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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 $R_3EC\equiv CCH_2Cl$ ($R_3E = Bu_3Sn, Ph_3Sn, Me_2PhSi, ^iPr_3Si, ^nPr_3Si, ^nBu_3Si$), obtained by a modified literature procedure, react with $LiPPh_2$ to afford the novel propargyl phosphanes $Ph_2PCH_2C\equiv CER_3$ in high yield, as viscous oils; $(Me_3Si)_2PCH_2C\equiv CSiPhMe_2$ is similarly obtained from $LiP(SiMe_3)_2$. In contrast, the reaction of $PhC\equiv CCH_2MgCl$ with $CIP(NEt_2)_2$ fails to produce a comparable propargyl phosphane, but generates preferentially (>70%) the novel phosphinoallene $(Et_2N)_2PC(Ph)=C=CH_2$, 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.

Introduction

Tertiary phosphanes are both ubiquitous and innumerable, being the subject of exhaustive efforts to control steric and electronic profiles through substituent modification, driven by their utility as ligands. The opportunities to impose steric bulk and/or asymmetry within the metal coordination sphere offer particular impetus, typically directed toward symmetric R_3P and chiral PRR'R'' derivatives respectively. Equally important are derivatives of the type R_2PR' ($R = aryl, alkyl$) that occupy the intermediate ground, allowing for subtle variation of sterics and electronics (variation of R'), while also imposing some level of asymmetry about the metal. Moreover, the ready availability of R_2PX ($X = halide, H$) renders a convenient scaffold with which to investigate more elaborate and functional substituents (R').

Despite prolific levels of activity in phosphane synthesis,¹ particularly systems of the type R_2PR' , surprising oversights remain, a case in point being the dearth of systems bearing a propargylic substituent (viz. $CH_2C\equiv CR'$). Indeed, while alkynyl phosphanes are common,² their propargyl counterparts are limited to $R_2PCH_2C\equiv CR'$ ($R = Ph, R' = H, ^3Me, ^4Ph; ^5R = Cy, ^iPr, R' = H, SiMe_3; ^6$), typically isolated as stabilised BH_3 adducts, $R_2PCH\{OSiMe_3\}C\equiv CPh$ ($R = Ph, Et$),⁷ $\{(Me_3Si)_2N\}RPCH_2C\equiv CSiMe_3$ ($R = Ph, ^8Et, ^8Cl^9$), the diphosphane $Ph_2PCH_2C\equiv CCH_2PPh_2$,¹⁰ and the bis-propargylphosphanes $RP\{CH_2C\equiv CR'\}_2$ ($R = Np, R' = H, SiMe_3; ^{11}R = CH_2CMe_2Et, R' = H; ^{11}R = Ph, R' = ^nBu; ^{12}R = Mes, R' = SiMe_3; ^{13}$), which are typically putative intermediates in the synthesis of macrocycles. The primary propargyl phosphane $H_2PCH_2C\equiv CH$ has also been reported.¹⁴

This lack of activity is surprising given continued interest in developing polyfunctional phosphorus-containing molecules, driven by their utility as ligands, optoelectronically active π -conjugates¹⁵ and, topically, frustrated Lewis pairs (FLPs).¹⁶ 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 - P, π - $C\equiv C$) bridging mode has been described for $[Cp_2Rh_2(CO)(\mu-\eta^1:\eta^1-CF_3C_2CF_3)\{PPh_2CH_2C\equiv CMe\}CO_2(CO)_6]$, obtained by reaction of $[Co_2(CO)_8]$ with the dirhodium complex $[Cp_2Rh_2(CO)(\mu-\eta^1:\eta^1-CF_3C_2CF_3)\{PPh_2CH_2C\equiv CMe\}]$.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, $[M(CO)_5(PR_2C\equiv CH)]$ ($M = Mo, R = Ph, ^{17}DBP; ^{18,\ddagger}Cr, ^{19}R = Ph, SiMe_3$), $[Mo(CO)_3(PH_2CH_2C\equiv CH)_3]$, $[Mo(CO)_4(PH_2C\equiv CH)^{20}]$ and $[Cp^RMn(CO)_2(PPh_{3-n}(CH_2C\equiv CH)_n)]$ ($Cp^R = Cp, n = 1, 2; Cp^R = Cp^{Me}, n = 1$).¹⁹ have been obtained directly from the respective phosphanes and suitable metal salts, as has the bimetallic complex $\{[HC\equiv CCH_2PPh_2]Ru(CO)_3(\mu-PPh_2)Co(CO)_3\}$.²¹ In contrast, $[Co(NO)(CO)(PPh_2CH_2C\equiv CH)_2]$ ²² and the ruthenium phthalocyaninato (Pc^{2-}) complex $[Ru(Pc)(PPh_2CH_2C\equiv CCH_3)_2]$ ²³ are obtained from the respective diphenylphosphane complexes, via *in situ* deprotonation ($BuLi$) and quenching with the appropriate propargylic bromide; $[CpMo\{\kappa^2-O, P-O\}Mes^*(CH_2C\equiv CH)]$ is similarly prepared, but without need for base.²⁴ Finally, $[W(CO)_5\{PPh(OMe)C(H)Me(C\equiv CSi^iPr_3)\}]$ was obtained upon methanolysis of the putative phosphalkene $[W(CO)_5\{P(Ph)=CMe(C\equiv CSi^iPr_3)\}]$.²⁵

Notably, no complexes of the group 10 metals have been described, though the formally related diphosphane-bridged complexes $[L_nM\{\mu-\eta^1:\eta^1-PPh_2CH_2C\equiv CCH_2PPh_2\}_2]$ ($L_nM = Cl_2Pt,$

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[†]Electronic Supplementary Information (ESI) available: Representative NMR spectra for compounds **8**, **15** and **16**, in lieu of bulk elemental analysis data. See DOI: 10.1039/x0xx00000x

(OC)₂Ni) have been reported,²⁶ alongside examples with other metals (L_nM = AuCl, CpCoI₂, CpFe(CO)₂⁺, CpFeBr(CO), CpMn(NO)(CO), CpMo(CO)₂(COCH₃),²⁶ Mo(CO)₄²⁷). The intriguing tetrameric complex [$\{\eta^2\text{-C,C-Mo(CO)}_4(\eta^2\text{-P,P-PPH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{PPh}_3)\}_3\text{Mo(CO)}$], has also been described.²⁷

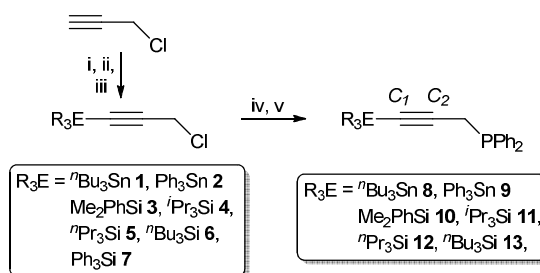
We have recently been interested in the synthesis and study of reactive and functional phosphanes²⁸ and organometallic phosphacarbonyls,²⁹ with the goal of developing novel ambiphilic systems^{28c} and molecular conductive and/or optoelectronically active molecules.^{29b} In continuing these works, we have had cause to access propargyl phosphanes of the type R₂P(CH₂C≡CER'₃) (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.* Ph₂P(CH₂C≡CER'₃) (E = Si, Sn), which we describe herein, along with attempts to obtain '(Et₂N)₂P' 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

Phosphane Synthesis

The silyl and stannyl chloropropargyl precursors R₃EC≡CCH₂Cl were prepared following a modified literature procedure (Scheme 1),³⁰ *via* the low-temperature (−78°C) lithiation of HC≡CCH₂Cl, 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 case, 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 (δ_H 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 HMBC; X = ¹¹⁹Sn, ²⁹Si); for the stannanes the ⁴J_{SnH} 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**,³¹ **2**,^{30,31} **3**³² and **4**³³ 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 ⁿBuLi) and the mixtures stirred overnight to afford the propargyl phosphanes Ph₂P(CH₂C≡CER'₃) (**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 ⁿBu₄Sn (1:4 of **8**) or Ph₃ⁿBuSn (1:1 with **9**), presumably due to metathesis of **1** and **2** with residual



Scheme 1: Reagents and Conditions: i) ⁿBuLi, −78°C, Et₂O, 30 min.; ii) R₃ECl, −78°C, 30 min.; iii) warm to ambient, stir 18 h.; iv) LiPPh₂, −78°C, Et₂O, 30 min; v) r.t. 18 h.

