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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 $R_3EC \equiv CCH_2Cl$ ($R_3E = {}^{n}Bu_3Sn$, Ph_3Sn , Me_2PhSi , ${}^{i}Pr_3Si$, ${}^{n}Pr_3Si$, ${}^{n}Bu_3Si$), obtained by a modified literature procedure, react with LiPPh₂ to afford the novel propargyl phosphanes $Ph_2PCH_2C \equiv CER_3$ in high yield, as viscous oils; (Me_3Si)₂PCH₂C $\equiv CSiPhMe_2$ 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) $\equiv C \equiv CH_2$, 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.

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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 R₂PR', surprising oversights remain, a case in point being the dearth of systems bearing a propargylic substituent (*viz.* CH₂C≡CR'). Indeed, while alkynyl phosphanes are common,² their propargyl counterparts are limited to R₂PCH₂C≡CR' (R = Ph, R' = H,³ Me,⁴ Ph;⁵ R = Cy, ⁱPr, R' = H, SiMe₃;⁶), typically isolated as stabilised BH₃ adducts, R₂PCH{OSiMe₃}C≡CPh (R = Ph, Et),⁷ {(Me₃Si)₂N}-RPCH₂C≡CCH₂C=CCH₂PPh₂,¹⁰ and the bis-propargylphosphanes RP{CH₂C≡CR'₂ (R = Np, R' = H, SiMe₃;¹¹ R = CH₂CMe₂Et, R' =

 $H_{3}^{11} R = Ph, R' = {}^{n}Bu_{3}^{12} R = Mes, R' = SiMe_{3}^{13}$), which are typically putative intermediates in the synthesis of macrocycles. The primary propargyl phosphane H_2PCH_2C =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=C) bridging mode has been described for [Cp₂Rh₂(CO)(μ - η ¹: η ¹-CF₃C₂CF₃){PPh₂CH₂C=CMe}CO₂(CO)₆], obtained by reaction of [Co₂(CO)₈] with the dirhodium complex [Cp₂Rh₂(CO)(μ - η ¹: η ¹-CF₃C₂CF₃){PPh₂CH₂C=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, SiMe₃), $[Mo(CO)_3(PH_2CH_2C \equiv CH)_3]$, $[Mo(CO)_4(PH_2C \equiv CH)^{20}]$ 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 $[{HC \equiv CCH_2Ph_2P}Ru(CO)_3(\mu-PPh_2)Co(CO)_3].^{21}$ In contrast, $[Co(NO)(CO)(PPh_2CH_2C \equiv CH)_2]^{22}$ and the ruthenium phthalocyaninato (Pc^{2-}) complex $[Ru(Pc)(PPh_2CH_2C \equiv CCH_3)_2]^{23}$



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E-mail: i.crossley@sussex.ac.uk; Fax: +44 (0)1273 876687; Tel: +44 (0)1273 877302 †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/c5dt03558a

[‡]DBP = dibenzophosphole.

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are obtained from the respective diphenylphosphane complexes, *via in situ* deprotonation (BuLi) and quenching with the appropriate propargylic bromide; $[CpMo\{\kappa^2-O,P-P(O)Mes^*-(CH_2C=CH)\}]$ is similarly prepared, but without need for base.²⁴ Finally, $[W(CO)_5\{PPh(OMe)C(H)Me(C=CSi^iPr_3)\}]$ was obtained upon methanolysis of the putative phosphaalkene $[W(CO)_5\{P(Ph)=CMe(C=CSi^iPr_3)\}]$.²⁵

Notably, no complexes of the group 10 metals have been described, though the formally related diphosphane-bridged complexes $[L_nM{\mu-\eta^1:\eta^1-PPh_2CH_2C=CCH_2PPh_2}]_2$ $(L_nM = Cl_2Pt, (OC)_2Ni)$ have been reported,²⁶ alongside examples with other metals $(L_nM = AuCl, CpCoI_2, CpFe(CO)_2^+, CpFeBr(CO), CpMn(NO)(CO), CpMo(CO)_2(COCH_3),^{26} Mo(CO)_4^{27})$. The intriguing tetrameric complex $[{\eta^2-C, C-Mo(CO)_4(\eta^2-P,P-PPh_2CH_2C=CCH_2PPh_3)}_3Mo(CO)]$, has also been described.²⁷

We have recently been interested in the synthesis and study of reactive and functional phosphanes²⁸ and organometallic phosphacarbons,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- $(CH_2C \equiv CER'_3)$ (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. $Ph_2P(CH_2C \equiv CER_3)$ (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 $R_3EC \equiv CCH_2Cl$ were prepared following a modified literature procedure (Scheme 1),³⁰ *via* the low-temperature (-78 °C) lithiation of HC \equiv CCH₂Cl, quenched with R_3SnCl (1 and 2) or R_3SiCl (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 ($\delta_{\rm H}$ 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; $X = {}^{119}Sn$, ${}^{29}Si$); for the stannanes the ${}^{4}J_{SnH}$ 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} 3³² and 4³³ 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 ^{*n*}BuLi) and the mixtures stirred overnight to afford the propargyl phosphanes Ph₂P(CH₂C=CER₃) (**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 ^{*n*}Bu₄Sn (1:4 of **8**) or ^{*n*}BuPh₃Sn (1:1 with **9**), presumably due to metathesis of **1** and **2** with residual ^{*n*}BuLi, as is common among Sn(*n*) 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 ^{*n*}Bu₄Sn (δ_{Sn} –12.0)³⁵ and ^{*n*}BuPh₃Sn (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

