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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 = $^nBu_3Sn$, 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 $ClP(NEt_2)_2$ 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,[3] Me,[4] Ph;[5] R = Cy, ^{i}Pr, 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,[8] Et,[8] Cl[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′ = ^{n}Bu;[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-conjugates[15] 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 $[Cp_2Rh_2(CO)(\mu\text{–}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)\{PPh_2CH_2C{\equiv}CMe\}CO_2(CO)_6]$, obtained by reaction of $[Co_2(CO)_8]$ with the dirhodium complex $[Cp_2Rh_2(CO)(\mu\text{–}\eta^1{:}\eta^1\text{-}CF_3C_2CF_3)\{PPh_2CH_2C{\equiv}CMe\}]$.[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] ‡ 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 $[\{HC{\equiv}CCH_2Ph_2P\}Ru(CO)_3(\mu\text{-}PPh_2)Co(CO)_3]$.[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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†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.

are obtained from the respective diphenylphosphane complexes, *via in situ* deprotonation (BuLi) and quenching with the appropriate propargylic bromide; [CpMo{κ^2-*O*,*P*-P(O)Mes*-(CH$_2$C≡CH)}] is similarly prepared, but without need for base.[24] Finally, [W(CO)$_5${PPh(OMe)C(H)Me(C≡CSi^{i}Pr$_3$)}] was obtained upon methanolysis of the putative phosphaalkene [W(CO)$_5${P(Ph)=CMe(C≡CSi^{i}Pr$_3$)}].[25]

Notably, no complexes of the group 10 metals have been described, though the formally related diphosphane-bridged complexes [L$_n$M{μ–η^1:η^1-PPh$_2$CH$_2$C≡CCH$_2$PPh$_2$}]$_2$ (L$_n$M = Cl$_2$Pt, (OC)$_2$Ni) have been reported,[26] alongside examples with other metals (L$_n$M = 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 [{η^2-*C*,*C*-Mo(CO)$_4$(η^2-*P*,*P*-PPh$_2$CH$_2$C≡CCH$_2$PPh$_3$)}$_3$Mo(CO)], has also been described.[27]

We have recently been interested in the synthesis and study of reactive and functional phosphanes[28] 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 R$_2$P-(CH$_2$C≡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$_2$P(CH$_2$C≡CER$_3$) (E = Si, Sn), which we describe herein, along with attempts to obtain '(Et$_2$N)$_2$P' 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

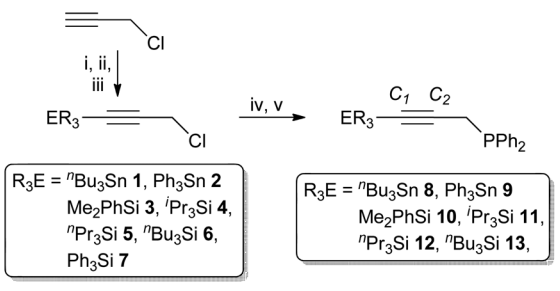
Phosphane synthesis

The silyl and stannyl chloropropargyl precursors R$_3$EC≡CCH$_2$Cl were prepared following a modified literature procedure (Scheme 1),[30] *via* the low-temperature (−78 °C) lithiation of HC≡CCH$_2$Cl, quenched with R$_3$SnCl (**1** and **2**) or R$_3$SiCl (**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 ^{1}H 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 (^{1}H–X HMBC; X = ^{119}Sn, ^{29}Si); for the stannanes the $^4J_{SnH}$ coupling (~10 Hz) is also large enough to resolve tin satellites. The ^{13}C{^{1}H}-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 LiPPh$_2$ in ether (formed by *in situ* lithiation of HPPh$_2$ with ^{n}BuLi) and the mixtures stirred overnight to afford the propargyl phosphanes Ph$_2$P(CH$_2$C≡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 ^{n}Bu$_4$Sn (1 : 4 of **8**) or ^{n}BuPh$_3$Sn (1 : 1 with **9**), presumably due to metathesis of **1** and **2** with residual ^{n}BuLi, 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 (^{1}H–X HMBC), with **8** and **9** also allowing for resolution of ^{119}Sn satellites ($^4J_{SnP}$ ~ 14 Hz) in the ^{31}P{^{1}H} spectra. The ^{119}Sn spectra of **8** and **9** indicate the presence of ^{n}Bu$_4$Sn (δ_{Sn} −12.0)[35] and ^{n}BuPh$_3$Sn (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 HPCy$_2$ as the only phosphorus-containing product, which presumably reflects the greater basicity and steric bulk of 'PCy$_2$' (*cf.* 'PPh$_2$'), favouring proton-abstraction



Scheme 1 Reagents and conditions: (i) ^{n}BuLi, −78 °C, Et$_2$O, 30 min; (ii) R$_3$ECl, −78 °C, 30 min; (iii) warm to ambient, stir 18 h; (iv) LiPPh$_2$, −78 °C, Et$_2$O, 30 min; (v) r.t. 18 h.

Table 1 Selected NMR spectroscopic data for proparylphosphanes **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]

[a] As C$_6$D$_6$ solutions. [b] Couplings in Hz.

from the chloropropargyls over S_N2 substitution. In contrast, reactions with $LiP(SiMe_3)_2$ did afford species consistent with the desired propargylphosphanes, though in admixture with several significant contaminants, which defied separation or characterisation. Nonetheless, $Me_2PhSiC{\equiv}CCH_2P(SiMe_3)_2$ (**14**) was obtained as the primary product (92% by $^{31}P\{^1H\}$-NMR) in admixture with $P(SiMe_3)_3$ (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≡CCH_2MgCl' under comparable conditions. However, our efforts to quench this reagent with $(Et_2N)_2PCl$ led to an unexpected outcome.

