DALTON
FULL PAPER

Didentate phosphine ligands with alkenyl and alkynyl linker units as building blocks for dendrimer fixation

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Using diethyl-2-methylmalonate as a starting material, the two diphosphines $HC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (**7**) and $H_2C{=}CHCH_2C(CH_3)(CH_2PPh_2)_2$ (**13**), containing alkynyl and alkenyl unit in the ligand backbone were prepared in multistep syntheses. These two ligands were employed in the synthesis of $[\{(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2\}PdCl_2]$ (**8**) and $[\{(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2\}PtCl_2]$ (**9**) as well as $[\{H_2C{=}CHCH_2C(CH_3)(CH_2PPh_2)_2\}PdI_2]$ (**14b**), all of which were characterized by X-ray diffraction. Reaction of $Si[(CH_2)_3SiMe_2Cl]_4$ (= "G[0]-$[Cl]_4$") with four molar equivalents of the *in situ* lithiated alkynyl diphosphine **7** cleanly yielded the four-fold functionalized derivative G[0]-$[C{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2]_4$ (**15**) which was converted to the metallated derivative G[0]-$[C{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2PdCl_2]_4$ (**16**). Since the fixation of the alkenyl-functionalized diphosphine ligand **13** to the SiH-silane $Si[(CH_2)_3SiMe_2H]_4$ (= "G[0]-$[H]_4$") by Pt-catalyzed hydrosilation proved to be unsuccessful due to the negative interference of the phosphine with Karstedt's catalyst, the chloro-substituted precursor of **13**, $H_2C{=}CHCH_2C(CH_3)(CH_2Cl)_2$ (**12**) was used. Hydrosilation of G[0]-$[H]_4$ with four molar equivalents of **12** readily gave the functionalized dendrimer G[0]-$[CH_2CH_2CH_2C(CH_3)(CH_2Cl)_2]_4$ (**17**) which was then reacted with eight equivalents of $LiPPh_2$ to yield the phosphinated derivative G[0]-$[CH_2CH_2CH_2C(CH_3)(CH_2PPh_2)_2]_4$ (**18**).

Introduction

The immobilization of homogeneous catalysts on inorganic solids or macromolecular supports has been an intensely studied strategy to solve the problem of catalyst recycling.[1–3] Many systems falling into this category have been investigated to date and their efficiency has been tested. However, leaching of the metal is a major practical problem, regardless of the method of catalyst fixation and the nature of the support material.[4] This may be suppressed to various degrees by using polydentate ligands which form thermally and kinetically stable complexes with the catalyst metal.[5]

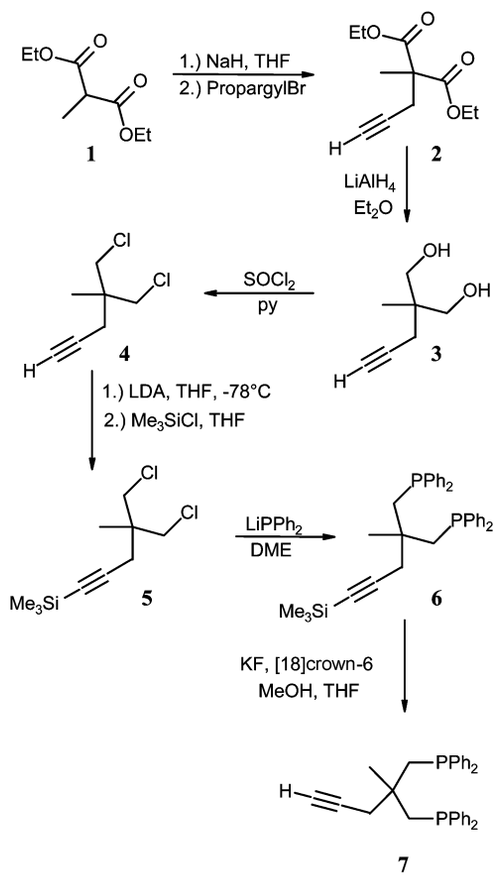
Due to the importance of phosphines in homogeneous catalysis, the immobilization of both chiral and achiral phosphine ligands has been studied in a range of such systems.[6] Since the first reports of the dendrimer fixation of molecular catalysts,[7] a variety of ligands and catalytically active complexes have been immobilized on the inside and outside of dendritic polymers.[8–10] In this paper we report the synthesis of two new didentate phosphines containing a propylene backbone which is linked to a propargyl or allyl unit. The latter allows the attachment of these chelating phosphines to carbosilane supports.

Results and discussion

Synthesis of a diphosphine containing an alkynyl linker unit

The synthesis of the didentate phosphine ligand containing an alkynyl anchor function in the ligand back bone is represented in Scheme 1. As the starting material we chose diethyl-2-methylmalonate **1** which was C-alkylated with 3-bromo-1-propyne to give the known compound **2**.[11] The diester was then reduced with $LiAlH_4$ yielding the dialcohol **3**, which was readily converted to the corresponding dichloride **4** using a standard synthetic protocol for such functional group interconversions.[12]

The direct conversion of compound **4** to the target phosphine by reaction with $LiPPh_2$ was relatively unselective and led to a product separation problem. This could be avoided by silylation of compound **4** in the alkynyl position, giving **5**, nucleophilic substitution of the chloride with $LiPPh_2$ and subsequent



Scheme 1 Synthesis of the alkynyl diphosphine **7** from diethyl-2-methylmalonate.