Table 1 Selected NMR spectroscopic data for proparylphosphanes $8{-}14^{\rm a}$

	$\delta_{ m P}$	$\delta_{\mathrm{H}} \left(\mathrm{CH}_2 \right) \left[J_{\mathrm{PH}} \right]^b$	$\delta_{\mathrm{C}}\left(\mathrm{C}_{1} ight)$	$\delta_{\mathrm{C}}\left(\mathrm{C}_{2} ight)$	$\delta_{\mathrm{E}}\left(\mathrm{E} ight)$
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]

^a As C₆D₆ solutions. ^b Couplings in Hz.

from the chloropropargyls over S_N^2 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 is generating 'PhC=CCH₂MgCl' under comparable conditions. However, our efforts to quench this reagent with $(Et_2N)_2$ PCl 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)₂PCl affords, after workup, a deep red oil comprising one predominant phosphoruscontaining product (15; 75%). The spectroscopic features of 15 confirm the presence of a ' $(Et_2N)_2P$ ' moiety (δ_P 90.9; cf. PhP- $(NEt_2)_2$ 97.9,³⁸ H₂C=C(H)-P(NEt_2)_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 ($\delta_{\rm H}$ 4.72. $\delta_{\rm C}$ 75.0) relative to both PhC=CCH₂Cl ($\delta_{\rm H}$ 4.39, $\delta_{\rm C}$ 31.2) and propargyl phosphanes, and exhibits appreciably greater magnitude coupling to phosphorus ($|J_{PH}| = 7.1 \text{ Hz}$) than 8–14. The unsaturated carbon centres are also heavily deshielded (δ_c 137.4 (J_{PC} 19.0 Hz) C_1 ; 209.9 (J_{PC} 11.3 Hz) C_2), 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.^{14,41} We thus confidently formulate 15 as (Et₂N)₂PC- $(Ph) = C = CH_2$ (Scheme 2).

The reaction of propargyl Grignard reagents with R₂PCl has been noted to afford mixtures that include allenyl-phosphanes, 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' ClP(NEt₂)₂ electrophile, as com-

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

	$\delta_{\rm H}(=\!$	$\delta_{\rm C}(=\!$	$\delta_{\rm C}$ (=C=)
$Mes(H)PC(Me) = C = CH_2$ $Mes(Me)PC(Me) = C = CH_2$ $Mes(Me_3Si)PC(Me) = C = CH_2$ $Mes(Cl)PC(Me) = C = CH_2$ $Ph_2PC(H) = C = CH_2$ $Ph_2PC(H) = C = CH_2$	4.40 4.64 4.55 4.57	71.12 73.26 72.35 74.65 71.7 70.7	208.0 204.9 206.4 205.5 213.2 210.3
$Ph_2PC(H) = C = C(Me)_2$	—	_	209.6

^a Chemical shifts in ppm. ^b Data sourced from ref. 14 and 41.



Scheme 2 Reagents and conditions: (i) Et_2O , $HgCl_2$ (5 mol%), Mg, \triangle , 4 h; (ii) (Et_2N)₂PCl, -78 °C, 30 min; (iii) r.t. 18 h; (iv) 2 equiv. HCl/Et₂O.

pared, for instance, with the notionally 'harder' PCl_3 , with which we encountered significantly greater complexity, yielding a largely intractable mixture.

In order to confirm or dismiss the presence of $Cl_2PC(Ph) =$ $C = CH_2$ within this mixture, we sought to prepare an authentic sample, treating 15 with HCl (2 equiv.). This effected 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 diasterotopicity 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 diasterotopicity of the '=CH₂' protons ($\delta_{\rm H}$ 4.63, d, $J_{\rm PH}$ 3 Hz). However, the 31 P shift ($\delta_{\rm P}$ 58.7, t, $J_{\rm PH}$ 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 propargylphosphanes

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

[§]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.



Scheme 3 Reagents and conditions: (i) $CH_2Cl_2,\ 12$ h; (ii) $C_6D_6,\ h\nu,\ 30$ min.

The propargylphosphanes **8**, **11** and **12** react with $[PtCl_2]_n$, as a suspension in CH₂Cl₂, to afford exclusively the complexes *cis*-[Pt{PPh₂(CH₂C=CER₃)}₂Cl₂] (ER₃ = ^{*n*}Bu₃Sn **17**, ^{*i*}Pr₃Si **18**, ^{*n*}Pr₃Si **19**, Scheme 3) in excess of 75% isolated yield. For the silanes, palladium analogues (ER₃ = ^{*i*}Pr₃Si **20**, ^{*n*}Pr₃Si **21**) are similarly obtained from $[PdCl_2]_n$, 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 data, which verify the structural integrity of the ligands and coordination of the phosphorus centres ($\Delta \delta_{\rm P} \sim +20$). For the platinum complexes 17-19, $|_{J_{PtP}}^{1}|$ values of *ca.* 3600 Hz are wholly consistent with assignment of a cis geometry, while the palladium complexes exhibit virtual coupling in the ¹H and ¹³C{¹H}-NMR resonances associated with the CH₂P moiety, consistent with a trans ligand arrangement. Notably, despite coordinative unsaturation of the metals, there is no evidence for either intra or intermolecular association of the pendant alkynyl moieties, the spectroscopic features of these units being little perturbed from the free ligands.

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

Conclusions

We have described the synthesis and characterisation of a series of novel propargylphosphanes that feature tin and silicon termini on the alkyne moiety. Attempts to increase the range of phosphanyl termini used *via* the reaction of R_2PCl with propargyl Grignard reagents proved unsuccessful, but allowed for the generation of the novel allenylphosphine $(Et_2N)_2PC(Ph)=C=CH_2$, the first time a species of this type has been obtained as the primary product (>70%) of such a reaction.