Table 1 Selected NMR spectroscopic data for propargylphosphanes **8** – **14**.^a

	δ _p	δ _H (CH ₂)[J _{PH}] ^b	δ _C (C ₁)	δ _C (C ₂)	δ _E (E)
8	−13.4	2.87 [1.6]	85.0	107.0	−68.4 [¹¹⁹ Sn]
9	−13.2	2.84 [3.0]	82.8	109.0	−168.4 [¹¹⁹ Sn]
10	−13.5	2.76 [2.9]	84.7	105.0	−22.9 [²⁹ Si]
11	−13.5	2.75 [2.3]	83.3	105.0	−3.03 [²⁹ Si]
12	−13.6	2.76 [2.5]	85.4	103.0	−14.5 [²⁹ Si]
13	−13.5	2.76 [2.3]	85.5	104.0	−12.9 [²⁹ Si]
14	−158.9	2.43 [1.3]	83.3	109.3	−22.8; 3.7 [²⁹ Si]

^aAs C₆D₆ solutions; ^bcouplings in Hz

ⁿBuLi, as is common among Sn(IV) organyls.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 (¹H-X HMBC), with **8** and **9** also allowing for resolution of ¹¹⁹Sn satellites (⁴J_{SnP} ~ 14 Hz) in the ³¹P{¹H} spectra. The ¹¹⁹Sn spectra of **8** and **9** indicate the presence of ⁿBu₄Sn (δ_{Sn} −12.0)³⁵ and Ph₃SnⁿBu (δ_{Sn} −98.3)³⁶ 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 'PCy₂' (*cf.* 'PPh₂'), favouring proton-abstraction from the chloropropargyls over S_N2 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, Me₂PhSiC≡CCH₂P(SiMe₃)₂ (**14**) was obtained as the primary product (92% by ³¹P{¹H}-NMR) in admixture with P(SiMe₃)₃ (4%) and a mono-silylphosphane (δ_p −84.4; 4%), which presumably result from disproportionation; indeed, the bulk composition is consistent with that of **14**.

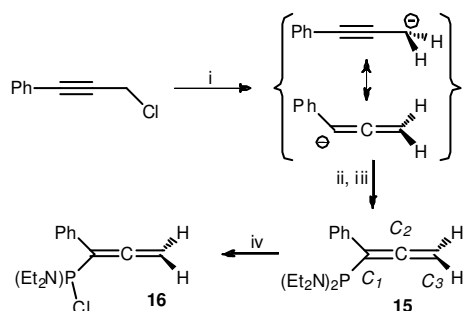
Given these difficulties, the generation of propargyl Grignard reagents from **1** to **7** was considered as an alternative approach; however, these reactions proved unreliable, presumably reflecting diminished reactivity of the halide in comparison to organo-propargyl derivatives. Indeed, though

less favoured than their bromide analogues, propargyl chlorides have been shown to form Grignard reagents,³⁷ and we encountered no difficulty in generating 'PhC≡CCH₂MgCl' under comparable conditions. However, our efforts to quench this reagent with (Et₂N)₂PdCl led to an unexpected outcome.

Formation of a phosphino-allene. The addition of freshly prepared 'PhC≡CCH₂MgCl' to a cooled (−78 °C) THF solution of (Et₂N)₂PdCl 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 '(Et₂N)₂P' moiety (δ_p 90.9; cf. PhP(NEt₂)₂ 97.9,³⁸ H₂C=C(H)-P(NEt₂)₂ 89.9³⁹), the ¹H NMR resonances integrating consistently against those for single equivalences of aromatic and methylenic fragments. However, the methylenic moiety is significantly deshielded (δ_H 4.72. δ_C 75.0) relative to both PhC≡CCH₂Cl (δ_H 4.39, δ_C 31.2) and propargyl phosphanes, and exhibits appreciably greater magnitude coupling to phosphorus (|J_{PH}| = 7.1 Hz) than **8** – **14**. The unsaturated carbon centres are also heavily deshielded (δ_C 137.4 (J_{PC} 19.0 Hz) C₁; 209.9 (J_{PC} 11.3 Hz) C₂), the latter in particular being more characteristic of an allenic,⁴⁰ rather than alkyne centre; indeed, these data are in good agreement with those for the limited range of phosphinoallenes⁵ (Table 2) described previously.^{14,41} We thus confidently formulate **15** as (Et₂N)₂PC(Ph)=C=CH₂ (Scheme 2).

The reaction of propargyl Grignard reagents with R₂PdCl has been noted to afford mixtures that include allenylphosphanes, their proportion being dependent on the nature of 'R'.⁴² However, this is to our knowledge the first example of an allenylphosphane 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(NEt₂)₂ electrophile, as compared, for instance, with the notionally 'harder' PdCl₂, with which we encountered significantly greater complexity, yielding a largely intractable mixture.

In order to confirm or dismiss the presence of Cl₂PC(Ph)=C=CH₂ within this mixture, we sought to prepare an authentic sample, treating **15** with HCl (2 equiv.). This effected



Scheme 2. Reagents and conditions: i) Et₂O, HgCl₂ (5 mol%), Mg, Δ, 4h.; ii) (Et₂N)₂PdCl, −78°C, 30 min; iii) r.t. 18 h.; iv) MeI/Et₂O; v) 2 equiv. HCl/Et₂O.

Table 2 Selected ¹H and ¹³C(¹H)-NMR data for precedent phosphinoallenes.^{a,b}

	δ _H (=CH ₂)	δ _C (=CH ₂)	δ _C (=C=)
Mes(H)PC(Me)=C=CH ₂	4.40	71.12	208.0
Mes(Me)PC(Me)=C=CH ₂	4.64	73.26	204.9
Mes(Me ₂ Si)PC(Me)=C=CH ₂	4.55	72.35	206.4
Mes(Cl)PC(Me)=C=CH ₂	4.57	74.65	205.5
Ph ₂ PC(H)=C=CH ₂	-	71.7	213.2
Ph ₂ PC(Me)=C=CH ₂	-	70.7	210.3
Ph ₂ PC(H)=C=C(Me) ₂	-	-	209.6

^achemical shifts in ppm. ^bdata sourced from references 14 and 41.

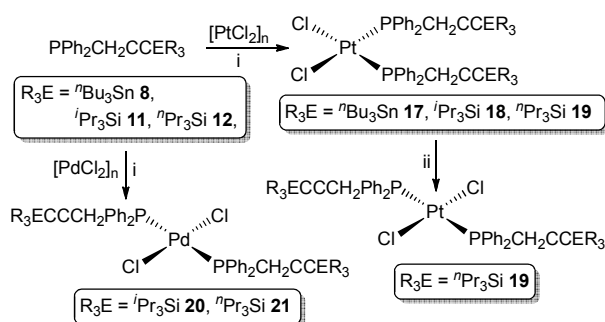
quantitative conversion to (Et₂N)(Cl)PC(Ph)=C=CH₂ (**16**), as evidenced by the ¹H NMR spectrum, which indicates loss of one diethylamino moiety (Et₂N vs Ph resonances) and emergence of diastereotopicity for the methylenic '=CH₂'. The phosphorus resonance of **16** is appreciably deshielded from that of **15**, consistent with replacement of NEt₂ by Cl (δ_p 122; cf. Ph(Cl)PNEt₂ 142.1⁴³). Upon further treatment with HCl there is superficial evidence for removal of the remaining diethylamino moiety, *viz.* loss of its ¹H NMR resonances, and of diastereotopicity of the '=CH₂' protons (δ_H 4.63, d, J_{PH} 3 Hz). However, the ³¹P shift (δ_p 58.7, t, J_{PH} 3 Hz) seems inconsistent with a species of the type R₂PCl₂; 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 Propargylphosphanes.