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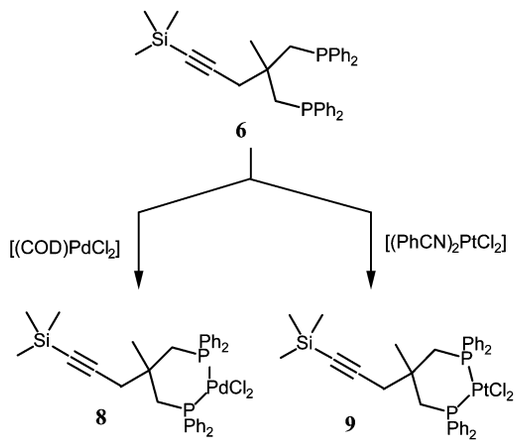
deprotection of **6** by reaction with KF under phase transfer conditions. This reaction sequence gave the target diphosphine $HC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (**7**) in good yield.

In order to establish the coordination behaviour of the functionalized diphosphine ligands as reference systems for the immobilized complexes, the silyl-protected ligand **6** was metallated by reaction with, respectively, one molar equivalent of $[(COD)PdCl_2]$ as well as $[(NCPh)_2PtCl_2]$ yielding the square planar complexes $[\{(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2\}PdCl_2]$ (**8**) and $[\{(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2\}PtCl_2]$ (**9**) (Scheme 2). The complete metallation of the phosphine



Scheme 2 Synthesis of the Pd and Pt complexes **8** and **9**.

ligands was established by ^{31}P NMR spectroscopy. In both cases the resonance of the phosphine, observed at δ −24.8 had disappeared and the corresponding coordination-shifted signals were observed at δ 17.2 and δ −1.4 for **8** and **9**, respectively. In the spectrum of the latter a set of satelites due to ^{195}Pt–^{31}P coupling is associated with the ^{31}P NMR resonance ($^1J_{PtP}$ = 3428 Hz). Single crystals suitable for an X-ray diffraction study were obtained for both complexes which are isomorphous in the solid state. The molecular structure of the palladium complex is displayed in Fig. 1 along with the principal bond lengths and interbond angles of **8** and **9**.

The metal centre in both complexes adopts the expected, slightly distorted, square planar arrangement. The diphosphine ligand is coordinated to the metal center forming a six-membered metallacycle which adopts a chair conformation. The corresponding interatomic distances and angles in both complexes are almost identical and resemble those of the $PdCl_2$ complex bearing the parent ligand system 1,3-bis(diphenylphosphanyl)propane.[13]

Synthesis of a diphosphine containing an alkenyl linker unit

As the starting material for the synthesis of a diphosphine ligand containing an alkenyl linker unit we chose the known diol **11** which is obtained from diethyl-2-methylmalonate **1** in a two-step synthesis (Scheme 3).[14] The dialcohol **11** is then converted to the chloride which is subjected to nucleophilic substitution by $LiPPh_2$ giving the diphosphine ligand $H_2C{=}CHCH_2C(CH_3)(CH_2PPh_2)_2$ (**13**).

Reaction of the diphosphine **13** with $[(COD)PdCl_2]$ gave the corresponding dichloropalladium complex $[\{H_2C{=}CHCH_2C(CH_3)(CH_2PPh_2)_2\}PdCl_2]$ (**14a**) which was converted to the diiodo complex $[\{H_2C{=}CHCH_2C(CH_3)(CH_2PPh_2)_2\}PdI_2]$ (**14b**) by halide exchange with NaI in CH_2Cl_2 (Scheme 4). A single crystal X-ray structure analysis of **14b** established the structural details of this type of compound. Its molecular structure, the first coordination sphere of which closely resembles that of compound **8**, is displayed in Fig. 2 along with the principal bond lengths and angles.

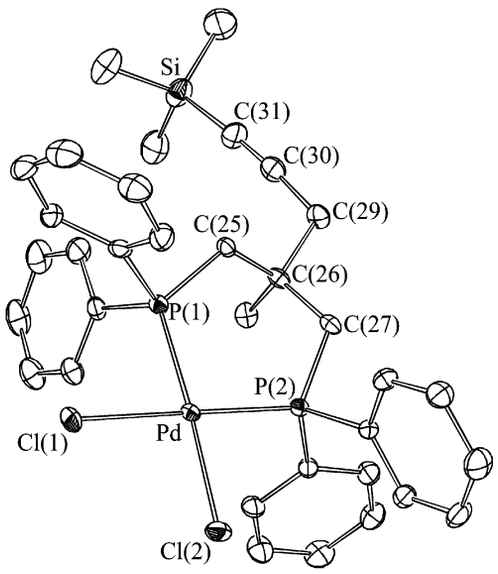
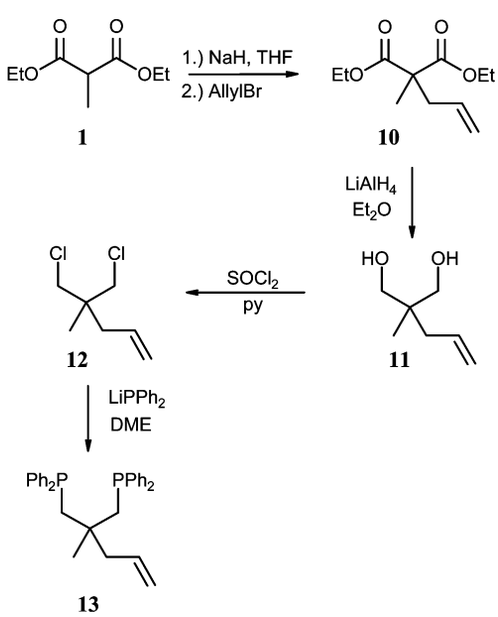