Representative phosphanes have been shown to form complexes $[M(PPh_2CH_2C \equiv CER_3)_2Cl_2]$ 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 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 an atmosphere of dry argon or dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å for DCM and THF) or potassium mirrors. Propargyl chloride, group 14 triorganohalides and HPPh2 were obtained from Sigma-Aldrich, purified by appropriate methods and degassed (freeze-thaw) before use. "BuLi (2.5 M in hexanes) was obtained from Sigma-Aldrich and titrated to establish concentration. Precious metal salts (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; ¹³C, 100.46 MHz; ³¹P, 161.71 MHz; ²⁹Si, 79.37 MHz; ¹¹⁹Sn, 148.97 MHz; ¹⁹⁵Pt, 85.53 MHz) or VNMRS 500 (¹H 499.91 MHz; ¹³C, 125.72 MHz) spectrometer. All spectra were referenced to Me₄Si, 85% H₃PO₄, Me₄Sn or K₂PtCl₆ as appropriate. Carbon-13 NMR data were assigned with recourse to the 2D (HSQC, HMBC) spectra; detailed connectivity and ²⁹Si chemical shifts were assessed using ¹H-X HMBC spectra (X = ²⁹Si; ¹¹⁹Sn; ³¹P). Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

Synthesis

^{*n*}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 ^{*n*}BuLi (2.5 M, 6.0 cm³, 1.5×10^{-2} mol). The mixture was stirred for 30 min., after which time ^{*n*}Bu₃SnCl (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.

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The mixture was held at $-78 \,^{\circ}$ 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: $\delta_{\rm H}$ 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). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 11.3 (s, <u>CH</u>₂Sn, ¹J_{117SnC} 365 Hz, ¹J_{119SnC} 382 Hz), 13.9 (s, <u>CH</u>₃), 27.3 (s, <u>CH</u>₂CH₂Sn, ²J_{117SnC} 58 Hz, ²J_{119SnC} 60 Hz), 29.3 (s, CH₃<u>C</u>H₂, ³J_{SnC} 24 Hz), 31.2 (s, J_{SnC} 8 Hz, CH₂Cl), 91.1 (s, <u>C</u>=CCH₂Cl), 105 (s, C=<u>C</u>CH₂Cl). ¹¹⁹Sn{¹H}-NMR: $\delta_{\rm Sn}$ -65.1. Anal. Found: C, 49.44; H, 7.86. Calcd for C₁₅H₂₉ClSn: C, 49.56; H, 8.04.

Ph₃**SnC**=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). ¹³C{¹H}-NMR: δ_C 30.8 (s, *J*_{SnC} 10 Hz, CH₂Cl), 88.5 (s, <u>*C*</u>=CCH₂Cl), 106.8 (s, <u>*C*≡<u>*C*</u>CH₂Cl), 128.8 (s, *p*-<u>*C*₆H₅), 129.5 (s, *m*-<u>*C*₆H₅), 130.1 (s, i-<u>*C*₆H₅), 136.7 (s, *o*-<u>*C*₆H₅). ¹¹⁹Sn{¹H}-NMR: δ_{Sn} −169.5. Anal. Found: C, 59.63; H, 4.12. Calcd for C₂₀H₁₇ClSn: C, 59.55; H, 4.05.</u></u></u></u></u>

Me₂**PhSiC**≡**CCH**₂**Cl** (3). As for 1, using propargyl chloride (3.73 g, 5.0 × 10⁻² mol), ^{*n*}BuLi (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: $\delta_{\rm H}$ 0.32 (s, $J_{\rm SiH}$ 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: $\delta_{\rm C}$ −1.2 (s, Si<u>C</u>H₃, ¹ $J_{\rm SiC}$ 58 Hz,), 30.5 (s, CH₂Cl), 90.1 (s, <u>C</u>=CCH₂Cl), 102.0 (s, C≡<u>*C*</u>CH₂Cl). ²⁹Si{¹H}-NMR: $\delta_{\rm Si}$ −21.6. Anal. Found: C, 63.18; H, 6.14. Calcd for C₁₁H₁₃ClSi: C, 63.29; H, 6.28.

ⁱ**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 ⁱPr₃SiCl (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: $\delta_{\rm H}$ 1.03 (m,³ H, SiC*H*), 1.11 (d, ³J_{HH} 6.5 Hz, 18H, CH₃), 3.53 (s, 2H, CH₂Cl). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 11.5 (s, Si<u>C</u>H, ¹J_{SiC} 57 Hz), 18.8 (s, <u>C</u>H₃), 30.6 (s, CH₂Cl), 88.4 (s, <u>C</u>=CCH₂Cl), 102.7 (s, C=<u>C</u>CH₂Cl). ²⁹Si{¹H}-NMR: $\delta_{\rm Si}$ -1.68. Anal. Found: C, 62.38; H, 9.85. Calcd for C₁₂H₂₃ClSi: C, 62.43; H, 10.04.

^{*n*}**Pr₃SiC**=CCH₂Cl (5). As for 1, using propargyl chloride (1.62 g, 2.2 × 10⁻² mol), ^{*n*}BuLi (2.5 M, 4.35 cm³, 1.1 × 10⁻² mol) and ^{*n*}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, <u>C</u>H₂Si, ¹J_{SiC} 56 Hz,), 17.9 (s, <u>C</u>H₃), 18.4 (s, <u>C</u>H₂CH₂Si, ²J_{SiC} 6 Hz), 30.7 (s, CH₂Cl), 90.2 (s, <u>C</u>=CCH₂Cl), 101.8 (s, C≡<u>C</u>CH₂Cl). ²⁹Si{¹H}-NMR: δ_{Si} −13.0. Anal. Found: C, 62.87; H, 9.79. Calcd for C₁₂H₂₃ClSi: C, 62.43; H, 10.04.