As previously noted (*vide supra*) the coordination chemistry of propargylphosphanes 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 propargylphosphanes **8**, **11** and **12** react with [PtCl₂]_n, as a suspension in CH₂Cl₂, to afford exclusively the complexes *cis*-[Pt{PPh₂(CH₂C≡CER₃)₂Cl₂] (ER₃ = ⁿBu₃Sn **17**, ⁱPr₃Si **18**, ⁿPr₃Si **19**, Scheme 3) in excess of 75% isolated yield. For the silanes, palladium analogues (ER₃ = ⁱPr₃Si **20**, ⁿPr₃Si **21**) are similarly obtained from [PdCl₂]_n, 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



Scheme 3. Reagents and conditions: i) CH₂Cl₂, 12 h.; ii) C₆D₆, h ν, 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**, $|^1J_{PtP}|$ 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 $^{13}C\{^1H\}$ -NMR resonances associated with the CH_2P 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 ($|^1J_{PtP}| = 2601$ Hz), consistent with *trans*-[Pt(PR₃)₂X₂], and ii) manifestation of virtual coupling for the CH_2P 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 propargylphosphanes that feature tin and silicon termini on the alkyne moiety. Attempts to increase the range of phosphanyl termini used *via* the reaction of R₂PCl with propargyl Grignard reagents proved unsuccessful, but allowed for the generation of the novel allenylphosphine (Et₂N)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 phosphanes have been shown to form complexes [M(PPh₂CH₂C≡CER₃)₂Cl₂] 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 (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. ⁿBuLi (2.5 M in hexanes) was obtained from Sigma-Aldrich and titrated to establish concentration. Precious metal salts (PtCl₂, PdCl₂) were obtained from STREM and used as supplied. HP(SiMe₃)₂ was prepared by literature procedure.⁴⁴ 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; ^{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 Me₄Si, 85% H₃PO₄, Me₄Sn or K₂PtCl₆ 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 1H -X HMBC spectra (X = ^{29}Si ; ^{119}Sn ; ^{31}P). Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

Synthesis

Bu₃SnC≡CCH₂Cl (1). In a modification of literature procedure, a solution of propargyl chloride (2.24 g, 3.0 × 10⁻² mol) in THF (ca 20 cm³) was cooled to -78°C before the drop-wise addition of ⁿBuLi (2.5 M, 6.0 cm³, 1.5 × 10⁻² mol). The mixture was stirred for 30 min., after which time ⁿBu₃SnCl (4.40 cm³, 1.5 × 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 HC≡CCH₂Cl 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 (C₆D₆, 30°C): 1H -NMR: δ_H 0.91 (t, $^3J_{HH}$ 7.3 Hz, 9 H, CH₃), 0.97 (t, $^3J_{HH}$ 6 Hz, J_{SnH} 54 Hz, 6H, CH₂Sn), 1.34 (m, 6H, CH₃CH₂), 1.61 (m, 6H, CH₂CH₂Sn), 3.70 (s, J_{SnH} 9.6 Hz, 2H, CH₂Cl). $^{13}C\{^1H\}$ -NMR: δ_C 11.3 (s, $\underline{CH_2}Sn$, $^1J_{117SnC}$ 365 Hz, $^1J_{119SnC}$ 382 Hz), 13.9 (s, $\underline{CH_3}$), 27.3 (s, $\underline{CH_2}CH_2Sn$, $^2J_{117SnC}$ 58 Hz, $^2J_{119SnC}$ 60 Hz), 29.3 (s, CH₃ $\underline{CH_2}$, $^3J_{SnC}$ 24 Hz), 31.2 (s, J_{SnC} 8 Hz, CH₂Cl), 91.1 (s, $\underline{C=C}CH_2Cl$), 105 (s, $C\equiv\underline{C}CH_2Cl$). $^{119}Sn\{^1H\}$ -NMR: δ_{Sn} -65.1. Anal. Found: C, 49.44; H, 7.86. Calcd. for C₁₅H₂₉ClSn: C, 49.56; H, 8.04.

Ph₃SnC≡CCH₂Cl (2). As for **1**, using propargyl chloride (2.03 g, 2.7 × 10⁻² mol), ⁿBuLi (2.5 M, 5.4 cm³, 1.3 × 10⁻² mol) and Ph₃SnCl (5.25 g, 1.3 × 10⁻² mol). Isolated as yellow oil. Yield: 3.96 g, 72%. NMR (C₆D₆, 30°C): 1H -NMR: δ_H 3.67 (s, J_{SnH} 10.5 Hz, 2H, CH₂Cl), 7.10 – 7.20 (m, 9H, *m/p*-C₆H₅), 7.60 – 7.65 (m, J_{SnH} 55 Hz, 6H, *o*-C₆H₅). $^{13}C\{^1H\}$ -NMR: δ_C 30.8 (s, J_{SnC} 10 Hz, CH₂Cl), 88.5 (s, $\underline{C=C}CH_2Cl$), 106.8 (s, $C\equiv\underline{C}CH_2Cl$), 128.8 (s, *p*-C₆H₅), 129.5 (s, *m*-C₆H₅), 130.1 (s, *i*-C₆H₅), 136.7 (s, *o*-C₆H₅). $^{119}Sn\{^1H\}$ -NMR: δ_{Sn} -169.5. Anal. Found: C, 59.63; H, 4.12. Calcd. for C₂₀H₁₇ClSn: C, 59.55; H, 4.05.

Me₂PhSiC≡CCH₂Cl (3). As for **1**, using propargyl chloride (3.73 g, 5.0 × 10⁻² mol), ⁿBuLi (2.5 M, 10.0 cm³, 2.5 × 10⁻² mol) and Me₂PhSiCl (4.26 g, 2.5 × 10⁻² mol). The crude product was distilled at 66 °C, 8.1 × 10⁻¹ mbar to afford colourless oil. Yield: 4.98 g, 96%. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 0.32 (s, J_{SiH} 8 Hz, 6 H, SiCH₃), 3.21 (s, 2H, CH₂Cl), 7.14 – 7.18 (m, 3H, *m/p*-C₆H₅), 7.55 – 7.59 (m, 2H, *o*-C₆H₅). ¹³C{¹H}-NMR: δ_C -1.2 (s, SiCH₃, ¹J_{SiC} 58 Hz), 30.5 (s, CH₂Cl), 90.1 (s, C=CCH₂Cl), 102.0 (s, C≡CCH₂Cl). ²⁹Si{¹H}-NMR: δ_{Si} -21.6. Anal. Found: C, 63.18; H, 6.14. Calcd. for C₁₁H₁₃ClSi: C, 63.29; H, 6.28.

Pr₃SiC≡CCH₂Cl (4). As for **1**, using propargyl chloride (6.24 g, 8.4 × 10⁻² mol), ⁿBuLi (2.5 M, 16.8 cm³, 4.2 × 10⁻² mol) and Pr₃SiCl (8.06 g, 4.2 × 10⁻² mol). The crude product was distilled at 52 °C, 3.0 × 10⁻¹ mbar to afford colourless oil. Yield: 5.76 g, 60%. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 1.03 (m, ³H, SiCH), 1.11 (d, ³J_{HH} 6.5 Hz, 18H, CH₃), 3.53 (s, 2H, CH₂Cl). ¹³C{¹H}-NMR: δ_C 11.5 (s, SiCH, ¹J_{SiC} 57 Hz), 18.8 (s, CH₃), 30.6 (s, CH₂Cl), 88.4 (s, C=CCH₂Cl), 102.7 (s, C≡CCH₂Cl). ²⁹Si{¹H}-NMR: δ_{Si} -1.68. Anal. Found: C, 62.38; H, 9.85. Calcd. for C₁₂H₂₃ClSi: C, 62.43; H, 10.04.

Pr₃SiC≡CCH₂Cl (5). As for **1**, using propargyl chloride (1.62 g, 2.2 × 10⁻² mol), ⁿBuLi (2.5 M, 4.35 cm³, 1.1 × 10⁻² mol) and Pr₃SiCl (2.09 g, 1.1 × 10⁻² mol). Obtained as orange oil. Yield: 2.33 g, 93%. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 0.60 (m, 6 H, SiCH₂), 0.99 (t, ³J_{HH} 7.2 Hz, 9H, CH₃), 1.47 (m, 6H, CH₃CH₂), 3.55 (s, 2H, CH₂Cl). ¹³C{¹H}-NMR: δ_C 16.2 (s, CH₂Si, ¹J_{SiC} 56 Hz), 17.9 (s, CH₃), 18.4 (s, CH₂CH₂Si, ²J_{SiC} 6 Hz), 30.7 (s, CH₂Cl), 90.2 (s, C=CCH₂Cl), 101.8 (s, C≡CCH₂Cl). ²⁹Si{¹H}-NMR: δ_{Si} -13.0. Anal. Found: C, 62.87; H, 9.79. Calcd. for C₁₂H₂₃ClSi: C, 62.43; H, 10.04.