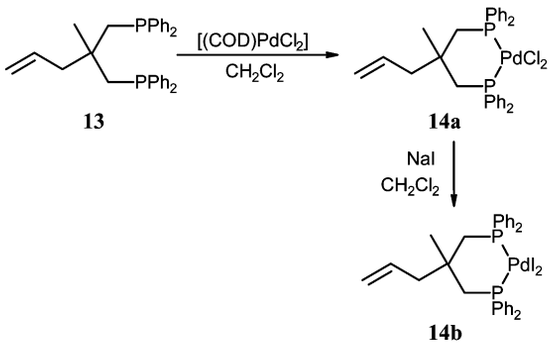
Fig. 1 Molecular structure of the palladium complex 8. Principal bond lengths (Å) and interbond angles (°): Pd–Cl(1) 2.349(1), Pd–P(2) 2.254(1), C(29)–C(30) 1.50(1), Pd–Cl(2) 2.354(2), P(1)–C(25) 1.811(5), C(30)–C(31) 1.207(9), Pd–P(1) 2.228(2), P(2)–C(27) 1.837(5), C(31)–Si 1.810(8), Cl(1)–Pd–Cl(2) 92.10(5), P(1)–Pd–P(2) 95.87(5), C(25)–C(26)–C(27) 110.0(5), Cl(1)–Pd–P(1) 84.24(5), Pd–P(1)–C(25) 116.77(3), C(29)–C(30)–C(31) 175.7(7), Cl(2)–Pd–P(2) 87.80(5), Pd–P(2)–C(27) 118.22(3), C(30)–C(31)–Si 173.8(7). Principal bond lengths (Å) and interbond angles (°) for the platinum analogue 9: Pt–Cl(1) 2.351(1), Pt–P(2) 2.234(1), C(29)–C(30) 1.480(1), Pt–Cl(2) 2.355(2), P(1)–C(25) 1.813(6), C(30)–C(31) 1.210(1), Pt–P(1) 2.216(2), P(2)–C(27) 1.833(6), C(31)–Si 1.841(8), Cl(1)–Pt–Cl(2) 89.72(6), P(1)–Pt–P(2) 96.92(6), C(25)–C(26)–C(27) 108.70(5), Cl(1)–Pt–P(1) 85.16(6), Pt–P(1)–C(25) 117.77(5), C(29)–C(30)–C(31) 174.30(9), Cl(2)–Pt–P(2) 88.20(6), Pt–P(2)–C(27) 119.36(4), C(30)–C(31)–Si 178.50(7).



Scheme 3 Synthesis of the alkenylphosphine **13** from diethyl-2-methylmalonate.

Fixation of the phosphine-linker units to polyfunctional carbosilanes

The end groups of carbosilane dendrimers have previously been modified by reaction with lithiated acetylenes,[15] however, this strategy has not been employed to date for the attachment of more complex ligand systems. The advantage of this approach is the reduced sensitivity of the silyl-C≡C bond compared with silyl-heteroatom units. The reaction of the known zeroth gener-



Scheme 4 Synthesis of the Pd complexes **14a** and **14b**.

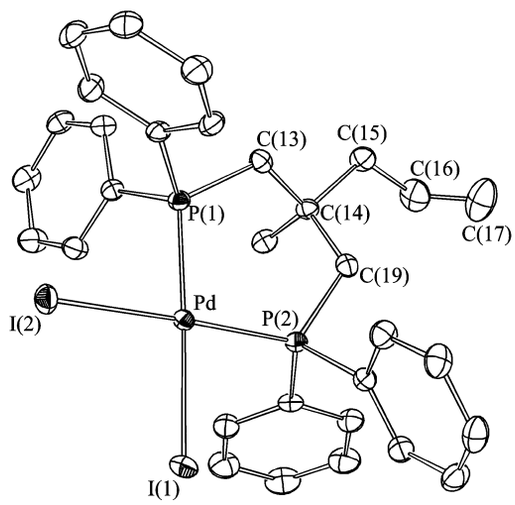


Fig. 2 Molecular structure of the diiodopalladium complex 14b. Principal bond lengths (Å) and interbond angles (°): Pd–P(1) 2.274(1), Pd–I(2) 2.6487(5), C(14)–C(15) 1.553(6), Pd–P(2) 2.261(1), P(1)–C(13) 1.835(5), C(15)–C(16) 1.486(7), Pd–I(1) 2.6508(4), P(2)–C(19) 1.817(5), C(16)–C(17) 1.319(8), I(1)–Pd–I(2) 90.02(1), P(1)–Pd–P(2) 94.85(4), C(13)–C(14)–C(19) 108.9(4), I(1)–Pd–P(2) 86.85(3), Pd–P(1)–C(13) 118.8(5), C(15)–C(16)–C(17) 124.2(6), I(2)–Pd–P(1) 88.34(3), Pd–P(2)–C(19) 118.5(9).

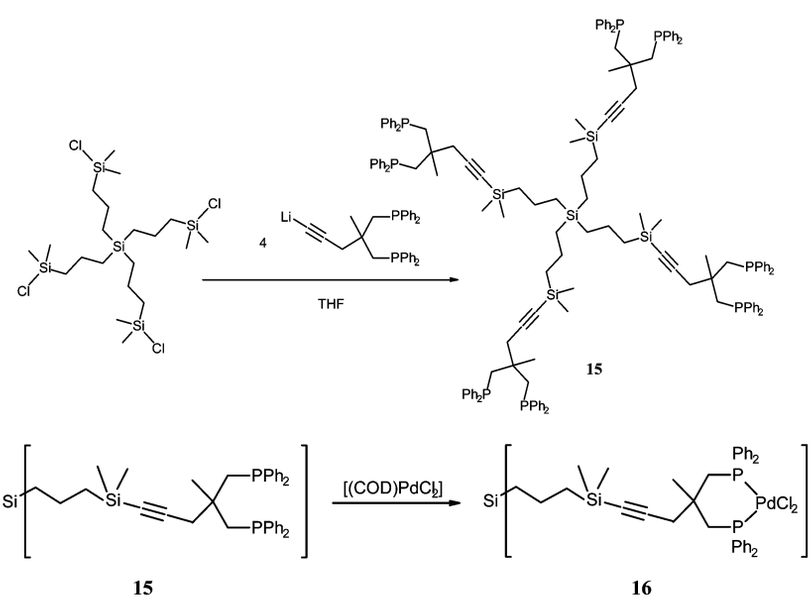
ation dendrimer $Si[(CH_2)_3SiMe_2Cl]_4$ (= "G[0]-[Cl]$_4$") [16] with four molar equivalents of the *in situ* lithiated alkynyl diphosphine **7** cleanly yielded the four-fold functionalized derivative $G[0]-[C{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2]_4$ (**15**) (Scheme 5). In the ^{29}Si NMR spectrum of **15** the signal of the central ^{29}Si nucleus is observed at δ 0.5 while the four outer alkynylsilyl groups give rise to a resonance at δ −17.9. The ν(C≡C) stretching vibration of **15** is found at 2168 cm^{-1} in the infrared spectrum, while the HC≡C band of the starting material is absent. The complete functionalization of the carbosilane core was confirmed by its FAB mass spectrum (molecular ion: m/z = 2282.6).