^{*n*}Bu₃SiC=CCH₂Cl (6). As for 1, using propargyl chloride (1.92 g, 2.5×10^{-2} mol), ^{*n*}BuLi (2.5 M, 5.2 cm³, 1.3×10^{-2} mol)

and ^{*n*}Bu₃SiCl (3.02 g, 1.29×10^{-2} mol). Obtained as orange oil. Yield: 3.08 g, 88%. NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 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: $\delta_{\rm C}$ 13.3 (s, <u>C</u>H₂Si, ¹J_{SiC} 57 Hz), 14.0 (s, <u>C</u>H₃), 26.5 (s, CH₃<u>C</u>H₂CH₂), 26.8 (s, <u>C</u>H₂CH₂Si, J_{SiC} 6 Hz), 30.7 (s, CH₂Cl), 90.3 (s, <u>C</u>=CCH₂Cl), 101.8 (s, C≡<u>C</u>CH₂Cl). ²⁹Sn{¹H</sup>-NMR: $\delta_{\rm Si}$ -11.3. Anal. Found: C, 66.39; H, 10.02. Calcd for C₁₅H₂₉ClSi: C, 66.01; H, 10.71.

Ph₃**SiC**≡**CCH**₂**Cl** (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 ⁿBu₃SiCl (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, <u>C</u>=CCH₂Cl), 104.9 (s, C≡<u>C</u>CH₂Cl), 128.4 (s, *p*-<u>C</u>₆H₅), 130.4 (s, *m*-<u>C</u>₆H₅), 133.4 (s, i-<u>C</u>₆H₅), 136.0 (s, *o*-<u>C</u>₆H₅). ²⁹Sn{¹H}-NMR: δ_{Si} −28.8. Anal. Found: C, 75.68; H, 5.11. Calcd for C₂₁H₁₇ClSi: C, 75.77; H, 5.15.

ⁿBu₃SnC=CCH₂PPh₂ (8). To an ethereal solution (ca. 20 cm³) of HPPh₂ (0.375 g, 2.02×10^{-3} mol) held at -78 °C was added drop-wise ^{*n*}BuLi (2.5 M, 0.808 cm³, 2.02 \times 10^{-3} mol); the mixture was stirred for 30 min. A solution of 1 $(0.733 \text{ g}, 2.02 \times 10^{-3} \text{ mol})$ 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: $\delta_{\rm H}$ 0.93 (m, CH_3), 1.36 (m, 12H, 2 × CH_2), 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: $\delta_{\rm C}$ 11.3 (s, <u>C</u>H₂Sn, ¹J_{117SnC} 366 Hz, ${}^{1}J_{119SnC}$ 383 Hz), 13.9 (s, CH₃), 20.4 (d, ${}^{1}J_{PC}$ 18 Hz, CH₂PPh₂), 27.4 (s, $\underline{C}H_2CH_2Sn$, J_{SnC} 58 Hz) 85.0 (d, J_{PC} 6 Hz, *C*=CCH₂PPh₂), 106.8 (d, *J*_{PC} 5 Hz, C=*C*CH₂PPh₂), 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- C_6H_5). 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).

Ph₃**SnC**≡**CCH**₂**PPh**₂ (9). As for 8, using HPPh₂ (0.309 g, 1.66 × 10⁻³ mol), ^{*n*}BuLi (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: $\delta_{\rm H}$ 2.84 (d, $J_{\rm PH}$ 3.0 Hz, $J_{\rm SnH}$ 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: $\delta_{\rm C}$ 20.2 (d, $J_{\rm PC}$ 21 Hz, $J_{\rm SnC}$ 11.9 Hz, CH₂P), 82.8 (d, $J_{\rm PC}$ 6 Hz, $J_{\rm SnC}$ 3.4 Hz, C≡CCH₂P), 109.3 (d, $J_{\rm PC}$ 3.4 Hz, <u>C</u>≡CCH₂P). ³¹P{¹H}-NMR: $\delta_{\rm P}$ −13.2 (s). ¹¹⁹Sn{¹H}-NMR: $\delta_{\rm Sn}$ −168.4 ($J_{\rm SnP}$ 14.8 Hz, 1Sn), −98.3 (s, BuSnPh₃, 1Sn).

Me₂PhSiC≡**CCH₂PPh₂ (10).** As for **8**, using HPPh₂ (0.780 g, 4.24 × 10⁻³ mol), ^{*n*}BuLi (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: $\delta_{\rm H}$ 0.30 (s, 6 H, SiCH₃), 2.75 (d, J_{PH} 2.9 Hz, 2H, CH₂P), 7.01–7.09 (m, 6H,

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 $m/p-P(C_6H_5)_2$, 7.17–7.22 (m, 4H, $o-P(C_6H_5)_2$), 7.39–7.46 (m, 3H, m/p-SiC₆ H_5), 7.52–7.58 (m, 2H, o-SiC₆ H_5). ¹³C{¹H}-NMR: $\delta_{\rm C}$ -0.6 (s, SiCH₃), 19.9 (d, $J_{\rm PC}$ 21 Hz, CH₂P), 85.7 (d, $J_{\rm PC}$ 5 Hz, $C \equiv CCH_2P$), 104.9 (d, J_{PC} 4 Hz, $C \equiv CCH_2P$), 128.7 (d, J_{PC} 6.5 Hz, $m-C_6H_5$), 129.0 (s, $p-C_6H_5$), 129.5 (s, $p-C_6H_5$), 133.2 (d, $J_{\rm PC}$ 19.5 Hz, $o-C_6H_5$), 134.2 (s, $o-C_6H_5$), 137.7 (s, $i-C_6H_5$), 138.1 (d, J_{PC} 16 Hz, i- C_6H_5). 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.