Bu₃SiC≡CCH₂Cl (6). As for **1**, using propargyl chloride (1.92 g, 2.5 × 10⁻² mol), ⁿBuLi (2.5 M, 5.2 cm³, 1.3 × 10⁻² mol) and Bu₃SiCl (3.02 g, 1.29 × 10⁻² mol). Obtained as orange oil. Yield: 3.08 g, 88%. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 0.67 (m, 6H, SiCH₂), 0.92 (t, ³J_{HH} 7.3 Hz, 9H, CH₃), 1.38 (m, 6H, CH₂CH₂Si), 1.46 (m, 6H, CH₃CH₂CH₂), 3.56 (s, 2H, CH₂Cl). ¹³C{¹H}-NMR: δ_C 13.3 (s, CH₂Si, ¹J_{SiC} 57 Hz), 14.0 (s, CH₃), 26.5 (s, CH₃CH₂CH₂), 26.8 (s, CH₂CH₂Si, ²J_{SiC} 6 Hz), 30.7 (s, CH₂Cl), 90.3 (s, C=CCH₂Cl), 101.8 (s, C≡CCH₂Cl). ²⁹Sn{¹H}-NMR: δ_{Si} -11.3. Anal. Found: C, 66.39; H, 10.02. Calcd. for C₁₅H₂₉ClSi: C, 66.01; H, 10.71.

Ph₃SiC≡CCH₂Cl (7). As for **1**, using propargyl chloride (1.00 g, 1.03 × 10⁻² mol), ⁿBuLi (2.5 M, 2.7 cm³, 6.7 × 10⁻³ mol) and Bu₃SiCl (3.83 g, 1.3 × 10⁻³ mol). The crude product was sublimed under reduced pressure (23.0 × 10⁻³ mbar) to afford a colourless solid. Yield: 3.04 g, 89%. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 3.49 (s, 2H, CH₂Cl), 7.14 – 7.16 (m, 9H, *m/p*-C₆H₅), 7.73 – 7.78 (m, 6H, *o*-C₆H₅). ¹³C{¹H}-NMR: δ_C 30.4 (s, CH₂Cl), 87.6 (s, C=CCH₂Cl), 104.9 (s, C≡CCH₂Cl), 128.4 (s, *p*-C₆H₅), 130.4 (s, *m*-C₆H₅), 133.4 (s, *i*-C₆H₅), 136.0 (s, *o*-C₆H₅). ²⁹Sn{¹H}-NMR: δ_{Si} -28.8. Anal. Found: C, 75.68; H, 5.11. Calcd. for C₂₁H₁₇ClSi: C, 75.77; H, 5.15.

Bu₃SnC≡CCH₂PPh₂ (8). To an ethereal solution (ca 20 cm³) of HPPPh₂ (0.375 g, 2.02 × 10⁻³ mol) held at -78 °C was added

drop-wise ⁿBuLi (2.5 M, 0.808 cm³, 2.02 × 10⁻³ mol); the mixture was stirred for 30 min. A solution of **1** (0.733 g, 2.02 × 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: 0.800 g (4:1 **8**:SnBu₄). NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 0.93 (m, CH₃), 1.36 (m, 12H, 2 × CH₂), 1.58 (m, 6H, CH₂), 2.87 (d, J_{PH} 1.6 Hz, J_{117SnC} 8.7 Hz, J_{119SnC} 12.4 Hz, 2H, CH₂P), 7.02 – 7.13 (m, 6H, *m/p*-C₆H₅), 7.43 – 7.51 (m, 4H, *o*-C₆H₅). ¹³C{¹H}-NMR: δ_C 11.3 (s, CH₂Sn, ¹J_{117SnC} 366 Hz, ¹J_{119SnC} 383 Hz), 13.9 (s, CH₃), 20.4 (d, ¹J_{PC} 18 Hz, CH₂PPh₂), 27.4 (s, CH₂CH₂Sn, J_{SnC} 58 Hz) 85.0 (d, J_{PC} 6 Hz, C=CCH₂PPh₂), 106.8 (d, J_{PC} 5 Hz, C≡CCH₂PPh₂), 128.6 (d, J_{PC} 6 Hz, *m*-C₆H₅), 128.9 (s, *p*-C₆H₅), 133.2 (d, J_{PC} 19 Hz, *o*-C₆H₅), 138.8 (d, J_{PC} 17 Hz, *i*-C₆H₅). ³¹P{¹H}-NMR: δ_P -13.4 (s, J_{SnP} 14.5 Hz). ¹¹⁹Sn{¹H}-NMR: δ_{Sn} -68.5 (d, J_{SnP} 14.5 Hz, 4Sn), -12.0 (s, 1Sn, Bu₄Sn).

Ph₃SnC≡CCH₂PPh₂ (9). As for **8**, using HPPPh₂ (0.309 g, 1.66 × 10⁻³ mol), ⁿBuLi (2.1 M, 0.80 cm³, 1.66 × 10⁻³ mol) and **2** (0.876 g, 1.66 × 10⁻³ mol). Isolated as yellow oil. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 2.84 (d, J_{PH} 3.0 Hz, J_{SnH} 14.8 Hz, 2H, CH₂P), 6.89 – 7.20 (m, Ar, *m/p*-C₆H₅), 7.37 – 7.70 (m, Ar, 6H, *o*-C₆H₅). ¹³C{¹H}-NMR: δ_C 20.2 (d, J_{PC} 21 Hz, J_{SnC} 11.9 Hz, CH₂P), 82.8 (d, J_{PC} 6 Hz, J_{SnC} 3.4 Hz, C=CCH₂P), 109.3 (d, J_{PC} 3.4 Hz, C≡CCH₂P). ³¹P{¹H}-NMR: δ_P -13.2 (s). ¹¹⁹Sn{¹H}-NMR: δ_{Sn} -168.4 (J_{SnP} 14.8 Hz, 1Sn), -98.3 (s, BuSnPh₃, 1Sn).

Me₂PhSiC≡CCH₂PPh₂ (10). As for **8**, using HPPPh₂ (0.780 g, 4.24 × 10⁻³ mol), ⁿBuLi (2.5 M, 1.7 cm³, 4.24 × 10⁻³ mol) and **3** (0.884 g, 4.24 × 10⁻³ mol). Isolated as brown oil. Yield: 1.19 g, 78 %. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 0.30 (s, 6 H, SiCH₃), 2.75 (d, J_{PH} 2.9 Hz, 2H, CH₂P), 7.01 – 7.09 (m, 6H, *m/p*-P(C₆H₅)₂), 7.17 – 7.22 (m, 4H, *o*-P(C₆H₅)₂), 7.39 – 7.46 (m, 3H, *m/p*-SiC₆H₅), 7.52 – 7.58 (m, 2H, *o*-SiC₆H₅). ¹³C{¹H}-NMR: δ_C -0.6 (s, SiCH₃), 19.9 (d, J_{PC} 21 Hz, CH₂P), 85.7 (d, J_{PC} 5 Hz, C=CCH₂P), 104.9 (d, J_{PC} 4 Hz, C≡CCH₂P), 128.7 (d, J_{PC} 6.5 Hz, *m*-C₆H₅), 129.0 (s, *p*-C₆H₅), 129.5 (s, *p*-C₆H₅), 133.2 (d, J_{PC} 19.5 Hz, *o*-C₆H₅), 134.2 (s, *o*-C₆H₅), 137.7 (s, *i*-C₆H₅), 138.1 (d, J_{PC} 16 Hz, *i*-C₆H₅). ³¹P{¹H}-NMR: δ_P -13.5 (s). ²⁹Si{¹H}-NMR: δ_{Si} -22.9. Anal. Found: C, 76.89; H, 6.34. Calcd. for C₂₃H₂₃PSi: C, 77.06; H, 6.47.

Pr₃SiC≡CCH₂PPh₂ (11). As for **8**, using HPPPh₂ (0.780 g, 4.24 × 10⁻³ mol), ⁿBuLi (2.5 M, 1.7 cm³, 4.24 × 10⁻³ mol) and **4** (0.976 g, 4.24 × 10⁻³ mol). Isolated as orange oil. Yield: 1.45 g, 90%. NMR (C₆D₆, 30°C): ¹H-NMR: δ_H 1.01 (m, 3H, SiCH), 1.09 (d, ³J_{HH} 6.8 Hz, 18H, CH₃), 2.75 (d, J_{PH} 2.3 Hz, 2H, CH₂P), 7.02 – 7.12 (m, 6H, *m/p*-P(C₆H₅)₂), 7.39 – 7.47 (m, 4H, *o*-P(C₆H₅)₂). ¹³C{¹H}-NMR: δ_C 11.7 (s, SiCH, ¹J_{SiC} 56 Hz), 18.9 (s, J_{SiC} 16 Hz, CH₃), 19.9 (d, J_{PC} 19.5 Hz, CH₂P), 83.3 (d, J_{PC} 5 Hz, C=CCH₂P), 104.7 (d, J_{PC} 4 Hz, C≡CCH₂P), 128.7 (d, J_{PC} 6.5 Hz, *m*-C₆H₅), 129.0 (s, *p*-C₆H₅), 133.1 (d, J_{PC} 19 Hz, *o*-C₆H₅), 138.3 (d, J_{PC} 16 Hz, *i*-C₆H₅). ³¹P{¹H}-NMR: δ_P -13.5 (s, J_{SiP} 20 Hz). ²⁹Si{¹H}-NMR: δ_{Si} -3.03. Anal. Found: C, 75.77; H, 8.64. Calcd. for C₂₄H₃₃PSi: C, 75.74; H, 8.74.