Stirring **15** with four molar equivalents of $[(COD)PdCl_2]$ yielded the metallated derivative $G[0]-[C{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2PdCl_2]_4$ (**16**). The ^{31}P NMR resonance, observed at δ −26.4 for the non-coordinated phosphine **15**, is characteristically shifted to δ 17.3 and both the absence to the free phosphine signal and the observation of the molecular ion peak in the FAB mass spectrum (m/z = 2955.9) indicate the complete metallation of the zeroth generation dendrimer.

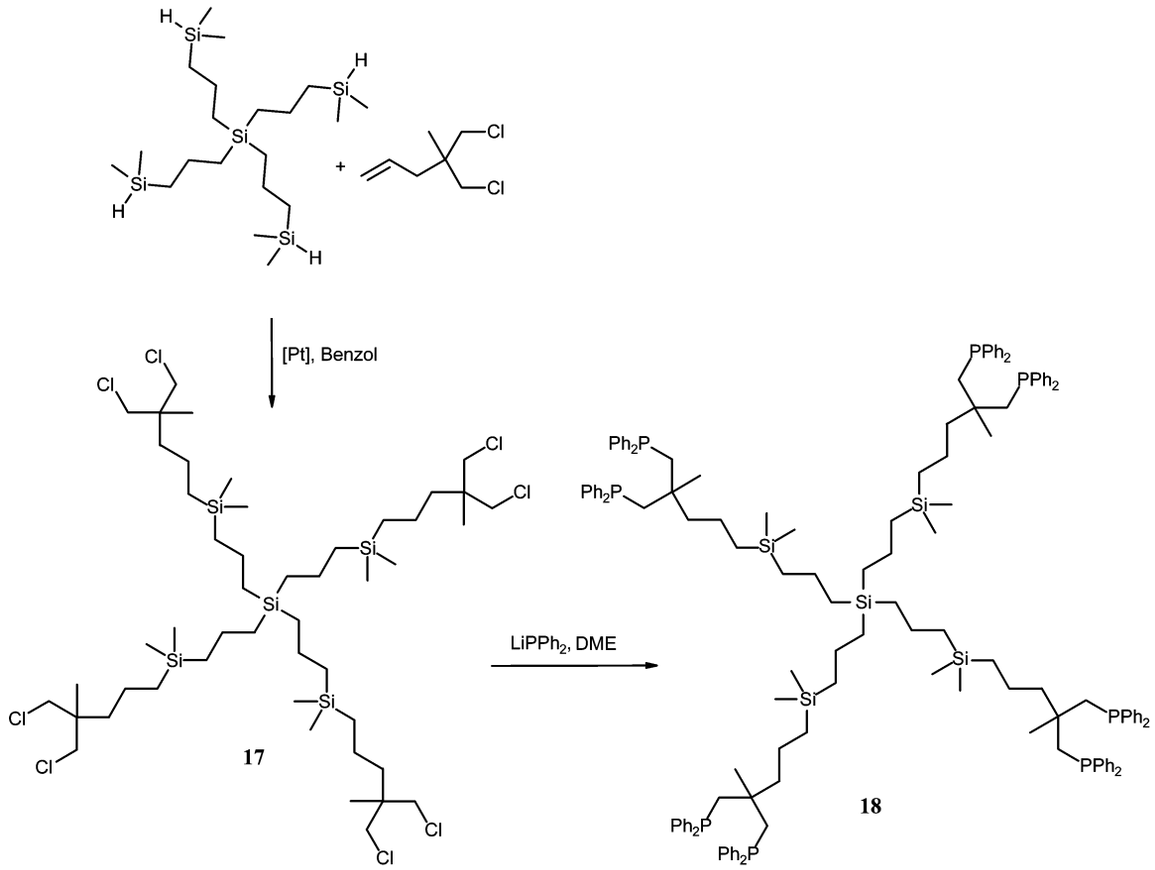
The fixation of the alkenyl-functionalized diphosphine ligand **13** to the SiH-silane $Si[(CH_2)_3SiMe_2H]_4$ ("G[0]-[H]$_4$") [16] by Pt-catalyzed hydrosilation proved to be unsuccessful due to the negative interference of the phosphine with Karstedt's catalyst, $[\{O(SiMe_2CH{=}CH_2)_2\}_3Pd_2]$. We therefore used the chloro-substituted precursor of **13**, $H_2C{=}CHCH_2C(CH_3)(CH_2Cl)_2$ (**12**). Hydrosilation of G[0]-[H]$_4$ with four molar equivalents of **12** readily gave the functionalized dendrimer $G[0]-[CH_2CH_2CH_2C(CH_3)(CH_2Cl)_2]_4$ (**17**) which was then reacted with an excess of $LiPPh_2$ to yield the phosphinated derivative $G[0]-[CH_2CH_2CH_2C(CH_3)(CH_2PPh_2)_2]_4$ (**18**) (Scheme 6). The latter was characterized by elemental analysis, NMR spectroscopy as well as FAB mass spectrometry (molecular ion: m/z = 2298.8).