Formation of a phosphino-allene

The addition of freshly prepared 'PhC≡CCH_2MgCl' to a cooled (−78 °C) THF solution of $(Et_2N)_2PCl$ affords, after work-up, a deep red oil comprising one predominant phosphorus-containing product (**15**; 75%). The spectroscopic features of **15** confirm the presence of a '$(Et_2N)_2P$' moiety (δ_P 90.9; *cf.* $PhP(NEt_2)_2$ 97.9,[38] $H_2C{=}C(H){-}P(NEt_2)_2$ 89.9 [39]), 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≡CCH_2Cl (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) 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 phosphinoalleneś (Table 2) described previously.[14,41] We thus confidently formulate **15** as $(Et_2N)_2PC(Ph){=}C{=}CH_2$ (Scheme 2).

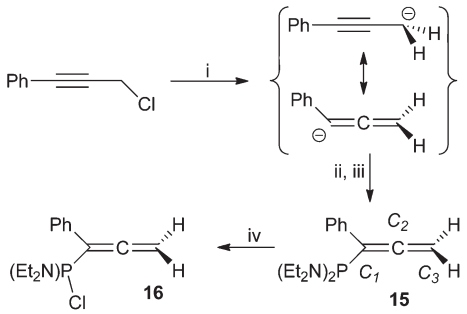
The reaction of propargyl Grignard reagents with R_2PCl has been noted to afford mixtures that include allenyl-phosphanes, their proportion being dependent on the nature of 'R'.[42] However, this is to our knowledge the first example of an allenylphosphane being obtained as the major product (>70%) in 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 sp^2, rather than sp^3 centre) or be the result of conjugate addition, favoured by the relatively 'soft' $ClP(NEt_2)_2$ electrophile, as compared, for instance, with the notionally 'harder' PCl_3, with which we encountered significantly greater complexity, yielding a largely intractable mixture.

ś 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.

Table 2 Selected ^1H and $^{13}C\{^1H\}$-NMR spectroscopic 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_3Si)PC(Me)=C=CH_2	4.55	72.35	206.4
Mes (Cl)PC(Me)=C=CH_2	4.57	74.65	205.5
$Ph_2PC(H){=}C{=}CH_2$	—	71.7	213.2
$Ph_2PC(Me){=}C{=}CH_2$	—	70.7	210.3
$Ph_2PC(H){=}C{=}C(Me)_2$	—	—	209.6

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

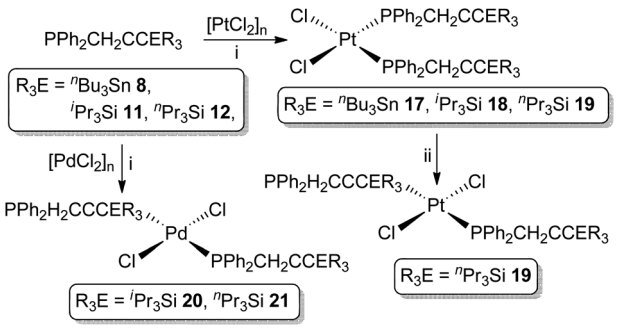


Scheme 2 Reagents and conditions: (i) Et_2O, $HgCl_2$ (5 mol%), Mg, △, 4 h; (ii) $(Et_2N)_2PCl$, −78 °C, 30 min; (iii) r.t. 18 h; (iv) 2 equiv. HCl/Et_2O.

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 $(Et_2N)(Cl)PC(Ph){=}C{=}CH_2$ (**16**), as evidenced by the ^1H NMR spectrum, which indicates loss of one diethylamino moiety (Et_2N *vs.* Ph resonances) and emergence of diasterotopicity for the methylenic '=CH_2'. The phosphorus resonance of **16** is appreciably deshielded from that of **15**, consistent with replacement of NEt_2 by Cl (δ_P 122; *cf.* $Ph(Cl)PNEt_2$ 142.1[43]). 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 '=CH_2' protons (δ_H 4.63, d, J_{PH} 3 Hz). However, the ^{31}P shift (δ_P 58.7, t, J_{PH} 3 Hz) seems inconsistent with a species of the type $RPCl_2$; moreover, several other, unidentified, species are apparent in both the ^1H and ^{31}P-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.



Scheme 3 Reagents and conditions: (i) CH_2Cl_2, 12 h; (ii) C_6D_6, *hν*, 30 min.

The propargylphosphanes **8**, **11** and **12** react with $[PtCl_2]_n$, as a suspension in CH_2Cl_2, to afford exclusively the complexes *cis*-$[Pt\{PPh_2(CH_2C{\equiv}CER_3)\}_2Cl_2]$ (ER_3 = ^{n}Bu$_3$Sn **17**, ^{i}Pr$_3$Si **18**, ^{n}Pr$_3$Si **19**, Scheme 3) in excess of 75% isolated yield. For the silanes, palladium analogues (ER_3 = ^{i}Pr$_3$Si **20**, ^{n}Pr$_3$Si **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 ($\Delta\delta_P \sim +20$). 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 ^{1}H 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*-$[Pt(PR_3)_2X_2]$, 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 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 $HPPh_2$ were obtained from Sigma-Aldrich, purified by appropriate methods and degassed (freeze–thaw) before use. ^{n}BuLi (2.5 M in hexanes) was obtained from Sigma-Aldrich and titrated to establish concentration. Precious metal salts ($PtCl_2$, $PdCl_2$) were obtained from STREM and used as supplied. $HP(SiMe_3)_2$ was prepared by literature procedure.[44] Deuterated solvents were supplied by Goss Scientific and purified by refluxing with potassium (hydrocarbon) or CaH_2 (chlorinated) for 3 days prior to use, being vacuum transferred and stored under inert atmosphere. Unless otherwise stated, NMR spectra were recorded on a Varian VNMRS 400 (^{1}H, 399.50 MHz; ^{13}C, 100.46 MHz; ^{31}P, 161.71 MHz; ^{29}Si, 79.37 MHz; ^{119}Sn, 148.97 MHz; ^{195}Pt, 85.53 MHz) or VNMRS 500 (^{1}H 499.91 MHz; ^{13}C, 125.72 MHz) spectrometer. All spectra were referenced to Me_4Si, 85% H_3PO_4, Me_4Sn or K_2PtCl_6 as appropriate. Carbon-13 NMR data were assigned with recourse to the 2D (HSQC, HMBC) spectra; detailed connectivity and ^{29}Si chemical shifts were assessed using ^{1}H–X HMBC spectra (X = ^{29}Si; ^{119}Sn; ^{31}P). Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

Synthesis

^{n}Bu$_3$SnC≡CCH$_2$Cl (1). In a modification of literature procedure, a solution of propargyl chloride (2.24 g, 3.0×10^{-2} mol) in THF (*ca.* 20 cm^3) was cooled to −78 °C before the drop-wise addition of ^{n}BuLi (2.5 M, 6.0 cm^3, 1.5×10^{-2} mol). The mixture was stirred for 30 min., after which time ^{n}Bu$_3$SnCl (4.40 cm^3, 1.5×10^{-2} mol) as solution in THF (*ca.* 10 cm^3) was added drop-wise, resulting in formation of a yellow solution.