${}^n\text{Pr}_3\text{SiC}\equiv\text{CCH}_2\text{PPh}_2$ (12). As for **8**, using HPPPh₂ (0.650 g, 3.49×10^{-3} mol), ${}^n\text{BuLi}$ (2.5 M, 1.4 cm^3 , 3.49×10^{-3} mol) and **5** (0.805 g, 3.49×10^{-3} mol). Isolated as brown oil. Yield: 1.00 g, 80%. NMR (C_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.58 (m, 6H, SiCH_2), 0.99 (t, ${}^3J_{\text{HH}}$ 7.0 Hz, 9H, CH_3), 1.42 (m, 6H, $\text{CH}_2\text{CH}_2\text{Si}$), 2.75 (d, J_{PH} 2.5 Hz, 2H, CH_2P), 7.04 – 7.12 (m, 6H, $m/p\text{-P}(\text{C}_6\text{H}_5)_2$), 7.40 – 7.46 (m, 4H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} 16.7 (s, $\underline{\text{C}}\text{H}_2\text{Si}$, ${}^1J_{\text{SiC}}$ 56 Hz), 18.0 (s, $\underline{\text{C}}\text{H}_3$), 18.5 (s, $\underline{\text{C}}\text{H}_2\text{CH}_2\text{Si}$, ${}^2J_{\text{SiC}}$ 8 Hz), 19.9 (d, J_{PC} 20 Hz, $\underline{\text{C}}\text{H}_2\text{P}$), 85.4 (d, J_{PC} 5.4 Hz, $\underline{\text{C}}\equiv\text{CCH}_2\text{P}$), 104.7 (d, J_{PC} 4 Hz, $\text{C}\equiv\text{CCH}_2\text{P}$), 128.5 (d, J_{PC} 6.6 Hz, $m\text{-C}_6\text{H}_5$), 129.0 (s, $p\text{-C}_6\text{H}_5$), 133.2 (d, J_{PC} 19 Hz, $o\text{-C}_6\text{H}_5$), 138.3 (d, J_{PC} 16.5 Hz, $i\text{-C}_6\text{H}_5$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} -13.6 (s, J_{SiP} 19.7 Hz). ${}^{29}\text{Si}\{^1\text{H}\}\text{-NMR}$: δ_{Si} -14.8. Anal. Found: C, 75.77; H, 8.59. Calcd. for $\text{C}_{24}\text{H}_{33}\text{PSi}$: C, 75.74; H, 8.74.

${}^n\text{Bu}_3\text{SiC}\equiv\text{CCH}_2\text{PPh}_2$ (13). As for **8**, using HPPPh₂ (0.650 g, 4.24×10^{-3} mol), ${}^n\text{BuLi}$ (2.5 M, 1.15 cm^3 , 2.87×10^{-3} mol) and **6** (0.784 g, 1.87×10^{-3} mol). Isolated as brown oil. Yield: 0.95 g, 79%. NMR (C_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.63 (m, 6H, SiCH_2), 0.93 (t, ${}^3J_{\text{HH}}$ 7.2 Hz, 9H, CH_3), 1.37 (m, 6H, $\text{CH}_2\text{CH}_2\text{Si}$), 1.41 (m, 6H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 2.76 (d, J_{PH} 2.3 Hz, 2H, CH_2P), 7.04 – 7.13 (m, 6H, $m/p\text{-P}(\text{C}_6\text{H}_5)_2$), 7.41 – 7.46 (m, 4H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} 13.7 (s, $\underline{\text{C}}\text{H}_2\text{Si}$), 14.1 (s, $\underline{\text{C}}\text{H}_3$), 19.9 (d, J_{PC} 20 Hz, $\underline{\text{C}}\text{H}_2\text{P}$), 26.7 (s, $\text{CH}_3\text{CH}_2\text{CH}_2$), 26.9 (s, $\underline{\text{C}}\text{H}_2\text{CH}_2\text{Si}$), 85.5 (d, J_{PC} 4.8 Hz, $\underline{\text{C}}\equiv\text{CCH}_2\text{P}$), 104.0 (d, J_{PC} 4.2 Hz, $\text{C}\equiv\text{CCH}_2\text{P}$), 128.6 (d, J_{PC} 6.4 Hz, $m\text{-C}_6\text{H}_5$), 129.0 (s, $p\text{-C}_6\text{H}_5$), 133.2 (d, J_{PC} 19 Hz, $o\text{-C}_6\text{H}_5$), 138.3 (d, J_{PC} 15.5 Hz, $i\text{-C}_6\text{H}_5$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} -13.5 (s, J_{SiP} 18.0 Hz). ${}^{29}\text{Si}\{^1\text{H}\}\text{-NMR}$: δ_{Si} -12.9. Anal. Found: C, 76.78; H, 9.32. Calcd. for $\text{C}_{27}\text{H}_{39}\text{PSi}$: C, 76.73; H, 9.30.

$\text{Me}_2\text{PhSiC}\equiv\text{CCH}_2\text{P}(\text{SiMe}_3)_2$ (14). In a manner similar to that described for **8**, using $\text{HP}(\text{SiMe}_3)_2$ (1.04 g, 5.84×10^{-3} mol), ${}^n\text{BuLi}$ (2.5 M, 2.3 cm^3 , 5.75×10^{-3} mol) and **3** (1.25 g, 6.00×10^{-3} mol). Isolated as orange oil. Yield: 1.84 g, 90%. NMR (C_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.25 (d, J_{PH} 4.8 Hz, 18H, $2 \times \text{Si}(\text{CH}_3)_3$), 0.44 (s, $2 \times \text{SiCH}_3$), 2.43 (d, J_{PH} 1.3 Hz, 2H, CH_2P), 7.20 – 7.25 (m, 3H, $m/p\text{-SiC}_6\text{H}_5$), 7.70 – 7.74 (m, 2H, $o\text{-SiC}_6\text{H}_5$). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} -0.6 (s, SiCH_3), 1.1 (d, J_{PC} 12.5 Hz, $\text{P}\{\text{SiCH}_3\}_2$), 5.5 (d, J_{PC} 23 Hz, $\underline{\text{C}}\text{H}_2\text{P}$), 83.3 (d, J_{PC} 4 Hz, $\underline{\text{C}}\equiv\text{CCH}_2\text{P}$), 109.3 (br., $\text{C}\equiv\text{CCH}_2\text{P}$), 128.2 (s, $m\text{-C}_6\text{H}_5$), 129.6 (s, $p\text{-C}_6\text{H}_5$), 134.2 (s, $o\text{-C}_6\text{H}_5$), 137.7 (s, $i\text{-C}_6\text{H}_5$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} -84.4 (s, 5%), -158.9 (s, **14**, 93%), -252.0 (s, 2%). ${}^{29}\text{Si}\{^1\text{H}\}\text{-NMR}$: δ_{Si} -23.0 (SiMe_2Ph), 3.42 ($\text{P}(\text{SiMe}_3)_2$). Anal. Found: C, 58.29; H, 8.86. Calcd. for $\text{C}_{17}\text{H}_{31}\text{PSi}_3$: C, 58.23; H, 8.91.