Conclusion

We have devised convenient synthetic routes to two new functionalized diphosphines which are suitable for catalyst immobilization on carbosilane dendrimers. The fixation has been demonstrated for the simplest case of zeroth generation dendritic systems. The use of these ligand systems in higher generation carbosilane dendrimers is the object of our current and future activities.



Scheme 5 Fixation of the lithiated alkynyl diphosphine **7** to $Si[(CH_2)_3SiMe_2Cl]_4$ (= "G[0]-[SCl]$_4$") giving the zeroth generation dendrimer **15** and its metallation to form the tetranuclear palladium complex **16**.



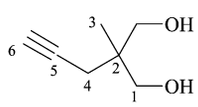
Scheme 6 Synthesis of the polyphosphine ligand **18**.

Experimental

All manipulations were performed under nitrogen (desiccant P_4O_{10}, Granusic®, J.T. Baker) on a high vacuum line using standard Schlenk techniques, or in a glovebox. Solvents and solutions were transferred by needle-septa techniques. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and stored over 4-Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite or by centrifugation. The ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT-NMR spectrometers. ^{1}H and ^{13}C data are listed in parts per million [ppm] relative to tetramethylsilane and were referenced using the residual protonated solvent peak (^{1}H) or the carbon resonance (^{13}C). ^{29}Si and ^{31}P NMR data are listed in ppm relative to, respectively, tetramethylsilane and 85% H_3PO_4 as external standards. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the chemistry department at Strasbourg. $HC{\equiv}CCH_2C(CH_3)(CO_2CH_2CH_3)_2$ (**2**),[11] $H_2C{=}CHCH_2C(CH_3)(CH_2OH)_2$ (**11**),[14] diphenylphosphine,[17] $[(COD)PdCl_2]$[18] and $[(PhCN)_2PtCl_2]$[19] were prepared according to published procedures. All other chemicals used as starting materials, as well as Karstedt's catalyst, were obtained commercially and used without further purification.

Preparations

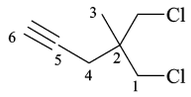
$HC{\equiv}CCH_2C(CH_3)(CH_2OH)_2$ (3). A solution of 6.94 g (32.7 mmol) of $HC{\equiv}CCH_2C(CH_3)(CO_2CH_2CH_3)_2$ (**2**) in 100 ml of Et_2O was slowly added to a stirred suspension of 1.36 g (38.9 mmol) of $LiAlH_4$ in 50 ml of Et_2O. After stirring for another 4 h at room temperature the product mixture was hydrolyzed by slow addition of 150 ml of iced diluted HCl. The organic layer was separated and the aqueous phase twice extracted with 50 ml of Et_2O. The combined organic phases were washed with 100 ml of H_2O and then dried over anhydrous Na_2SO_4. After removal of the solvent by distillation, the colourless solid residue was extracted with and recrystallized from toluene to give $HC{\equiv}CCH_2C(CH_3)(CH_2OH)_2$ (**3**) as a colourless, microcrystalline solid.



Yield: 3.60 g (28.1 mmol, 86%).M.p.: 69 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.90 (s, 3 H, H-3), 2.0 (t, 1 H, $^{4}J_{HH}$ = 2.8 Hz, H-6), 2.29 (d, 2 H, $^{4}J_{HH}$ = 2.8 Hz, H-4), 3.56–3.64 (m, 4 H, H-1). $\{^{1}H\}^{13}C$-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 18.6 (CH_3, C-3), 23.7 (CH_2, C-4), 39.2 (C, C-2), 69.1 (CH_2, C-1), 70.1 (CH, C-6), 81.1 (C, C-5).IR (film): ν = 3341 (s), 3283 (m), 2960 (m), 2926 (m), 2874 (m), 1474 (m), 1424 (m), 1394 (m), 1365 (m), 1252 (m), 1224 (m), 1134 (m), 1056 (s), 1029 (s), 961 (m), 908 (m), 677 (m), 631 (m) cm^{-1}. $C_7H_{12}O_2$ (128.17 g mol^{-1}): calcd.: C 65.60 H 9.44; found: C 65.62 H 9.52 %.

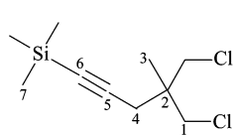
$HC{\equiv}C{-}CH_2C(CH_3)(CH_2Cl)_2$ (4). To a solution of 3.76 g (29.3 mmol) of $HC{\equiv}CCH_2C(CH_3)(CH_2OH)_2$ (**3**) in 5.10 g (5.20 ml, 64.5 mmol) of dry pyridine, which was stirred at 0 °C were slowly added 7.67 g (4.70 ml, 64.5 mmol) of $SOCl_2$. The reaction mixture was stirred at 115 °C for 3 h and then cooled to room temperature. After addition of 100 ml iced dilute HCl and 50 ml of CH_2Cl_2, the aqueous phase was separated and twice extracted with 50 ml of CH_2Cl_2. The combined organic layers were washed with 100 ml of dilute HCl, 100 ml of a saturated NaCl solution and 100 ml of H_2O and then dried over anhydrous Na_2SO_4. After removal of the

solvent by distillation under normal pressure, the remaining residue was fractionated under reduced pressure (35 Torr) to give compound $HC{\equiv}CCH_2C(CH_3)(CH_2Cl)_2$ (**4**) as a colourless liquid.