The mixture was held at −78 °C for a further 30 min. with continued stirring before being allowed to warm to ambient temperature overnight. Solvent and excess $HC{\equiv}CCH_2Cl$ were removed under reduced pressure and the product extracted with pentane, stripped of volatiles and dried *in vacuo* as yellow oil. Yield: 5.09 g, 94%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.91 (t, $^3J_{HH}$ 7.3 Hz, 9 H, CH_3), 0.97 (t, $^3J_{HH}$ 6 Hz, J_{SnH} 54 Hz, 6H, CH_2Sn), 1.34 (m, 6H, CH_3CH_2), 1.61 (m, 6H, CH_2CH_2Sn), 3.70 (s, J_{SnH} 9.6 Hz, 2H, CH_2Cl). ^{13}C{^{1}H}-NMR: δ_C 11.3 (s, $\underline{C}H_2$Sn, $^1J_{117SnC}$ 365 Hz, $^1J_{119SnC}$ 382 Hz), 13.9 (s, $\underline{C}H_3$), 27.3 (s, $\underline{C}H_2CH_2$Sn, $^2J_{117SnC}$ 58 Hz, $^2J_{119SnC}$ 60 Hz), 29.3 (s, $CH_3\underline{C}H_2$, $^3J_{SnC}$ 24 Hz), 31.2 (s, J_{SnC} 8 Hz, CH_2Cl), 91.1 (s, $\underline{C}{=}CCH_2Cl$), 105 (s, $C{\equiv}\underline{C}CH_2Cl$). ^{119}Sn{^{1}H}-NMR: δ_{Sn} −65.1. Anal. Found: C, 49.44; H, 7.86. Calcd for $C_{15}H_{29}ClSn$: C, 49.56; H, 8.04.

$Ph_3SnC{\equiv}CCH_2Cl$ (2). As for **1**, using propargyl chloride (2.03 g, 2.7×10^{-2} mol), ^{n}BuLi (2.5 M, 5.4 cm^3, 1.3×10^{-2} mol) and Ph_3SnCl (5.25 g, 1.3×10^{-2} mol). Isolated as yellow oil. Yield: 3.96 g, 72%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 3.67 (s, J_{SnH} 10.5 Hz, 2H, CH_2Cl), 7.10–7.20 (m, 9H, *m*/*p*-C_6H_5), 7.60–7.65 (m, J_{SnH} 55 Hz, 6H, *o*-C_6H_5). ^{13}C{^{1}H}-NMR: δ_C 30.8 (s, J_{SnC} 10 Hz, CH_2Cl), 88.5 (s, $\underline{C}{=}CCH_2Cl$), 106.8 (s, $C{\equiv}\underline{C}CH_2Cl$), 128.8 (s, *p*-$\underline{C}_6H_5$), 129.5 (s, *m*-$\underline{C}_6H_5$), 130.1 (s, i-$\underline{C}_6H_5$), 136.7 (s, *o*-$\underline{C}_6H_5$). ^{119}Sn{^{1}H}-NMR: δ_{Sn} −169.5. Anal. Found: C, 59.63; H, 4.12. Calcd for $C_{20}H_{17}ClSn$: C, 59.55; H, 4.05.

$Me_2PhSiC{\equiv}CCH_2Cl$ (3). As for **1**, using propargyl chloride (3.73 g, 5.0×10^{-2} mol), ^{n}BuLi (2.5 M, 10.0 cm^3, 2.5×10^{-2} mol) and $Me_2PhSiCl$ (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 (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.32 (s, J_{SiH} 8 Hz, 6 H, SiCH_3), 3.21 (s, 2H, CH_2Cl), 7.14–7.18 (m, 3H, *m*/*p*-C_6H_5), 7.55–7.59 (m, 2H, *o*-C_6H_5). ^{13}C{^{1}H}-NMR: δ_C −1.2 (s, Si$\underline{C}H_3$, $^1J_{SiC}$ 58 Hz,), 30.5 (s, CH_2Cl), 90.1 (s, $\underline{C}{=}CCH_2Cl$), 102.0 (s, $C{\equiv}\underline{C}CH_2Cl$). ^{29}Si{^{1}H}-NMR: δ_{Si} −21.6. Anal. Found: C, 63.18; H, 6.14. Calcd for $C_{11}H_{13}ClSi$: C, 63.29; H, 6.28.

$^i Pr_3SiC{\equiv}CCH_2Cl$ (4). As for **1**, using propargyl chloride (6.24 g, 8.4×10^{-2} mol), ^{n}BuLi (2.5 M, 16.8 cm^3, 4.2×10^{-2} mol) and $^i Pr_3SiCl$ (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 (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 1.03 (m,^{3} H, SiCH), 1.11 (d, $^3J_{HH}$ 6.5 Hz, 18H, CH_3), 3.53 (s, 2H, CH_2Cl). ^{13}C{^{1}H}-NMR: δ_C 11.5 (s, Si$\underline{C}$H, $^1J_{SiC}$ 57 Hz), 18.8 (s, $\underline{C}H_3$), 30.6 (s, CH_2Cl), 88.4 (s, $\underline{C}{=}CCH_2Cl$), 102.7 (s, $C{\equiv}\underline{C}CH_2Cl$). ^{29}Si{^{1}H}-NMR: δ_{Si} −1.68. Anal. Found: C, 62.38; H, 9.85. Calcd for $C_{12}H_{23}ClSi$: C, 62.43; H, 10.04.