ⁱ $Pr_3SiC \equiv CCH_2PPh_2$ (11). As for 8, using HPPh₂ (0.780 g, 4.24×10^{-3} mol), ^{*n*}BuLi (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, ³*J*_{HH} 6.8 Hz, 18H, C*H*₃), 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: $\delta_{\rm C}$ 11.7 (s, SiCH, ¹ $J_{\rm SiC}$ 56 Hz), 18.9 (s, $J_{\rm SiC}$ 16 Hz, *C*H₃), 19.9 (d, *J*_{PC} 19.5 Hz, *C*H₂P), 83.3 (d, *J*_{PC} 5 Hz, *C*≡CCH₂P), 104.7 (d, *J*_{PC} 4 Hz, C≡*C*CH₂P), 128.7 (d, *J*_{PC} 6.5 Hz, *m*-*C*₆H₅), 129.0 (s, p-C₆H₅), 133.1 (d, J_{PC} 19 Hz, o-C₆H₅), 138.3 (d, J_{PC} 16 Hz, i- C_6H_5). 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*}Pr₃SiC=CCH₂PPh₂ (12). As for 8, using HPPh₂ (0.650 g, 3.49×10^{-3} mol), ^{*n*}BuLi (2.5 M, 1.4 cm³, 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 (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.58 (m, 6H, SiCH₂), 0.99 (t, ${}^{3}J_{HH}$ 7.0 Hz, 9H, CH₃), 1.42 (m, 6H, CH₂CH₂Si), 2.75 (d, $J_{\rm PH}$ 2.5 Hz, 2H, CH₂P), 7.04–7.12 (m, 6H, m/p-P(C₆H₅)₂), 7.40–7.46 (m, 4H, o-P(C₆ H_5)₂). ¹³C{¹H}-NMR: δ_C 16.7 (s, CH_2Si , ${}^{1}J_{\text{SiC}}$ 56 Hz,), 18.0 (s, CH₃), 18.5 (s, CH₂CH₂Si, ${}^{2}J_{\text{SiC}}$ 8 Hz), 19.9 (d, J_{PC} 20 Hz, CH₂P), 85.4 (d, J_{PC} 5.4 Hz, C=CCH₂P), 104.7 (d, J_{PC} 4 Hz, C=<u>C</u>CH₂P), 128.5 (d, J_{PC} 6.6 Hz, *m*-C₆H₅), 129.0 (s, p-C₆H₅), 133.2 (d, J_{PC} 19 Hz, o-C₆H₅), 138.3 (d, J_{PC} 16.5 Hz, i- C_6H_5). ³¹P{¹H}-NMR: δ_P –13.6 (s, J_{SiP} 19.7 Hz). ²⁹Si{¹H}-NMR: δ_{si} –14.8. Anal. Found: C, 75.77; H, 8.59. Calcd for C₂₄H₃₃PSi: C, 75.74; H, 8.74.

^{*n*}Bu₃SiC=CCH₂PPh₂ (13). As for 8, using HPPh₂ (0.650 g, 4.24×10^{-3} mol), ^{*n*}BuLi (2.5 M, 1.15 cm³, 2.87 × 10⁻³ mol) and 6 (0.784 g, 1.87 \times 10^{-3} mol). Isolated as brown oil. Yield: 0.95 g, 79%. NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.6.3 (m, 6H, $SiCH_2$, 0.93 (t, ${}^{3}J_{HH}$ 7.2 Hz, 9H, CH_3), 1.37 (m, 6H, CH_2CH_2Si), 1.41 (m, 6H, CH₃CH₂CH₂), 2.76 (d, J_{PH} 2.3 Hz, 2H, CH₂P), 7.04–7.13 (m, 6H, m/p-P(C₆H₅)₂), 7.41–7.46 (m, 4H, o-P(C₆H₅)₂). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 13.7 (s, CH₂Si), 14.1 (s, CH₃), 19.9 (d, $J_{\rm PC}$ 20 Hz, <u>CH</u>₂P), 26.7 (s, CH₃<u>C</u>H₂CH₂), 26.9 (s, <u>C</u>H₂CH₂Si), 85.5 (d, *J*_{PC} 4.8 Hz, *C*=CCH₂P), 104.0 (d, *J*_{PC} 4.2 Hz, C=CCH₂P), 128.6 (d, J_{PC} 6.4 Hz, m- C_6H_5), 129.0 (s, p- C_6H_5), 133.2 (d, J_{PC} 19 Hz, $o-C_6H_5$), 138.3 (d, J_{PC} 15.5 Hz, $i-C_6H_5$). ³¹P{¹H}-NMR: $\delta_{\rm P}$ –13.5 (s, $J_{\rm SiP}$ 18.0 Hz). ²⁹Si{¹H}-NMR: $\delta_{\rm Si}$ –12.9. Anal. Found: C, 76.78; H, 9.32. Calcd for C₂₇H₃₉PSi: C, 76.73; H, 9.30.