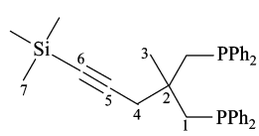


Yield: 3.00 g (18.2 mmol, 62%).B.p.: 72 °C/35 Torr. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 1.16 (s, 3 H, H-3), 2.05 (t, 1 H, $^4J_{HH}$ = 2.6 Hz, H-6), 2.34 (d, 2 H, $^4J_{HH}$ = 2.6 Hz, H-4), 3.52–3.60 (m, 4 H, H-1). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 20.3 (CH_3, C-3), 25.7 (CH_2, C-4), 40.0 (C, C-2), 49.7 (CH_2, C-1), 71.5 (CH, C-6), 79.3 (C, C-5). IR (film): ν = 3299 (s), 2972 (m), 2878 (m), 1459 (m), 1436 (m), 1380 (m), 1297 (m), 1272 (m), 886 (m), 849 (m), 783 (m), 742 (m), 703 (m), 647 (s) cm^{-1}. $C_7H_{10}Cl_2$ (165.06 g mol^{-1}): calcd.: C 50.94 H 6.11; found: C 50.81 H 6.20 %.

$(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2Cl)_2$ (5). To a stirred solution of 2.91 g (17.6 mmol) $HC{\equiv}CCH_2C(CH_3)(CH_2Cl)_2$ (**4**) in 30 ml of THF, which was cooled at −78 °C, 13.8 ml (22 mmol) of a 1.6 M solution of LDA were slowly added. The reaction mixture was stirred first at −78 °C for 1 h and then for another hour at room temperature. The solution was cooled again to −78 °C and 2.67 g (24.6 mmol) of Me_3SiCl were added with a syringe and the reaction mixture was subsequently stirred at ambient temperature for 17 h. After removal of the volatiles *in vacuo* the residue was extracted with 50 ml of CH_2Cl_2, the extract washed with 2 × 30 ml of H_2O and then dried over anhydrous $NaSO_4$. After removal of the solvent by distillation at normal pressure the crude reaction product was fractionated at reduced pressure (0.6 Torr) to give $(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2Cl)_2$ (**5**) as a colourless liquid. Yield: 3.99 g (16.8 mmol, 96%). B.p.: 82–83 °C/0.60 Torr. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.14 (s, 9 H, H-7), 1.15 (s, 3 H, H-3), 2.37 (s, 2 H, H-4), 3.50–3.59 (m, 4 H, H-1). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 0.0 (CH_3, C-7), 20.5 (CH_3, C-3), 27.3 (CH_2, C-4), 40.2 (C, C-2), 49.9 (CH_2, C-1), 88.3 (C, C-6), 101.8 (C, C-5). {^{1}H}^{29}Si-NMR (79.49 MHz, $CDCl_3$, 295 K): δ −18.4 (s). IR (film): ν = 2959 (m), 2177 (m), 1460 (m), 1435 (m), 1379 (m), 1296 (m), 1250 (m), 1037 (m), 844 (s), 781 (m), 760 (m), 700 (m), 648 (m) cm^{-1}. $C_{10}H_{18}Cl_2Si$ (237.24 g mol^{-1}): calcd.: C 50.63 H 7.65; found: C 50.42 H 7.52.

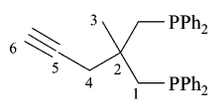


$(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (6). A 2 M solution of *n*-BuLi in *n*-hexane (12.1 ml = 24.2 mmol) was added dropwise to a stirred solution of 4.51 g (24.2 mmol) of $HPPh_2$ in 40 ml DME which was cooled at −10 °C. After stirring for another 30 min at room temperature a solution of 2.45 g (10.3 mmol) of $(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2Cl)_2$ (**5**) in 10 ml of DME was added. The reaction mixture was stirred at ambient temperature for 24 h and the volatiles subsequently removed *in vacuo*. The residue was extracted with 20 ml of toluene, the extract washed with 3 × 10 ml of H_2O and then dried over anhydrous Na_2SO_4. After removal of the solvent *in vacuo* the remaining oily residue was taken up in methanol from which the product crystallized at −30 °C. Compound $(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (**6**) was obtained as a colourless solid.



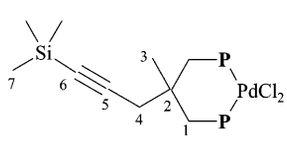
Yield: 4.26 g (7.93 mmol, 77%). M.p.: 81 °C. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.16 (s, 9 H, H-7), 1.03 (s, 3 H, H-3), 2.46–2.48 (m, 4 H, H-1), 2.5 (s, 2 H, H-4), 7.29–7.46 (m, 20 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 0.1 (s, CH_3, C-7), 27.3 (t, CH_3, $^3J_{PC}$ = 8.5 Hz, C-3), 33.2 (t, CH_2, $^3J_{PC}$ = 9.7 Hz, C-4), 38.2 (t, C, $^1J_{PC}$ = 14.6 Hz, C-2), 41.3 (dd, CH_2, $^3J_{PC}$ = 17.0 Hz, $^1J_{PC}$ = 8.5 Hz, C-1), 87.6 (s, C, C-6), 105.0 (s, C, C-5), 128.3–128.6 (m, aromat. C), 132.8–134.5 (m, aromat. C), 139.4–139.8 (m, aromat. C).{^{1}H}^{31}P-NMR (161.9 MHz, $CDCl_3$, 295 K): δ −24.8 (s). {^{1}H}^{29}Si-NMR (79.49 MHz, $CDCl_3$, 295 K): δ −19.0 (s). IR (film): ν = 3052 (m), 2955 (m), 2899 (m), 2170 (s), 1584 (w), 1480 (m), 1433 (m), 1248 (m), 1185 (m), 1093 (m), 1026 (m), 841 (s), 739 (s), 694 (m) cm^{-1}. $C_{34}H_{38}P_2Si$ (536.71 g mol^{-1}): calcd.: C 76.09 H 7.14; found: C 76.27 H 7.11 %.

$HC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (7). To a stirred solution of 682 mg (1.27 mmol) of $(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (**6**) in 10 ml of a 1:1 solvent mixture of methanol and THF were added 377 mg (6.49 mmol) of solid KF and 355 mg (1.31 mmol) of [18]crown-6. The reaction mixture was stirred at room temperature for 7 d and all volatiles were subsequently removed *in vacuo*. The residue was extracted with 10 ml of toluene, washed with 3 × 10 ml of degassed water and then dried over anhydrous Na_2SO_4. Recrystallization of the crude product from methanol at −30 °C gave $HC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (**7**) as a colourless, soft solid.