$^n Pr_3SiC{\equiv}CCH_2Cl$ (5). As for **1**, using propargyl chloride (1.62 g, 2.2×10^{-2} mol), ^{n}BuLi (2.5 M, 4.35 cm^3, 1.1×10^{-2} mol) and $^n Pr_3SiCl$ (2.09 g, 1.1×10^{-2} mol). Obtained as orange oil. Yield: 2.33 g, 93%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.60 (m, 6 H, SiCH_2), 0.99 (t, $^3J_{HH}$ 7.2 Hz, 9H, CH_3), 1.47 (m, 6H, CH_3CH_2), 3.55 (s, 2H, CH_2Cl). ^{13}C{^{1}H}-NMR: δ_C 16.2 (s, $\underline{C}H_2$Si, $^1J_{SiC}$ 56 Hz,), 17.9 (s, $\underline{C}H_3$), 18.4 (s, $\underline{C}H_2CH_2$Si, $^2J_{SiC}$ 6 Hz), 30.7 (s, CH_2Cl), 90.2 (s, $\underline{C}{=}CCH_2Cl$), 101.8 (s, $C{\equiv}\underline{C}CH_2Cl$). ^{29}Si{^{1}H}-NMR: δ_{Si} −13.0. Anal. Found: C, 62.87; H, 9.79. Calcd for $C_{12}H_{23}ClSi$: C, 62.43; H, 10.04.

$^n Bu_3SiC{\equiv}CCH_2Cl$ (6). As for **1**, using propargyl chloride (1.92 g, 2.5×10^{-2} mol), ^{n}BuLi (2.5 M, 5.2 cm^3, 1.3×10^{-2} mol) and $^n Bu_3SiCl$ (3.02 g, 1.29×10^{-2} mol). Obtained as orange oil. Yield: 3.08 g, 88%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.67 (m, 6H, SiCH_2), 0.92 (t, $^3J_{HH}$ 7.3 Hz, 9H, CH_3), 1.38 (m, 6H, CH_2CH_2Si), 1.46 (m, 6H, $CH_3CH_2CH_2$), 3.56 (s, 2H, CH_2Cl). ^{13}C{^{1}H}-NMR: δ_C 13.3 (s, $\underline{C}H_2$Si, $^1J_{SiC}$ 57 Hz), 14.0 (s, $\underline{C}H_3$), 26.5 (s, $CH_3\underline{C}H_2CH_2$), 26.8 (s, $\underline{C}H_2CH_2$Si, J_{SiC} 6 Hz), 30.7 (s, CH_2Cl), 90.3 (s, $\underline{C}{=}CCH_2Cl$), 101.8 (s, $C{\equiv}\underline{C}CH_2Cl$). ^{29}Sn{^{1}H}-NMR: δ_{Si} −11.3. Anal. Found: C, 66.39; H, 10.02. Calcd for $C_{15}H_{29}ClSi$: C, 66.01; H, 10.71.

$Ph_3SiC{\equiv}CCH_2Cl$ (7). As for **1**, using propargyl chloride (1.00 g, 1.03×10^{-2} mol), ^{n}BuLi (2.5 M, 2.7 cm^3, 6.7×10^{-3} mol) and $^n Bu_3SiCl$ (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 (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 3.49 (s, 2H, CH_2Cl), 7.14–7.16 (m, 9H, *m*/*p*-C_6H_5), 7.73–7.78 (m, 6H, *o*-C_6H_5). ^{13}C{^{1}H}-NMR: δ_C 30.4 (s, CH_2Cl), 87.6 (s, $\underline{C}{=}CCH_2Cl$), 104.9 (s, $C{\equiv}\underline{C}CH_2Cl$), 128.4 (s, *p*-$\underline{C}_6H_5$), 130.4 (s, *m*-$\underline{C}_6H_5$), 133.4 (s, i-$\underline{C}_6H_5$), 136.0 (s, *o*-$\underline{C}_6H_5$). ^{29}Sn{^{1}H}-NMR: δ_{Si} −28.8. Anal. Found: C, 75.68; H, 5.11. Calcd for $C_{21}H_{17}ClSi$: C, 75.77; H, 5.15.

$^n Bu_3SnC{\equiv}CCH_2PPh_2$ (8). To an ethereal solution (*ca.* 20 cm^3) of $HPPh_2$ (0.375 g, 2.02×10^{-3} mol) held at −78 °C was added drop-wise ^{n}BuLi (2.5 M, 0.808 cm^3, 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 cm^3) was then added drop-wise and the mixture maintained at −78 °C while stirring for 30 min. The mixture was allowed to warm to ambient temperature while stirring overnight. Volatiles were removed under reduced pressure and the product extracted with pentane; the solvent was removed and the product dried *in vacuo* to afford yellow oil. Yield: 0.800 g (4 : 1 **8** : $SnBu_4$). NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.93 (m, CH_3), 1.36 (m, 12H, 2 × CH_2), 1.58 (m, 6H, CH_2), 2.87 (d, J_{PH} 1.6 Hz, J_{117SnC} 8.7 Hz, J_{119SnC} 12.4 Hz, 2H, CH_2P), 7.02–7.13 (m, 6H, *m*/*p*-C_6H_5), 7.43–7.51 (m, 4H, *o*-C_6H_5). ^{13}C{^{1}H}-NMR: δ_C 11.3 (s, $\underline{C}H_2$Sn, $^1J_{117SnC}$ 366 Hz, $^1J_{119SnC}$ 383 Hz), 13.9 (s, $\underline{C}H_3$), 20.4 (d, $^1J_{PC}$ 18 Hz, $\underline{C}H_2PPh_2$), 27.4 (s, $\underline{C}H_2CH_2$Sn, J_{SnC} 58 Hz) 85.0 (d, J_{PC} 6 Hz, $\underline{C}{=}CCH_2PPh_2$), 106.8 (d, J_{PC} 5 Hz, $C{\equiv}\underline{C}CH_2PPh_2$), 128.6 (d, J_{PC} 6 Hz, *m*-C_6H_5), 128.9 (s, *p*-C_6H_5), 133.2 (d, J_{PC} 19 Hz, *o*-C_6H_5), 138.8 (d, J_{PC} 17 Hz, i-C_6H_5). ^{31}P{^{1}H}-NMR: δ_P −13.4 (s, J_{SnP} 14.5 Hz). ^{119}Sn{^{1}H}-NMR: δ_{Sn} −68.5 (d, J_{SnP} 14.5 Hz, 4Sn), −12.0 (s, 1Sn, Bu_4Sn).