 $Me_2PhSiC \equiv CCH_2P(SiMe_3)_2$ (14). In a manner similar to that described for 8, using HP(SiMe₃)₂ (1.04 g, 5.84 \times 10^{-3} mol), ^{*n*}BuLi (2.5 M, 2.3 cm³, 5.75 × 10^{-3} mol) and 3 $(1.25 \text{ g}, 6.00 \times 10^{-3} \text{ mol})$. Isolated as orange oil. Yield: 1.84 g, 90%. NMR (C₆D₆, 30 °C): ¹H-NMR: δ_H 0.25 (d, J_{PH} 4.8 Hz, 18H, $2 \times Si(CH_3)_3$), 0.44 (s, $2 \times SiCH_3$), 2.43 (d, J_{PH} 1.3 Hz, 2H,

 CH_2P), 7.20–7.25 (m, 3H, m/p-SiC₆ H_5), 7.70–7.74 (m, 2H, o-SiC₆ H_5). ¹³C{¹H}-NMR: $\delta_{\rm C}$ -0.6 (s, SiCH₃), 1.1 (d $J_{\rm PC}$ 12.5 Hz, $P{SiCH}_{3}_{2}$, 5.5 (d, J_{PC} 23 Hz, $CH_{2}P$), 83.3 (d, J_{PC} 4 Hz, $C = CCH_2P$, 109.3 (br., $C = CCH_2P$), 128.2 (s, $m - C_6H_5$), 129.6 (s, $p-C_6H_5$), 134.2 (s, $o-C_6H_5$), 137.7 (s, $i-C_6H_5$). ³¹P{¹H}-NMR: $\delta_{\rm P}$ -84.4 (s, 5%), -158.9 (s, 14, 93%), -252.0 (s, 2%). ²⁹Si{¹H}-NMR: δ_{Si} –23.0 (SiMe₂Ph), 3.42 (P(SiMe₃)₂). Anal. Found: C, 58.29; H, 8.86. Calcd for C₁₇H₃₁PSi₃: C, 58.23; H, 8.91.

 $\{(Et_2N)_2P\}C(Ph)=C=CH_2$ (15). To a THF suspension (ca. 30 cm³) of excess, pre-activated magnesium turnings containing HgCl₂ (0.100 g, 3.68×10^{-4} mol) as initiator, was added drop-wise PhC=CCH₂Cl (1.00 g, 6.65×10^{-3} mol) as solution in THF (ca. 10 cm³); 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 (Et₂N)₂PCl (1.39 cm³, 6.65 \times 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 (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.89 (t, ${}^{3}J_{\rm HH}$ 7.0 Hz, 12H, CH₃), 3.05 (q, ${}^{3}J_{\rm HH}$ 7.0 Hz, 8H, CH_2 , 4.69 (d, J_{PH} 7.0 Hz, 2H, = CH_2), 7.11–7.15 (m, 3H, m/p- C_6H_5), 7.63–7.59 (m, 2H, o- C_6H_5). ¹³C{¹H}-NMR: δ_C 14.8 (d, ${}^{3}J_{PC}$ 3.2 Hz, CH₃), 43.4 (d, ${}^{3}J_{PC}$ 17.4 Hz, NCH₂), 75.0 (s, =CH₂), 105.9 (d, JPC 13.5 Hz, i-C6H5), 137.4 (d, JPC 19 Hz, PhC- $\{P(NEt_2)_2\} = C$, 127.8 (s, *o*-*C*₆H₅), 127.9 (overlapped *m*-/*p*-*C*₆H₅), 209.9 (d, J_{PC} 11.4 Hz, =C=). ³¹P{¹H}-NMR: δ_P 91.0 (s, br, 74%). Propargyl tautomer (5%): NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 1.02 (t, ${}^{3}J_{\rm HH}$ 7.2 Hz, 12H, CH₃), 2.71 (d, $J_{\rm PH}$ 5.8 Hz, 2H, CH₂P), 2.87 (m, 8H, NCH₂). ¹³C 1 H-NMR: δ_{C} 14.0 (d, ³ J_{PC} 5 Hz, CH₃), 19.8 (m, CH₂P), 42.8 (d, ³J_{PC} 17 Hz, NCH₂), 81.5 (s, C=CH₂P), 87.6 (s, C=CH₂P). ³¹P{¹H}-NMR: δ_{P} 83.2 (s, br, 5%).

{(Et₂N)(Cl)P}C(Ph)=C=CH₂ (16). To an ethereal solution of 15 held at -78 °C was added drop-wise two equivalent of HCl (1 M 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 (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.81 (t, ${}^{3}J_{\rm HH}$ 6.9 Hz, 6H, CH₃), 2.94 (q, ${}^{3}J_{\rm HH}$ 7.4 Hz, 4H, CH₂), 4.89 (dd, ${}^{2}J_{HH}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, =CH₂), 4.93 (dd, ${}^{2}J_{\rm HH}$ 13.0 Hz, $J_{\rm PH}$ 5.7 Hz, 1H, =CH₂), 6.94–7.02 (m, 1H, p-C₆H₅), 7.11 (7, J_{HH} 7.8 Hz, 2H, m-C₆H₅), 7.50 (d, J_{HH} 7.8 Hz, 2H, o-C₆ H_5). ¹³C{¹H}-NMR: δ_C 13.9 (d, ³ J_{PC} 6.2 Hz, <u>C</u>H₃), 43.9 (d, ${}^{3}J_{PC}$ 13 Hz, NCH₂), 77.6 (s, =CH₂), 105.3 (d, J_{PC} 40 Hz, Ph<u>C</u>{PCl(NEt₂)}=C), 135.4 (d, J_{PC} 24 Hz, i-C₆H₅), 127.6 (d, J_{PC} 1.5 Hz, $o-C_6H_5$), 127.98 (s, $p-C_6H_5$) 128.9 (s, $m-C_6H_5$), 210.6 (d, J_{PC} 8.4 Hz, =<u>C</u>=). ³¹P{¹H}-NMR: δ_{P} 122.0 (s, br, 77%).