Yield: 378 mg (811 μmol, 64 %). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 1.09 (s, 3 H, H-3), 2.03 (t, 1 H, $^4J_{HH}$ = 2.46 Hz, H-6), 2.44–2.57 (m, 6 H, H-1,4), 7.33–7.53 (m, 20 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 27.2 (t, CH_3, $^3J_{PC}$ = 9.2 Hz, C-3), 32.2 (t, CH_2, $^3J_{PC}$ = 10.9 Hz, C-4), 37.9 (t, C, $^1J_{PC}$ = 13.4 Hz, C-2), 41.1 (dd, CH_2, $^3J_{PC}$ = 16.8 Hz, $^1J_{PC}$ = 8.5 Hz, C-1), 71.2 (s, CH, C-6), 81.9 (s, C, C-5), 128.3–128.6 (m, aromat. C), 132.8–134.5 (m, aromat. C), 139.3–139.7 (m, aromat. C). {^{1}H}^{31}P-NMR (121.51 MHz, $CDCl_3$, 295 K): δ −25.3 (s). IR (film): ν = 3296 (m), 3051 (m), 2953 (m), 2845 (m), 1480 (s), 1433 (s), 1373 (w), 1303 (w), 1268 (w), 1181 (w), 1093 (m), 1019 (w), 996 (w), 821 (w), 740 (s), 695 (s) cm^{-1}. $C_{31}H_{30}P_2$ (464.53 g mol^{-1}): calcd.: C 80.15 H 6.51; found: C 80.37 H 6.63 %.

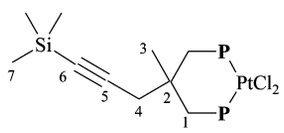
$[\{(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2\}PdCl_2]$ (8). A solution of 123 mg (432 μmol) of $[(COD)PdCl_2]$ in 20 ml of CH_2Cl_2 was added to a solution of 232 mg (432 μmol) of $(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2$ (**6**) in 15 ml of CH_2Cl_2 and the reaction mixture stirred for 14 h at room temperature to give a colourless solution. After reducing the volume to 15 ml, the product was precipitated by addition of pentane, washed with 3 × 20 ml of *n*-pentane and then dried *in vacuo* to give $[\{(CH_3)_3SiC{\equiv}CCH_2C(CH_3)(CH_2PPh_2)_2\}PdCl_2]$ (**8**) as a colourless microcrystalline solid.



Yield: 283 mg (398 μmol, 92 %). M.p.: 270 °C (dec.). ^{1}H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ 0.46 (s, 9 H, H-7), 0.72 (s, 3 H, H-3), 2.46 (s, 2 H, H-4), 2.68–2.90 (m, 4 H, H-1), 7.79–8.53 (m, 20 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ 0.1 (s, CH_3, C-7), 26.2 (t, CH_3, $^3J_{PC}$ = 4.9 Hz,

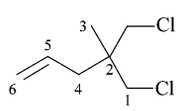
C-3), 36.9 (m, CH_2, C-1), 38.6 (s, C, C-2), 38.8 (t, CH_2, $^3J_{PC}$ = 11.0 Hz, C-4), 90.3 (s, C, C-6), 101.9 (s, C, C-5), 128.8–136.0 (m, aromat. C). $\{^1H\}^{31}P$-NMR (121.51 MHz, $CDCl_3$, 295 K): δ 17.2 (s). $\{^1H\}^{29}Si$-NMR (79.49 MHz, CD_2Cl_2, 295 K): δ −19.4 (s). IR (film): ν = 3056(m), 2956 (m), 2901 (m), 2171 (m), 1483 (m), 1435 (s), 1384 (w), 1311 (w), 1248 (m), 1185 (w), 1098 (s), 1029 (m), 998 (w), 839 (s), 726 (m), 692 (m) cm^{-1}. $C_{34}H_{38}Cl_2P_2PdSi$ (714.03 g mol^{-1}): calcd.: C 57.19 H 5.36; found: C 56.93 H 5.28 %.

[{$(CH_3)_3SiC\equiv CCH_2C(CH_3)(CH_2PPh_2)_2$}$PtCl_2$] (9). A solution of 217 mg (460 μmol) of [$(PhCN)_2PtCl_2$] in 20 ml of CH_2Cl_2 was added to a solution of 247 mg (460 μmol) of $(CH_3)_3SiC\equiv CCH_2C(CH_3)(CH_2PPh_2)_2$ (**6**) in 15 ml of CH_2Cl_2 and the reaction mixture stirred for 14 h at room temperature to give a colourless solution. After reducing the volume to 15 ml, the product was precipitated by addition of pentane, washed with 3 × 20 ml of *n*-pentane and then dried *in vacuo* to give [{$(CH_3)_3SiC\equiv CCH_2C(CH_3)(CH_2PPh_2)_2$}$PtCl_2$] (**9**) as a colourless microcrystalline solid.