$Ph_3SnC{\equiv}CCH_2PPh_2$ (9). As for **8**, using $HPPh_2$ (0.309 g, 1.66×10^{-3} mol), ^{n}BuLi (2.1 M, 0.80 cm^3, 1.66×10^{-3} mol) and **2** (0.876 g, 1.66×10^{-3} mol). Isolated as yellow oil. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 2.84 (d, J_{PH} 3.0 Hz, J_{SnH} 14.8 Hz, 2H, CH_2P), 6.89–7.20 (m, Ar, *m*/*p*-C_6H_5), 7.37–7.70 (m, *Ar*, 6H, *o*-C_6H_5). ^{13}C{^{1}H}-NMR: δ_C 20.2 (d, J_{PC} 21 Hz, J_{SnC} 11.9 Hz, CH_2P), 82.8 (d, J_{PC} 6 Hz, J_{SnC} 3.4 Hz, $C{=}\underline{C}CH_2P$), 109.3 (d, J_{PC} 3.4 Hz, $\underline{C}{\equiv}CCH_2P$). ^{31}P{^{1}H}-NMR: δ_P −13.2 (s). ^{119}Sn{^{1}H}-NMR: δ_{Sn} −168.4 (J_{SnP} 14.8 Hz, 1Sn), −98.3 (s, $BuSnPh_3$, 1Sn).

$Me_2PhSiC{\equiv}CCH_2PPh_2$ (10). As for **8**, using $HPPh_2$ (0.780 g, 4.24×10^{-3} mol), ^{n}BuLi (2.5 M, 1.7 cm^3, 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 (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.30 (s, 6 H, SiCH_3), 2.75 (d, J_{PH} 2.9 Hz, 2H, CH_2P), 7.01–7.09 (m, 6H,

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*-SiC_6H_5), 7.52–7.58 (m, 2H, *o*-SiC_6H_5). ^{13}C{^{1}H}-NMR: δ_C −0.6 (s, Si$\underline{C}$H$_3$), 19.9 (d, J_{PC} 21 Hz, $\underline{C}$H$_2$P), 85.7 (d, J_{PC} 5 Hz, $\underline{C}$≡CCH$_2$P), 104.9 (d, J_{PC} 4 Hz, C≡$\underline{C}$CH$_2$P), 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_{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). ^{31}P{^{1}H}-NMR: δ_P −13.5 (s). ^{29}Si{^{1}H}-NMR: δ_{Si} −22.9. Anal. Found: C, 76.89; H, 6.34. Calcd for $C_{23}H_{23}PSi$: C, 77.06; H, 6.47.

^{i}Pr$_3$SiC≡CCH$_2$PPh$_2$ (11). As for **8**, using HPPh$_2$ (0.780 g, 4.24 × 10^{-3} mol), ^{n}BuLi (2.5 M, 1.7 cm^3, 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 (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 1.01 (m, 3H, SiC*H*), 1.09 (d, $^3J_{HH}$ 6.8 Hz, 18H, CH_3), 2.75 (d, J_{PH} 2.3 Hz, 2H, CH_2P), 7.02–7.12 (m, 6H, *m*/*p*-P(C_6H_5)$_2$), 7.39–7.47 (m, 4H, *o*-P(C_6H_5)$_2$). ^{13}C{^{1}H}-NMR: δ_C 11.7 (s, Si$\underline{C}$H, $^1J_{SiC}$ 56 Hz), 18.9 (s, J_{SiC} 16 Hz, $\underline{C}$H$_3$), 19.9 (d, J_{PC} 19.5 Hz, $\underline{C}$H$_2$P), 83.3 (d, J_{PC} 5 Hz, $\underline{C}$≡CCH$_2$P), 104.7 (d, J_{PC} 4 Hz, C≡$\underline{C}$CH$_2$P), 128.7 (d, J_{PC} 6.5 Hz, *m*-C_6H_5), 129.0 (s, *p*-C_6H_5), 133.1 (d, J_{PC} 19 Hz, *o*-C_6H_5), 138.3 (d, J_{PC} 16 Hz, i-C_6H_5). ^{31}P{^{1}H}-NMR: δ_P −13.5 (s, J_{SiP} 20 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −3.03. Anal. Found: C, 75.77; H, 8.64. Calcd for $C_{24}H_{33}PSi$: C, 75.74; H, 8.74.

^{n}Pr$_3$SiC≡CCH$_2$PPh$_2$ (12). As for **8**, using HPPh$_2$ (0.650 g, 3.49 × 10^{-3} mol), ^{n}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}H-NMR: δ_H 0.58 (m, 6H, SiCH_2), 0.99 (t, $^3J_{HH}$ 7.0 Hz, 9H, CH_3), 1.42 (m, 6H, CH_2CH$_2$Si), 2.75 (d, J_{PH} 2.5 Hz, 2H, CH_2P), 7.04–7.12 (m, 6H, *m*/*p*-P(C_6H_5)$_2$), 7.40–7.46 (m, 4H, *o*-P(C_6H_5)$_2$). ^{13}C{^{1}H}-NMR: δ_C 16.7 (s, $\underline{C}$H$_2$Si, $^1J_{SiC}$ 56 Hz,), 18.0 (s, $\underline{C}$H$_3$), 18.5 (s, $\underline{C}$H$_2$CH$_2$Si, $^2J_{SiC}$ 8 Hz), 19.9 (d, J_{PC} 20 Hz, $\underline{C}$H$_2$P), 85.4 (d, J_{PC} 5.4 Hz, $\underline{C}$≡CCH$_2$P), 104.7 (d, J_{PC} 4 Hz, C≡$\underline{C}$CH$_2$P), 128.5 (d, J_{PC} 6.6 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} 16.5 Hz, i-C_6H_5). ^{31}P{^{1}H}-NMR: δ_P −13.6 (s, J_{SiP} 19.7 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −14.8. Anal. Found: C, 75.77; H, 8.59. Calcd for $C_{24}H_{33}PSi$: C, 75.74; H, 8.74.