Platinum and palladium complexes

In a typical procedure, to a suspension of the $[MCl_2]_n$ (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(PPh₂CH₂C≡CSnBu₃)₂Cl₂] (17). Yield: 78%. NMR (C₆D₆, 30 °C): ¹H-NMR: δ_H 0.81 (m, 12H, SnCH₂), 0.88 (m, 18H, CH₃), 1.27 (m, 12H, CH₂), 1.44 (m, 12H, CH₂), 3.78 (m, *J*_{PH} ~ 5 Hz, 4H, CH₂P), 6.90-7.01 (m, 12H, *m/p*-C₆H₅), 7.63-7.77 (m, 8H, *o*-C₆H₅). ¹³C{¹H}-NMR: δ_C 11.1 (s, <u>C</u>H₂Sn, ¹*J*_{117SnC} 365 Hz, ¹*J*_{119SnC} 381 Hz), 13.9 (s, <u>C</u>H₃), 23.8 (d, ¹*J*_{PC} 27 Hz, <u>C</u>H₂PPh₂), 27.4 (s, <u>C</u>H₂CH₂Sn, *J*_{117SnC} 58.8, *J*_{119SnC} 60.7 Hz), 29.2 (s, *J*_{SnC} 10 Hz, CH₃<u>C</u>H₂), 88.7 (m, <u>C</u>=CCH₂PPh₂), 104.0 (m, C≡<u>C</u>CH₂PPh₂), 127.9 (br, *m*-P(C₆H₅)₂), 129.a (br, i-P(C₆H₅)₂), 131.1 (s, *p*-P(C₆H₅)₂), 134.4 (m, *o*-P(C₆H₅)₂). ³¹P{¹H}-NMR: δ_P 6.0 (s, *J*_{PtP} 3618 Hz). ¹¹⁹Sn{¹H}-NMR: δ_{Sn} -68.2 (m). ¹⁹⁵Pt{¹H}-NMR: δ_{Pt} -4407 (t, *J*_{PtP} 3618 Hz). Anal. Found: C, 50.23; H, 5.95. Calcd for C₅₄H₇₈Cl₂P₂PtSn₂ Si: C, 50.18; H, 6.08.

cis-[Pt(PPh₂CH₂C≡CSiPrⁱ₃)₂Cl₂] (18). Yield: 86%. NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.84 (sept., ³*J*_{HH} 7.1 Hz, 6H, SiC*H*), 0.93 (d, ³*J*_{HH} 7.1 Hz, 36H, C*H*₃), 3.87 (d, *J*_{PC} 10.8 Hz, 4H, CH₂P), 6.82–6.88 (m, 8H, *m*-P(C₆H₅)₂), 6.91–6.95 (m, 4H, *p*-P(C₆H₅)₂), 7.51–7.57 (m, 8H, *o*-P(C₆H₅)₂). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 11.6 (s, Si<u>C</u>H), 18.8 (s, <u>C</u>H₃), 23.9 (d, *J*_{PC} 40 Hz, <u>C</u>H₂P), 85.8 (m, <u>C</u>=CCH₂P), 101.9 (m, C≡<u>C</u>CH₂P), 127.9 (m, *m*-C₆H₅), 131.1 (s, *p*-C₆H₅), 134.2 (m, *o*-C₆H₅), 134.6 (m, i-C₆H₅). ³¹P{¹H}-NMR: $\delta_{\rm P}$ 5.83 (s, *J*_{PtP} 3614 Hz). ²⁹Si{¹H}-NMR: $\delta_{\rm Si}$ −2.98. ¹⁹⁵Pt{¹H}-NMR: $\delta_{\rm Pt}$ −4399 (t, *J*_{PtP} 3614 Hz). Anal. Found: C, 56.03; H, 6.39. Calcd for C₄₈H₆₆Cl₂P₂PtSi₂: C, 56.13; H, 6.48.

cis-[Pt(PPh₂CH₂C=CSiPr^{*n*}₃)₂Cl₂] (19). Yield: 78%. NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.41 (m, 12H, SiCH₂), 0.93 (t, ³J_{HH} 7.2 Hz, 18H, CH₃), 1.23 (m, 12H, CH₂CH₂Si), 3.81 (d, J_{PH} 10 Hz, 4H, CH₂P), 6.86–6.93 (m, 8H, *m*-P(C₆H₅)₂), 6.94–7.00 (m, 4H, *o*-P(C₆H₅)₂), 7.54–7.62 (m, 8H, *o*-P(C₆H₅)₂). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 16.3 (s, <u>C</u>H₂Si, ¹J_{SiC} 55 Hz,), 17.8 (s, <u>C</u>H₃), 18.5 (s, <u>C</u>H₂CH₂Si, ²J_{SiC} 7.4 Hz), 23.9 (d, J_{PC} 46 Hz, <u>C</u>H₂P), 88.0 (m, <u>C</u>=CCH₂Cl), 101.4 (m, C=<u>C</u>CH₂P), 128.2 (m, *m*-C₆H₅), 129.0 (s, *p*-C₆H₅), 131.1 (s, *o*-C₆H₅), 134.3 (m, i-C₆H₅). ³¹P{¹H}-NMR: $\delta_{\rm P}$ 5.95 (s, J_{PtP} 3614 Hz). ²⁹Si{¹H}-NMR: $\delta_{\rm Si}$ –13.9. ¹⁹⁵Pt{¹H}-NMR: $\delta_{\rm Pt}$ -4403 (t, J_{PtP} 3614 Hz). Anal. Found: C, 56.13; H, 6.45. Calcd for C₄₈H₆₆Cl₂P₂PtSi₂: C, 56.13; H, 6.48.