$\{(\text{Et}_2\text{N})_2\text{P}\}(\text{Ph})\text{C}(\text{Ph})\text{C}=\text{CH}_2$ (15). To a THF suspension (ca 30 cm^3) of excess, pre-activated magnesium turnings containing HgCl_2 (0.100 g, 3.68×10^{-4} mol) as initiator, was added drop-wise $\text{PhC}\equiv\text{CCH}_2\text{Cl}$ (1.00 g, 6.65×10^{-3} mol) as solution in THF (ca 10 cm^3); upon complete addition the mixture was brought to reflux for 4 h. After allowing to cool to ambient temperature, the mixture was filtered (*via* cannula) directly into a pre-cooled (-78°C) THF solution of $(\text{Et}_2\text{N})_2\text{P}(\text{Cl})$ (1.39 cm^3 , 6.65×10^{-3} mol). The resulting red solution was stirred for 30 minutes at this temperature, before allowing it to attain ambient temperature and stir overnight. The resulting orange solution was stripped

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_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.89 (t, ${}^3J_{\text{HH}}$ 7.0 Hz, 12H, CH_3), 3.05 (q, ${}^3J_{\text{HH}}$ 7.0 Hz, 8H, CH_2), 4.69 (d, J_{PH} 7.0 Hz, 2H, $=\text{CH}_2$), 7.11 – 7.15 (m, 3H, $m/p\text{-C}_6\text{H}_5$), 7.63 – 7.59 (m, 2H, $o\text{-C}_6\text{H}_5$). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} 14.8 (d, ${}^3J_{\text{PC}}$ 3.2 Hz, $\underline{\text{C}}\text{H}_3$), 43.4 (d, ${}^3J_{\text{PC}}$ 17.4 Hz, NCH_2), 75.0 (s, $=\text{CH}_2$), 105.9 (d, J_{PC} 13.5 Hz, $i\text{-C}_6\text{H}_5$), 137.4 (d, J_{PC} 19 Hz, $\text{PhC}\{(\text{NET}_2)_2\}=\text{C}$), 127.8 (s, $o\text{-C}_6\text{H}_5$), 127.9 (overlapped $m/p\text{-C}_6\text{H}_5$), 209.9 (d, J_{PC} 11.4 Hz, $=\underline{\text{C}}=$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} 91.0 (s, br, 74%). **Propargyl tautomer (5%)**: NMR (C_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 1.02 (t, ${}^3J_{\text{HH}}$ 7.2 Hz, 12H, CH_3), 2.71 (d, J_{PH} 5.8 Hz, 2H, CH_2P), 2.87 (m, 8H, NCH_2). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} 14.0 (d, ${}^3J_{\text{PC}}$ 5 Hz, $\underline{\text{C}}\text{H}_3$), 19.8 (m, $\underline{\text{C}}\text{H}_2\text{P}$), 42.8 (d, ${}^3J_{\text{PC}}$ 17 Hz, NCH_2), 81.5 (s, $\text{C}\equiv\text{CCH}_2\text{P}$), 87.6 (s, $\underline{\text{C}}\equiv\text{CCH}_2\text{P}$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} 83.2 (s, br, 5%).

$\{(\text{Et}_2\text{N})(\text{Cl})\text{P}\}(\text{Ph})\text{C}(\text{Ph})\text{C}=\text{CH}_2$ (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_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.81 (t, ${}^3J_{\text{HH}}$ 6.9 Hz, 6H, CH_3), 2.94 (q, ${}^3J_{\text{HH}}$ 7.4 Hz, 4H, CH_2), 4.89 (dd, ${}^2J_{\text{HH}}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, $=\text{CH}_2$), 4.93 (dd, ${}^2J_{\text{HH}}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, $=\text{CH}_2$), 6.94 – 7.02 (m, 1H, $p\text{-C}_6\text{H}_5$), 7.11 (7, J_{HH} 7.8 Hz, 2H, $m\text{-C}_6\text{H}_5$), 7.50 (d, J_{HH} 7.8 Hz, 2H, $o\text{-C}_6\text{H}_5$). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} 13.9 (d, ${}^3J_{\text{PC}}$ 6.2 Hz, $\underline{\text{C}}\text{H}_3$), 43.9 (d, ${}^3J_{\text{PC}}$ 13 Hz, NCH_2), 77.6 (s, $=\underline{\text{C}}\text{H}_2$), 105.3 (d, J_{PC} 40 Hz, $\text{PhC}\{(\text{NET}_2)_2\}=\text{C}$), 135.4 (d, J_{PC} 24 Hz, $i\text{-C}_6\text{H}_5$), 127.6 (d, J_{PC} 1.5 Hz, $o\text{-C}_6\text{H}_5$), 127.98 (s, $p\text{-C}_6\text{H}_5$), 128.9 (s, $m\text{-C}_6\text{H}_5$), 210.6 (d, J_{PC} 8.4 Hz, $=\underline{\text{C}}=$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} 122.0 (s, br, 77 %).

Platinum and palladium complexes. In a typical procedure, to a suspension of the $[\text{MCl}_2]_n$ ($\text{M} = \text{Pt}, \text{Pd}$) 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.

$\text{cis-}[\text{Pt}(\text{PPh}_2\text{CH}_2\text{C}\equiv\text{CSnBu}_3)_2\text{Cl}_2]$ (17). Yield: 78%. NMR (C_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.81 (m, 12H, SnCH_2), 0.88 (m, 18H, CH_3), 1.27 (m, 12H, CH_2), 1.44 (m, 12H, CH_2), 3.78 (m, $J_{\text{PH}} \sim 5\text{ Hz}$, 4H, CH_2P), 6.90 – 7.01 (m, 12H, $m/p\text{-C}_6\text{H}_5$), 7.63 – 7.77 (m, 8H, $o\text{-C}_6\text{H}_5$). ${}^{13}\text{C}\{^1\text{H}\}\text{-NMR}$: δ_{C} 11.1 (s, $\underline{\text{C}}\text{H}_2\text{Sn}$, ${}^1J_{117\text{SnC}}$ 365 Hz, ${}^1J_{119\text{SnC}}$ 381 Hz), 13.9 (s, $\underline{\text{C}}\text{H}_3$), 23.8 (d, ${}^1J_{\text{PC}}$ 27 Hz, $\underline{\text{C}}\text{H}_2\text{PPh}_2$), 27.4 (s, $\underline{\text{C}}\text{H}_2\text{CH}_2\text{Sn}$, $J_{117\text{SnC}}$ 58.8, $J_{119\text{SnC}}$ 60.7 Hz), 29.2 (s, J_{SnC} 10 Hz, CH_3CH_2), 88.7 (m, $\underline{\text{C}}\equiv\text{CCH}_2\text{PPh}_2$), 104.0 (m, $\text{C}\equiv\text{CCH}_2\text{PPh}_2$), 127.9 (br, $m\text{-P}(\text{C}_6\text{H}_5)_2$), 129.0 (br, $i\text{-P}(\text{C}_6\text{H}_5)_2$), 131.1 (s, $p\text{-P}(\text{C}_6\text{H}_5)_2$), 134.4 (m, $o\text{-P}(\text{C}_6\text{H}_5)_2$). ${}^{31}\text{P}\{^1\text{H}\}\text{-NMR}$: δ_{P} 6.0 (s, J_{PtP} 3618 Hz). ${}^{119}\text{Sn}\{^1\text{H}\}\text{-NMR}$: δ_{Sn} -68.2 (m). ${}^{195}\text{Pt}\{^1\text{H}\}\text{-NMR}$: δ_{Pt} -4407 (t, J_{PtP} 3618 Hz). Anal. Found: C, 50.23; H, 5.95. Calcd. for $\text{C}_{54}\text{H}_{78}\text{Cl}_2\text{P}_2\text{PtSn}_2$: C, 50.18; H, 6.08.

$\text{cis-}[\text{Pt}(\text{PPh}_2\text{CH}_2\text{C}\equiv\text{CSiPr}^f)_2\text{Cl}_2]$ (18). Yield: 86%. NMR (C_6D_6 , 30°C): ${}^1\text{H-NMR}$: δ_{H} 0.84 (sept., ${}^3J_{\text{HH}}$ 7.1 Hz, 6H, SiCH), 0.93 (d,

$^3J_{\text{HH}}$ 7.1 Hz, 36H, CH_3), 3.87 (d, J_{PC} 10.8 Hz, 4H, CH_2P), 6.82 – 6.88 (m, 8H, $m\text{-P}(\text{C}_6\text{H}_5)_2$), 6.91 – 6.95 (m, 4H, $p\text{-P}(\text{C}_6\text{H}_5)_2$), 7.51 – 7.57 (m, 8H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ_{C} 11.6 (s, SiCH), 18.8 (s, CH_3), 23.9 (d, J_{PC} 40 Hz, CH_2P), 85.8 (m, $\text{C}=\text{CCH}_2\text{P}$), 101.9 (m, $\text{C}\equiv\text{CCH}_2\text{P}$), 127.9 (m, $m\text{-C}_6\text{H}_5$), 131.1 (s, $p\text{-C}_6\text{H}_5$), 134.2 (m, $o\text{-C}_6\text{H}_5$), 134.6 (m, $i\text{-C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_{P} 5.83 (s, J_{PTP} 3614 Hz). $^{29}\text{Si}\{^1\text{H}\}$ -NMR: δ_{Si} -2.98. $^{195}\text{Pt}\{^1\text{H}\}$ -NMR: δ_{Pt} -4399 (t, J_{PTP} 3614 Hz). Anal. Found: C, 56.03; H, 6.39. Calcd. for $\text{C}_{48}\text{H}_{66}\text{Cl}_2\text{P}_2\text{PtSi}_2$: C, 56.13; H, 6.48.

