)3), 7.92 – 7.98 (m, 8H, o-P(C6H4)3). 13C{1H}-NMR: δs 11.6 (s, SiCH3), 18.8 (s, CH3), 18.9 (s, CH2Si, JHe 13.6 Hz, CH2P), 45.8 (d, JHe 2.9 Hz, C6CCH2Cl), 101.3 (d, JHe 5.6 Hz, C6CCH2P), 128.0 (m, m-C6H4), 129.3 (t, JHe 24 Hz, i-C6H4), 130.9 (s, p-C6H4), 134.6 (t, JHe 6 Hz, o-C6H4). 31P{1H}-NMR: δp 16.0 (s). 25Si{1H}-NMR: δs 2.75. Anal. Found: C, 61.07; H, 6.94. Calcld. for C48H66Cl2P2Si3: C, 61.43; H, 7.09.

cis/trans isomerisation of [Pt(PPh3)2Cl2CSiPr3]2Cl (19). In a borosilicate NMR tube was placed cis-19 as solution in C6D6. 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 (C6D6, 30°C): 1H-NMR: δi 0.46 (m, 12H, SiCH3), 0.92 (t, JHe 7.3 Hz, 18H, CH3), 1.25 (m, 12CH, CH2SiCH3), 3.77 (t, JHe 4.3 Hz, 4H, CH2P), 7.03 – 7.13 (m, 12H, m-P(C6H4)3), 7.95 – 8.01 (m, 8H, o-P(C6H4)3). 13C{1H}-NMR: δs 16.4 (s, CH2Si), 17.8 (s, CH3), 18.5 (s, CH2SiCH3), 23.8 (t, JHe 24 Hz, CH2P), 88.0 (m, C6CCH2Cl), 101.4 (t, JHe 6.3 Hz, C6CCH2P), 128.2 (m, m-C6H4), 128.8 (s, p-C6H4), 130.9 (s, o-C6H4), 134.7 (t, JHe 6.0 Hz, i-C6H4). 31P{1H}-NMR: δp 11.5 (s, JHeP 2601 Hz). 25Si{1H}-NMR: δs 13.2. 195Pt{1H}-NMR: δp 3939 (t, JHeP 2601 Hz).

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Notes and references
† DBP = dibenzophosphole
§ 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. Berndt, R. Veillard, C. Alayrac, A.-C. Gaumont, Molecules, 2012, 17, 14573-14587.
Synopsis – for table of contents use only

The propargyl phosphanes Ph₂PCH₂C≡CER₃ (R₃E = nBu₃Sn, Ph₃Sn, Me₂PhSi, Pr₃Si, nBu₂Si) 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.