^{n}Bu$_3$SiC≡CCH$_2$PPh$_2$ (13). As for **8**, using HPPh$_2$ (0.650 g, 4.24 × 10^{-3} mol), ^{n}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}H-NMR: δ_H 0.6.3 (m, 6H, SiCH_2), 0.93 (t, $^3J_{HH}$ 7.2 Hz, 9H, CH_3), 1.37 (m, 6H, CH_2CH$_2$Si), 1.41 (m, 6H, CH$_3$CH_2CH$_2$), 2.76 (d, J_{PH} 2.3 Hz, 2H, CH_2P), 7.04–7.13 (m, 6H, *m*/*p*-P(C_6H_5)$_2$), 7.41–7.46 (m, 4H, *o*-P(C_6H_5)$_2$). ^{13}C{^{1}H}-NMR: δ_C 13.7 (s, $\underline{C}$H$_2$Si), 14.1 (s, $\underline{C}$H$_3$), 19.9 (d, J_{PC} 20 Hz, $\underline{C}$H$_2$P), 26.7 (s, CH$_3\underline{C}$H$_2$CH$_2$), 26.9 (s, $\underline{C}$H$_2$CH$_2$Si), 85.5 (d, J_{PC} 4.8 Hz, $\underline{C}$≡CCH$_2$P), 104.0 (d, J_{PC} 4.2 Hz, C≡$\underline{C}$CH$_2$P), 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). ^{31}P{^{1}H}-NMR: δ_P −13.5 (s, J_{SiP} 18.0 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −12.9. Anal. Found: C, 76.78; H, 9.32. Calcd for $C_{27}H_{39}PSi$: C, 76.73; H, 9.30.

Me$_2$PhSiC≡CCH$_2$P(SiMe$_3$)$_2$ (14). In a manner similar to that described for **8**, using HP(SiMe$_3$)$_2$ (1.04 g, 5.84 × 10^{-3} mol), ^{n}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}H-NMR: δ_H 0.25 (d, J_{PH} 4.8 Hz, 18H, 2 × Si(CH_3)$_3$), 0.44 (s, 2 × SiCH_3), 2.43 (d, J_{PH} 1.3 Hz, 2H, CH_2P), 7.20–7.25 (m, 3H, *m*/*p*-SiC_6H_5), 7.70–7.74 (m, 2H, *o*-SiC_6H_5). ^{13}C{^{1}H}-NMR: δ_C −0.6 (s, Si$\underline{C}$H$_3$), 1.1 (d J_{PC} 12.5 Hz, P{Si$\underline{C}$H)$_3$}$_2$), 5.5 (d, J_{PC} 23 Hz, $\underline{C}$H$_2$P), 83.3 (d, J_{PC} 4 Hz, $\underline{C}$≡CCH$_2$P), 109.3 (br., C≡$\underline{C}$CH$_2$P), 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). ^{31}P{^{1}H}-NMR: δ_P −84.4 (s, 5%), −158.9 (s, **14**, 93%), −252.0 (s, 2%). ^{29}Si{^{1}H}-NMR: δ_{Si} −23.0 (SiMe$_2$Ph), 3.42 (P(SiMe$_3$)$_2$). Anal. Found: C, 58.29; H, 8.86. Calcd for $C_{17}H_{31}PSi_3$: C, 58.23; H, 8.91.

{(Et$_2$N)$_2$P}C(Ph)=C=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 PhC≡CCH$_2$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 (Et$_2$N)$_2$PCl (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}H-NMR: δ_H 0.89 (t, $^3J_{HH}$ 7.0 Hz, 12H, CH_3), 3.05 (q, $^3J_{HH}$ 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). ^{13}C{^{1}H}-NMR: δ_C 14.8 (d, $^3J_{PC}$ 3.2 Hz, $\underline{C}$H$_3$), 43.4 (d, $^3J_{PC}$ 17.4 Hz, N$\underline{C}$H$_2$), 75.0 (s, =$\underline{C}$H$_2$), 105.9 (d, J_{PC} 13.5 Hz, i-C_6H_5), 137.4 (d, J_{PC} 19 Hz, Ph$\underline{C}$-{P(NEt$_2$)$_2$}=C), 127.8 (s, *o*-C_6H_5), 127.9 (overlapped *m*-/*p*-C_6H_5), 209.9 (d, J_{PC} 11.4 Hz, =$\underline{C}$=). ^{31}P{^{1}H}-NMR: δ_P 91.0 (s, br, 74%). Propargyl tautomer (5%): NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 1.02 (t, $^3J_{HH}$ 7.2 Hz, 12H, CH_3), 2.71 (d, J_{PH} 5.8 Hz, 2H, CH_2P), 2.87 (m, 8H, NCH_2). ^{13}C{^{1}H}-NMR: δ_C 14.0 (d, $^3J_{PC}$ 5 Hz, $\underline{C}$H$_3$), 19.8 (m, $\underline{C}$H$_2$P), 42.8 (d, $^3J_{PC}$ 17 Hz, N$\underline{C}$H$_2$), 81.5 (s, C≡$\underline{C}$CH$_2$P), 87.6 (s, $\underline{C}$≡CCH$_2$P). ^{31}P{^{1}H}-NMR: δ_P 83.2 (s, br, 5%).