cis-[Pt(PPh₂CH₂C≡CSiPrⁿ)₂Cl₂] (19). Yield: 78%. NMR (C_6D_6 , 30°C): ^1H -NMR: δ_{H} 0.41 (m, 12H, SiCH_2), 0.93 (t, $^3J_{\text{HH}}$ 7.2 Hz, 18H, CH_3), 1.23 (m, 12H, $\text{CH}_2\text{CH}_2\text{Si}$), 3.81 (d, J_{PH} 10 Hz, 4H, CH_2P), 6.86 – 6.93 (m, 8H, $m\text{-P}(\text{C}_6\text{H}_5)_2$), 6.94 – 7.00 (m, 4H, $o\text{-P}(\text{C}_6\text{H}_5)_2$), 7.54 – 7.62 (m, 8H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ_{C} 16.3 (s, CH_2Si , $^1J_{\text{SiC}}$ 55 Hz), 17.8 (s, CH_3), 18.5 (s, $\text{CH}_2\text{CH}_2\text{Si}$, $^2J_{\text{SiC}}$ 7.4 Hz), 23.9 (d, J_{PC} 46 Hz, CH_2P), 88.0 (m, $\text{C}=\text{CCH}_2\text{Cl}$), 101.4 (m, $\text{C}\equiv\text{CCH}_2\text{P}$), 128.2 (m, $m\text{-C}_6\text{H}_5$), 129.0 (s, $p\text{-C}_6\text{H}_5$), 131.1 (s, $o\text{-C}_6\text{H}_5$), 134.3 (m, $i\text{-C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_{P} 5.95 (s, J_{PTP} 3614 Hz). $^{29}\text{Si}\{^1\text{H}\}$ -NMR: δ_{Si} -13.9. $^{195}\text{Pt}\{^1\text{H}\}$ -NMR: δ_{Pt} -4403 (t, J_{PTP} 3614 Hz). Anal. Found: C, 56.13; H, 6.45. Calcd. for $\text{C}_{48}\text{H}_{66}\text{Cl}_2\text{P}_2\text{PtSi}_2$: C, 56.13; H, 6.48.

trans-[Pd(PPh₂CH₂C≡CSiPr¹)₂Cl₂] (20). Yield: 88%. NMR (C_6D_6 , 30°C): ^1H -NMR: δ_{H} 0.90 (m, 6H, SiCH), 0.97 (d, $^3J_{\text{HH}}$ 6.7 Hz, 36H, CH_3), 3.74 (t, J_{PH} 3.9 Hz, 2H, CH_2P), 7.05 – 7.11 (m, 12H, $m/p\text{-P}(\text{C}_6\text{H}_5)_2$), 7.92 – 7.98 (m, 8H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ_{C} 11.6 (s, SiCH), 18.8 (s, CH_3), 18.9 (t, J_{PC} 13.6 Hz, CH_2P), 85.8 (d, J_{PC} 2.9 Hz, $\text{C}=\text{CCH}_2\text{Cl}$), 101.3 (d, J_{PC} 5.6 Hz, $\text{C}\equiv\text{CCH}_2\text{P}$), 128.0 (m, $m\text{-C}_6\text{H}_5$), 129.3 (t, J_{PC} 24 Hz, $i\text{-C}_6\text{H}_5$), 130.9 (s, $p\text{-C}_6\text{H}_5$), 134.6 (t, J_{PC} 6 Hz, $o\text{-C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_{P} 16.0 (s). $^{29}\text{Si}\{^1\text{H}\}$ -NMR: δ_{Si} -2.75. Anal. Found: C, 61.07; H, 6.94. Calcd. for $\text{C}_{48}\text{H}_{66}\text{Cl}_2\text{P}_2\text{PdSi}_2$: C, 61.43; H, 7.09.

trans-[Pd(PPh₂CH₂C≡CSiPrⁿ)₂Cl₂] (21). Yield: 89%. NMR (C_6D_6 , 30°C): ^1H -NMR: δ_{H} 0.45 (m, 12H, SiCH_2), 0.91 (t, $^3J_{\text{HH}}$ 7.0 Hz, 18H, CH_3), 1.25 (m, 12H, $\text{CH}_2\text{CH}_2\text{Si}$), 3.75 (t, J_{PH} 4 Hz, 4H, CH_2P), 7.03 – 7.12 (m, 12H, $m/p\text{-P}(\text{C}_6\text{H}_5)_2$), 7.89 – 7.98 (m, 8H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ_{C} 16.4 (s, CH_2Si , $^1J_{\text{SiC}}$ 57 Hz), 17.8 (s, CH_3), 18.5 (s, $\text{CH}_2\text{CH}_2\text{Si}$, $^2J_{\text{SiC}}$ 6 Hz), 18.8 (t, J_{PC} 13.5 Hz, CH_2P), 97.9 (d, J_{PC} 2.8 Hz, $\text{C}=\text{CCH}_2\text{Cl}$), 100.8 (d, J_{PC} 4.9 Hz, $\text{C}\equiv\text{CCH}_2\text{P}$), 128.2 (m, $m\text{-C}_6\text{H}_5$), 129.2 (t, J_{PC} 24 Hz, $i\text{-C}_6\text{H}_5$), 130.9 (s, $p\text{-C}_6\text{H}_5$), 134.7 (t, J_{PC} 5.5 Hz, $o\text{-C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_{P} 15.9 (s, J_{SiP} 23 Hz). $^{29}\text{Si}\{^1\text{H}\}$ -NMR: δ_{Si} -13.8. Anal. Found: C, 61.08; H, 7.00. Calcd. for $\text{C}_{48}\text{H}_{66}\text{Cl}_2\text{P}_2\text{PdSi}_2$: C, 61.43; H, 7.09.

cis-/trans- isomerisation of [Pt(PPh₂CH₂C≡CSiPrⁿ)₂Cl₂] (19). In a borosilicate NMR tube was placed **cis-19** as solution in C_6D_6 . 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 (C_6D_6 , 30°C): ^1H -NMR: δ_{H} 0.46 (m, 12H, SiCH_2), 0.92 (t, $^3J_{\text{HH}}$ 7.3 Hz, 18H, CH_3), 1.25 (m, 12H, $\text{CH}_2\text{CH}_2\text{Si}$), 3.77 (t, J_{PH} 4.3 Hz, 4H, CH_2P), 7.03 – 7.13 (m, 12H, $m/p\text{-P}(\text{C}_6\text{H}_5)_2$), 7.95 – 8.01 (m, 8H, $o\text{-P}(\text{C}_6\text{H}_5)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR: δ_{C} 16.4 (s, CH_2Si), 17.8 (s, CH_3), 18.5 (s, $\text{CH}_2\text{CH}_2\text{Si}$), 23.8 (t, J_{PC} 24 Hz, CH_2P), 88.0 (m, $\text{C}=\text{CCH}_2\text{Cl}$), 101.4 (t, J_{PC} 6.3 Hz, $\text{C}\equiv\text{CCH}_2\text{P}$), 128.2

(m, $m\text{-C}_6\text{H}_5$), 128.8 (s, $p\text{-C}_6\text{H}_5$), 130.9 (s, $o\text{-C}_6\text{H}_5$), 134.7 (t, J_{PC} 6.0 Hz, $i\text{-C}_6\text{H}_5$). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ_{P} 11.5 (s, J_{PTP} 2601 Hz). $^{29}\text{Si}\{^1\text{H}\}$ -NMR: δ_{Si} -13.2. $^{195}\text{Pt}\{^1\text{H}\}$ -NMR: δ_{Pt} -3993 (t, J_{PTP} 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.