trans-[Pd(PPh₂CH₂C≡CSiPrⁱ₃)₂Cl₂] (20). Yield: 88%. NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.90 (m, 6H, SiC*H*), 0.97 (d, ³*J*_{HH} 6.7 Hz, 36H, C*H*₃), 3.74 (t, *J*_{PH} 3.9 Hz, 2H, CH₂P), 7.05–7.11 (m, 12H, *m/p*-P(C₆*H*₅)₂), 7.92–7.98 (m, 8H, *o*-P(C₆*H*₅)₂). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 11.6 (s, Si<u>C</u>H), 18.8 (s, <u>C</u>H₃), 18.9 (t, *J*_{PC} 13.6 Hz, <u>C</u>H₂P), 85.8 (d, *J*_{PC} 2.9 Hz, <u>C</u>=CCH₂Cl), 101.3 (d, *J*_{PC} 5.6 Hz, C≡<u>C</u>CH₂P), 128.0 (m, *m*-C₆H₅), 129.3 (t, *J*_{PC} 24 Hz, i-C₆H₅), 130.9 (s, *p*-C₆H₅), 134.6 (t, *J*_{PC} 6 Hz, *o*-C₆H₅). ³¹P{¹H}-NMR: $\delta_{\rm P}$ 16.0 (s). ²⁹Si{¹H}-NMR: $\delta_{\rm Si}$ –2.75. Anal. Found: C, 61.07; H, 6.94. Calcd for C₄₈H₆₆Cl₂P₂PdSi₂: C, 61.43; H, 7.09.

trans-[Pd(PPh₂CH₂C=CSiPrⁿ₃)₂Cl₂] (21). Yield: 89%. NMR (C₆D₆, 30 °C): ¹H-NMR: $\delta_{\rm H}$ 0.45 (m, 12H, SiCH₂), 0.91 (t, ³J_{HH} 7.0 Hz, 18H, CH₃), 1.25 (m, 12H, CH₂CH₂Si), 3.75 (t, J_{PH} 4 Hz, 4H, CH₂P), 7.03–7.12 (m, 12H, *m*/*p*-P(C₆H₅)₂), 7.89–7.98 (m, 8H, *o*-P(C₆H₅)₂). ¹³C{¹H}-NMR: $\delta_{\rm C}$ 16.4 (s, <u>C</u>H₂Si, ¹J_{SiC} 57 Hz,), 17.8 (s, <u>C</u>H₃), 18.5 (s, <u>C</u>H₂CH₂Si, ²J_{SiC} 6 Hz), 18.8 (t, J_{PC} 13.5 Hz, <u>C</u>H₂P), 97.9 (d, J_{PC} 2.8 Hz, <u>C</u>=CCH₂Cl), 100.8 (d, J_{PC} 4.9 Hz, C=<u>C</u>CH₂P), 128.2 (m, *m*-C₆H₅), 129.2 (t, J_{PC} 24 Hz, i-C₆H₅), 130.9 (s, *p*-C₆H₅), 134.7 (t, J_{PC} 5.5 Hz, *o*-C₆H₅). ³¹P{¹H}-NMR: δ_P 15.9 (s, J_{SiP} 23 Hz). ²⁹Si{¹H}-NMR: δ_{Si} −13.8. Anal. Found: C, 61.08; H, 7.00. Calcd for C₄₈H₆₆Cl₂P₂PdSi₂: C, 61.43; H, 7.09.

cis-/trans-Isomerisation of [Pt(PPh₂CH₂C≡CSiPrⁿ₃)₂Cl₂] (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: δ_H 0.46 (m, 12H, SiCH₂), 0.92 (t, ³J_{HH} 7.3 Hz, 18H, CH₃), 1.25 (m, 12H, CH₂CH₂Si), 3.77 (t, J_{PH} 4.3 Hz, 4H, CH₂P), 7.03–7.13 (m, 12H, *m/p*-P(C₆H₅)₂), 7.95–8.01 (m, 8H, *o*-P(C₆H₅)₂). ¹³C{¹H}-NMR: δ_C 16.4 (s, <u>C</u>H₂Si), 17.8 (s, <u>C</u>H₃), 18.5 (s, <u>C</u>H₂CH₂Si), 23.8 (t, J_{PC} 24 Hz, <u>C</u>H₂P), 88.0 (m, <u>C</u>=CCH₂Cl), 101.4 (t, J_{PC} 6.3 Hz, C≡<u>C</u>CH₂P), 128.2 (m, *m*-C₆H₅), 128.8 (s, *p*-C₆H₅), 130.9 (s, *o*-C₆H₅), 134.7 (t, J_{PC} 6.0 Hz, i-C₆H₅). ³¹P{¹H}-NMR: δ_P 11.5 (s, J_{PtP} 2601 Hz). ²⁹Si{¹H}-NMR: δ_{Si} −13.2. ¹⁹⁵Pt{¹H}-NMR: δ_{Pt} −3993 (t, J_{PtP} 2601 Hz).

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