{(Et$_2$N)(Cl)P}C(Ph)=C=CH$_2$ (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 (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.81 (t, $^3J_{HH}$ 6.9 Hz, 6H, CH$_3$), 2.94 (q, $^3J_{HH}$ 7.4 Hz, 4H, CH$_2$), 4.89 (dd, $^2J_{HH}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, =CH$_2$), 4.93 (dd, $^2J_{HH}$ 13.0 Hz, J_{PH} 5.7 Hz, 1H, =CH$_2$), 6.94–7.02 (m, 1H, *p*-C$_6$H$_5$), 7.11 (7, J_{HH} 7.8 Hz, 2H, *m*-C$_6$H$_5$), 7.50 (d, J_{HH} 7.8 Hz, 2H, *o*-C$_6$H$_5$). ^{13}C{^{1}H}-NMR: δ_C 13.9 (d, $^3J_{PC}$ 6.2 Hz, $\underline{C}$H$_3$), 43.9 (d, $^3J_{PC}$ 13 Hz, N$\underline{C}$H$_2$), 77.6 (s, =$\underline{C}$H$_2$), 105.3 (d, J_{PC} 40 Hz, Ph$\underline{C}$(PCl(NEt$_2$)}=C), 135.4 (d, J_{PC} 24 Hz, i-C$_6$H$_5$), 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, =$\underline{C}$=). ^{31}P{^{1}H}-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 respect-

ive ligand (**8**, **11** or **12**). The mixture was stirred overnight then stripped of volatiles under reduced pressure to afford the complexes as yellow solids, which were recrystallised from DCM/ether.

***cis*-[Pt(PPh$_2$CH$_2$C≡CSnBu$_3$)$_2$Cl$_2$] (17).** Yield: 78%. NMR (C_6D_6, 30 °C): ^{1}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_{PH} ~ 5 Hz, 4H, CH$_2$P), 6.90–7.01 (m, 12H, *m*/*p*-C$_6H_5$), 7.63–7.77 (m, 8H, *o*-C$_6H_5$). ^{13}C{^{1}H}-NMR: δ_C 11.1 (s, $\underline{C}$H$_2$Sn, $^1J_{117SnC}$ 365 Hz, $^1J_{119SnC}$ 381 Hz), 13.9 (s, $\underline{C}$H$_3$), 23.8 (d, $^1J_{PC}$ 27 Hz, $\underline{C}$H$_2$PPh$_2$), 27.4 (s, $\underline{C}$H$_2$CH$_2$Sn, J_{117SnC} 58.8, J_{119SnC} 60.7 Hz), 29.2 (s, J_{SnC} 10 Hz, CH$_3\underline{C}$H$_2$), 88.7 (m, $\underline{C}$≡CCH$_2$PPh$_2$), 104.0 (m, C≡$\underline{C}$CH$_2$PPh$_2$), 127.9 (br, *m*-P(C$_6H_5$)$_2$), 129.a (br, i-P(C$_6H_5$)$_2$), 131.1 (s, *p*-P(C$_6H_5$)$_2$), 134.4 (m, *o*-P(C$_6H_5$)$_2$). ^{31}P{^{1}H}-NMR: δ_P 6.0 (s, J_{PtP} 3618 Hz). ^{119}Sn{^{1}H}-NMR: δ_{Sn} −68.2 (m). ^{195}Pt{^{1}H}-NMR: δ_{Pt} −4407 (t, J_{PtP} 3618 Hz). Anal. Found: C, 50.23; H, 5.95. Calcd for $C_{54}H_{78}Cl_2P_2PtSn_2$ Si: C, 50.18; H, 6.08.

***cis*-[Pt(PPh$_2$CH$_2$C≡CSiPr$^i_3$)$_2$Cl$_2$] (18).** Yield: 86%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.84 (sept., $^3J_{HH}$ 7.1 Hz, 6H, SiC*H*), 0.93 (d, $^3J_{HH}$ 7.1 Hz, 36H, CH_3), 3.87 (d, J_{PC} 10.8 Hz, 4H, CH$_2$P), 6.82–6.88 (m, 8H, *m*-P(C$_6H_5$)$_2$), 6.91–6.95 (m, 4H, *p*-P(C$_6H_5$)$_2$), 7.51–7.57 (m, 8H, *o*-P(C$_6H_5$)$_2$). ^{13}C{^{1}H}-NMR: δ_C 11.6 (s, Si$\underline{C}$H), 18.8 (s, $\underline{C}$H$_3$), 23.9 (d, J_{PC} 40 Hz, $\underline{C}$H$_2$P), 85.8 (m, $\underline{C}$≡CCH$_2$P), 101.9 (m, C≡$\underline{C}$CH$_2$P), 127.9 (m, *m*-C_6H$_5$), 131.1 (s, *p*-C_6H$_5$), 134.2 (m, *o*-C_6H$_5$), 134.6 (m, i-C_6H$_5$). ^{31}P{^{1}H}-NMR: δ_P 5.83 (s, J_{PtP} 3614 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −2.98. ^{195}Pt{^{1}H}-NMR: δ_{Pt} −4399 (t, J_{PtP} 3614 Hz). Anal. Found: C, 56.03; H, 6.39. Calcd for $C_{48}H_{66}Cl_2P_2PtSi_2$: C, 56.13; H, 6.48.

***cis*-[Pt(PPh$_2$CH$_2$C≡CSiPr$^n_3$)$_2$Cl$_2$] (19).** Yield: 78%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.41 (m, 12H, SiCH_2), 0.93 (t, $^3J_{HH}$ 7.2 Hz, 18H, CH_3), 1.23 (m, 12H, CH_2CH$_2$Si), 3.81 (d, J_{PH} 10 Hz, 4H, CH_2P), 6.86–6.93 (m, 8H, *m*-P(C$_6H_5$)$_2$), 6.94–7.00 (m, 4H, *o*-P(C$_6H_5$)$_2$), 7.54–7.62 (m, 8H, *o*-P(C$_6H_5$)$_2$). ^{13}C{^{1}H}-NMR: δ_C 16.3 (s, $\underline{C}$H$_2$Si, $^1J_{SiC}$ 55 Hz,), 17.8 (s, $\underline{C}$H$_3$), 18.5 (s, $\underline{C}$H$_2$CH$_2$Si, $^2J_{SiC}$ 7.4 Hz), 23.9 (d, J_{PC} 46 Hz, $\underline{C}$H$_2$P), 88.0 (m, $\underline{C}$≡CCH$_2$Cl), 101.4 (m, C≡$\underline{C}$CH$_2$P), 128.2 (m, *m*-C_6H$_5$), 129.0 (s, *p*-C_6H$_5$), 131.1 (s, *o*-C_6H$_5$), 134.3 (m, i-C_6H$_5$). ^{31}P{^{1}H}-NMR: δ_P 5.95 (s, J_{PtP} 3614 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −13.9. ^{195}Pt{^{1}H}-NMR: δ_{Pt} −4403 (t, J_{PtP} 3614 Hz). Anal. Found: C, 56.13; H, 6.45. Calcd for $C_{48}H_{66}Cl_2P_2PtSi_2$: C, 56.13; H, 6.48.