- For recent reviews see: D. W. Allen, *Organophosphorus Chem.*, 2015, **44**, 1-55; D. W. Allen, *Organophosphorus Chem.*, 2014, **43**, 1-51 and preceding volumes in the series; D. H. Valentine Jr., J. H. Hillhouse, *Synthesis*, 2003, 2437-2460; *ibid*, 2003, 317-334.
- For a recent review see: E. Bernoud, R. Veillard, C. Alayrac, A.-C. Gaumont, *Molecules*, 2012, **17**, 14573-14587.
- R. J. Detz, S. A. Heras, R. de Gelder, P. W. N. M. van Leeuwen, H. Hiemstra, J. N. H. Reek, J. H. van Maarseveen, *Org. Lett.*, 2006, **8**, 3227-3230.
- T. D. Simone, R. S. Dickson, B. W. Skelton, A. H. White, *Inorg. Chim. Acta*, 1995, **240**, 323-333.
- N. Maigrot, M. Melaimi, L. Ricard, P. Le Floch, *Heteratom Chem.*, 2003, **14**, 326-333.
- M. Gandelman, E. M. Schuster, G. Nisnevich, US Patent US8318960 B2, 2012.
- M. Reisser, A. Maier, G. Maas, *Synlett*, 2002, 1459-1462.
- T. J. Taylor, A. P. Soto, K. Huynh, A. J. Lough, A. C. Swain, N. C. Norman, C. A. Russell, I. Manners, *Macromolecules*, 2010, **43**, 7446-7452.
- T. W. Mackewitz, M. Regitz, *Liebigs. Ann.*, 1996, 327.
- R. B. King, A. Efraty, *Inorg. Chim. Acta*, 1970, **4**, 123-128.
- T. W. Mackewitz, D. Ulrich, U. Bergstrasser, S. Leininger, M. Regitz, *Liebigs. Ann.*, 1997, 1827-1839.
- R. Popp, R. Gleiter, F. Rominger, *Tetrahedron Lett.*, 2000, **41**, 4075-4078.
- M. Mirza-Aghayan, R. Boukherroub, G. Oba, G. Manuel, M. Koenig, *J. Organomet. Chem.*, 1998, **564**, 61-70.
- R. H. Shay, B. N. Diel, D. M. Schubert, A. D. Norman, *Inorg. Chem.*, 1988, **27**, 2378-2382.
- T. Baumgartner, *Acc. Chem. Res.*, 2014, **47**, 1613-1622; T. Baumgartner, R. Reau, *Chem. Rev.*, 2006, **106**, 4681-4727 and references therein.
- D. W. Stephan, *J. Am. Chem. Soc.*, 2015, **137**, 10018-10032; D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46-76 and references therein.
- K. Maitra, V. J. Catalano, J. H. Nelson, *J. Organomet. Chem.*, 1997, **529**, 409-422.
- K. Maitra, W. L. Wilson, M. M. Jemin, C. Yeung, W. S. Rader, K. D. Redwine, D. P. Striplin, V. J. Catalano, J. H. Nelson, S. Song, E. C. Alyea, *Synth. React. Inorg. Metal-Org. Chem.*, 1996, **26**, 967-996; W. L. Wilson, N. W. Alcock, E. C. Alyea, S. Song, J. H. Nelson, *Bull. Soc. Chim. Fr.*, 1993, **130**, 673 – 682.
- H. Lang, U. Lay, M. Leise, L. Zsolnai, *Z. Naturforsch. B*, 1993, **48**, 27-36.
- B. N. Diel, P. F. Brandt, R. C. Haltiwanger, M. L. J. Hackney, A. D. Norman, *Inorg. Chem.*, 1989, **28**, 2811-2816

- 21 R. Regragui, P. H. Dixneuf, *New J. Chem.*, 1988, **12**, 547-550.
- 22 J. T. Lin, S. Y. Wang, Y. C. Chou, M. L. Gong, Y.-M. Shiow, H.-M. Gau, Y. S. Wen, *J. Organomet. Chem.*, 1996, **508**, 183-193.
- 23 J.-S. Huang, G.-A. Yu, J. Xie, K.-M. Wong, N. Zhu, C.-M. Che, *Inorg. Chem.*, 2008, **47**, 9166-9181.
- 24 M. Alonso, M. A. Alvarez, E. Garcia, D. Garcia-Vivó, M. A. Ruiz, *Inorg. Chem.*, 2010, **49**, 8962-8976.
- 25 A. I. Arkhynchuk, A. Orthaber, V. A. Mihali, A. Ehlers, K. Lammertsma, S. Ott, *Chem. Eur. J.*, 2013, **19**, 13692-13704.
- 26 R. B. King, A. Efraty, *Inorg. Chim. Acta*, 1970, **4**, 123-128.
- 27 G. Hogarth, J. Y. Pang, *J. Organomet. Chem.*, 1996, **515**, 193-203.
- 28 (a) A. J. Saunders, I. R. Crossley, M. P. Coles, S. M. Roe, *Chem. Commun.*, 2012, 48, 5766-5768; (b) C. E. Averre, M. P. Coles, I. R. Crossley, I. J. Day, *Dalton Trans.*, 2012, **41**, 278-284; (c) V. K. Greenacre, M. B. Ansell, S. M. Roe, I. R. Crossley, *Eur. J. Inorg. Chem.*, 2014, 5053-5062.
- 29 (a) V. K. Greenacre, N. Trathen, I. R. Crossley, *Organometallics*, 2015, **34**, 2533-2542; (b) N. Trathen, M. C. Leech, I. R. Crossley, V. K. Greenacre, S. M. Roe, *Dalton Trans.*, 2014, **43**, 9004-9007; (c) N. Trathen, V. K. Greenacre, I. R. Crossley, S. M. Roe, *Organometallics*, 2013, **32**, 2501-2504.
- 30 K. Ruitenbergh, H. Westmijze, H. Kleijn, P. Vermeer, *J. Organomet. Chem.*, 1984, **277**, 227-234.
- 31 K. Kiyokawa, N. Tachikake, M. Yasuda, A. Baba, *Angew. Chem. Int. Ed.*, 2011, **50**, 10393-10396.
- 32 S. K. Woo, L. M. Geary, M. J. Kirsche, *Angew. Chem. Int. Ed.*, 2012, **51**, 7830-7834.
- 33 O. Tsutsumi, K. Nishiguchi, *J. Am. Chem. Soc.*, 1998, **120**, 1938-1939; R. L. Phillips, I.-B. Kim, L. M. Tolbert, U. H. F. Bunz, *J. Am. Chem. Soc.*, 2008, **130**, 6952-6954.
- 34 See for example: H. Gilman, S. Rosenberg, *J. Org. Chem.*, 1959, **24**, 2063-2064; D. Seyferth, M. A. Weiner, *J. Am. Chem. Soc.*, 1962, **84**, 361-364; D. Seyferth, T. Wada, *Inorg. Chem.*, 1962, **1**, 78-83; D. Seyferth, L. G. Vaughan, R. Suzuki, *J. Organomet. Chem.*, 1964, **1**, 437-448; D. Seyferth, G. B. Womack, *Organometallics*, 1986, **5**, 2360-2370; J. J. Eisch, J. E. Galle, *J. Organomet. Chem.*, 1988, **341**, 293-313; A. K. Brisdon, I. R. Crossley, R. G. Pritchard, J. E. Warren, *Inorg. Chem.*, 2002, **41**, 4748-4755.
- 35 J.-P. Quintard, G. Dumartin, *J. Organomet. Chem.*, 1984, **266**, 123-138.
- 36 P. R. Deacon, N. Devylder, M. S. Hill, M. F. Mahon, K. C. Molloy, G. J. Price, *J. Organomet. Chem.*, 2003, **687**, 46-56.
- 37 G. Pattenden, D. Whybrow, *Tetrahedron Lett.*, 1979, **20**, 1885-1888; K. V. Baker, J. M. Brown, N. Hughes, A. J. Skarnulis, A. Sexton, *J. Org. Chem.*, 1991, **56**, 698-703; G. Courtois, M. Harama, L. Miginiac, *J. Organomet. Chem.*, 1980, **198**, 1-14.
- 38 K. S. Dunne, S. E. Lee, V. Gouveneur, *J. Organomet. Chem.*, 2006, **691**, 5246-5259.
- 39 R. B. King, P. M. Sundaram, *J. Org. Chem.*, 1984, **49**, 1784-1789.
- 40 See for example: R. L. Danheiser, Y. M. Choi, M. Menichincheri, E. J. Stoner, *J. Org. Chem.*, 1993, **58**, 322-327.
- 41 B. Németh, B. Khater, T. Veszprémi, J.-C. Guillemin, *Dalton Trans.*, 2009, 3526-3535; J.-C. Guillemin, P. Savignac, J.-M. Denis, *Inorg. Chem.*, 1991, **30**, 2170-2173; F. Nief, F. Mathey, *Tetrahedron*, 1991, **47**, 6673-6680; W. Hewertson, I. C. Taylor, S. Trippett, *J. Chem. Soc. C*, 1970, 1835-1839.
- 42 M. P. Simonnin, C. Charrier, *Org. Magnetic Resonance*, 1969, **1**, 27-49.
- 43 N. Allefeld, M. Grasse, N. Ignat'ev, B. Hoge, *Chem. Eur. J.*, 2014, **20**, 8615-8620.
- 44 H. Burfer, U. Groetze, *J. Organomet. Chem.*, 1968, **12**, 451.

Synopsis – for table of contents use only

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