***trans*-[Pd(PPh$_2$CH$_2$C≡CSiPr$^i_3$)$_2$Cl$_2$] (20).** Yield: 88%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.90 (m, 6H, SiC*H*), 0.97 (d, $^3J_{HH}$ 6.7 Hz, 36H, CH_3), 3.74 (t, J_{PH} 3.9 Hz, 2H, CH$_2$P), 7.05–7.11 (m, 12H, *m*/*p*-P(C$_6H_5$)$_2$), 7.92–7.98 (m, 8H, *o*-P(C$_6H_5$)$_2$). ^{13}C{^{1}H}-NMR: δ_C 11.6 (s, Si$\underline{C}$H), 18.8 (s, $\underline{C}$H$_3$), 18.9 (t, J_{PC} 13.6 Hz, $\underline{C}$H$_2$P), 85.8 (d, J_{PC} 2.9 Hz, $\underline{C}$≡CCH$_2$Cl), 101.3 (d, J_{PC} 5.6 Hz, C≡$\underline{C}$CH$_2$P), 128.0 (m, *m*-C_6H$_5$), 129.3 (t, J_{PC} 24 Hz, i-C_6H$_5$), 130.9 (s, *p*-C_6H$_5$), 134.6 (t, J_{PC} 6 Hz, *o*-C_6H$_5$). ^{31}P{^{1}H}-NMR: δ_P 16.0 (s). ^{29}Si{^{1}H}-NMR: δ_{Si} −2.75. Anal. Found: C, 61.07; H, 6.94. Calcd for $C_{48}H_{66}Cl_2P_2PdSi_2$: C, 61.43; H, 7.09.

***trans*-[Pd(PPh$_2$CH$_2$C≡CSiPr$^n_3$)$_2$Cl$_2$] (21).** Yield: 89%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.45 (m, 12H, SiCH_2), 0.91 (t, $^3J_{HH}$ 7.0 Hz, 18H, CH_3), 1.25 (m, 12H, CH_2CH$_2$Si), 3.75 (t, J_{PH} 4 Hz, 4H, CH_2P), 7.03–7.12 (m, 12H, *m*/*p*-P(C$_6H_5$)$_2$), 7.89–7.98 (m, 8H, *o*-P(C$_6H_5$)$_2$). ^{13}C{^{1}H}-NMR: δ_C 16.4 (s, $\underline{C}$H$_2$Si, $^1J_{SiC}$ 57 Hz,), 17.8 (s, $\underline{C}$H$_3$), 18.5 (s, $\underline{C}$H$_2$CH$_2$Si, $^2J_{SiC}$ 6 Hz), 18.8 (t, J_{PC} 13.5 Hz, $\underline{C}$H$_2$P), 97.9 (d, J_{PC} 2.8 Hz, $\underline{C}$≡CCH$_2$Cl), 100.8 (d, J_{PC} 4.9 Hz, C≡$\underline{C}$CH$_2$P), 128.2 (m, *m*-C_6H$_5$), 129.2 (t, J_{PC} 24 Hz, i-C_6H$_5$), 130.9 (s, *p*-C_6H$_5$), 134.7 (t, J_{PC} 5.5 Hz, *o*-C_6H$_5$). ^{31}P{^{1}H}-NMR: δ_P 15.9 (s, J_{SiP} 23 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −13.8. Anal. Found: C, 61.08; H, 7.00. Calcd for $C_{48}H_{66}Cl_2P_2PdSi_2$: C, 61.43; H, 7.09.

***cis*-/*trans*-Isomerisation of [Pt(PPh$_2$CH$_2$C≡CSiPr$^n_3$)$_2$Cl$_2$] (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 ^{1}H NMR): 58%. NMR (C_6D_6, 30 °C): ^{1}H-NMR: δ_H 0.46 (m, 12H, SiCH_2), 0.92 (t, $^3J_{HH}$ 7.3 Hz, 18H, CH_3), 1.25 (m, 12H, CH_2CH$_2$Si), 3.77 (t, J_{PH} 4.3 Hz, 4H, CH_2P), 7.03–7.13 (m, 12H, *m*/*p*-P(C$_6H_5$)$_2$), 7.95–8.01 (m, 8H, *o*-P(C$_6H_5$)$_2$). ^{13}C{^{1}H}-NMR: δ_C 16.4 (s, $\underline{C}$H$_2$Si), 17.8 (s, $\underline{C}$H$_3$), 18.5 (s, $\underline{C}$H$_2$CH$_2$Si), 23.8 (t, J_{PC} 24 Hz, $\underline{C}$H$_2$P), 88.0 (m, $\underline{C}$≡CCH$_2$Cl), 101.4 (t, J_{PC} 6.3 Hz, C≡$\underline{C}$CH$_2$P), 128.2 (m, *m*-C_6H$_5$), 128.8 (s, *p*-C_6H$_5$), 130.9 (s, *o*-C_6H$_5$), 134.7 (t, J_{PC} 6.0 Hz, i-C_6H$_5$). ^{31}P{^{1}H}-NMR: δ_P 11.5 (s, J_{PtP} 2601 Hz). ^{29}Si{^{1}H}-NMR: δ_{Si} −13.2. ^{195}Pt{^{1}H}-NMR: δ_{Pt} −3993 (t, J_{PtP} 2601 Hz).

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