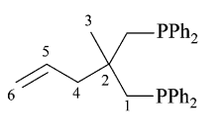
Yield: 360 mg (437 μmol, 95 %). M.p.: 269 °C (dec.). ^1H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ 0.13 (s, 9 H, H-7), 0.40 (s, 3 H, H-3), 2.07 (s, 2 H, H-4), 2.40–2.61 (m, 4 H, H-1), 7.48–8.19 (m, 20 H, aromat. H). $\{^1H\}^{13}C$-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ 0.1 (s, CH_3, C-7), 26.1 (t, CH_3, $^3J_{PC}$ = 4.9 Hz, C-3), 36.4 (m, CH_2, C-1), 38.7 (s, C, C-2), 39.4 (t, CH_2, $^3J_{PC}$ = 11.0 Hz, C-4), 90.2 (s, C, C-6), 101.2 (s, C, C-5), 128.7–136.9 (m, aromat. C). $\{^1H\}^{31}P$-NMR (121.52 MHz, CD_2Cl_2, 295 K): −1.4 (s), −2.0 (d, $^1J_{PtP}$ = 3428.4 Hz). $\{^1H\}^{29}Si$-NMR (79.49 MHz, CD_2Cl_2, 295 K): δ −18.8 (s). IR (film): ν = 3053 (m), 2957 (m), 2907 (m), 2171 (m), 1435 (s), 1249 (m), 1099 (s), 1024 (w), 841 (s), 755 (m), 727 (m), 694 (s) cm^{-1}. $C_{34}H_{38}Cl_2P_2PtSi$ (802.69 g mol^{-1}): calcd.: C 50.88 H 4.77; found: C 50.61 H 4.79 %.

$H_2C\equiv CHCH_2C(CH_3)(CH_2Cl)_2$ (12). To a stirred solution of 7.39 g (56.8 mmol) of 2-allyl-2-methyl-1,3-propanediol (**11**) in 9.88 g (10.1 ml, 125 mmol) of dry pyridine, which was cooled at 0 °C, were slowly added 14.9 g (9.11 ml, 125 mmol) of $SOCl_2$. The reaction mixture was heated at 115 °C for 3 h and, after cooling to room temperature, 100 ml of iced dilute HCl and 50 ml of CH_2Cl_2 were added. The aqueous phase was separated and twice extracted with 50 ml of CH_2Cl_2. The combined organic phases were washed first with 100 ml of a saturated aqueous solution of NaCl, then with 100 ml of H_2O and finally dried over anhydrous Na_2SO_4. After removal of the solvent by distillation at normal presure the residue was fractionated at reduced pressure (25 Torr) to give $H_2C=CHCH_2C(CH_3)(CH_2Cl)_2$ (**12**) as a colourless liquid.

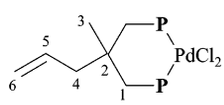


Yield: 7.21 g (43.15 mmol, 76 %). B.p.: 74 °C/25 Torr. ^1H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 1.03 (s, 3 H, H-3), 2.15 (d, 2 H, $^3J_{HH}$ = 7.6 Hz, H-4), 3.41–3.50 (m, 4 H, H-1), 5.66–5.80 (m, 1 H, H-5). $\{^1H\}^{13}C$-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 20.2 (CH_3, C-3), 39.5 (CH_2, C-4), 39.8 (C, C-2), 50.1 (CH_2, C-1), 119.3 (CH_2, C-6), 132.1 (CH, C-5). IR (film): ν = 3079 (w), 2977 (m), 1640 (m), 1461 (m), 1432 (s), 1378 (m), 1296 (m), 1274 (m), 999 (m), 923 (s), 887 (w), 851 (w), 740 (s), 639 (m) cm^{-1}. $C_7H_{12}Cl_2$ (167.08 g mol^{-1}): calcd.: C 50.32 H 7.24; found: C 50.28 H 7.31 %.

$H_2C\equiv CHCH_2C(CH_3)(CH_2PPh_2)_2$ (13). To a stirred solution of 4.17 g (22.4 mmol) of $HPPh_2$ in 30 ml of DME, which was cooled at −30 °C were added 8.96 ml of a 2.5 M solution of *n*-BuLi in hexane (22.4 mmol). After stirring the resulting deep red solution at room temperature for 30 min, a solution of 1.71 g (10.2 mmol) of $H_2C=CHCH_2C(CH_3)(CH_2Cl)_2$ (**12**) was added. After stirring for another 24 h the volatiles were removed *in vacuo*, the residue extracted with 20 ml of toluene and the extract, after washing with 2 × 10 ml of degassed H_2O, dried over anhydrous Na_2SO_4. After removal of the solvent *in vacuo*, the crude product was recrystallized from methanol at −30 °C to give $H_2C=CHCH_2C(CH_3)(CH_2PPh_2)_2$ (**13**) as a soft colourless solid. Yield: 3.85 g (8.25 mmol, 81 %). ^1H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.99 (s, 3 H, H-3), 2.30–2.45 (m, 6 H, H-1,4), 4.99–5.06 (m, 2 H, H-6), 5.64–5.78 (m, 1 H, H-5), 7.27–7.49 (m, 20 H, aromat. H). $\{^1H\}^{13}C$-NMR (75.48 MHz, $CDCl_3$, 295 K): δ 27.7 (t, CH_3, $^3J_{PC}$ = 9.2 Hz, C-3), 37.9 (t, C, $^2J_{PC}$ = 13.4 Hz, C-2), 41.6 (dd, CH_2, $^3J_{PC}$ = 16.5 Hz, $^1J_{PC}$ = 8.5 Hz, C-1), 46.4 (t, CH_2, $^3J_{PH}$ = 8.6 Hz, C-4), 118.2 (s, CH_2, C-6), 127.2–129.4 (m, aromat. C), 132.8–133.1 (m, aromat. C), 134.6 (s, CH, C-5), 139.8–139.9 (m, aromat. C). $\{^1H\}^{31}P$-NMR (121.51 MHz, $CDCl_3$, 295 K): δ −25.7 (s). IR (film): ν = 3067 (m), 2953 (m), 2856 (m), 1636 (w), 1583 (w), 1479 (m), 1432 (s), 1373 (m), 1304 (m), 1184 (m), 1091 (m), 1025 (m), 997 (m), 915 (m), 821 (m), 738 (s), 694 (s) cm^{-1}. $C_{31}H_{32}P_2$ (466.54 g mol^{-1}): calcd.: C 79.81, H 6.91 found: C 79.63, H 6.99.

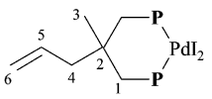


[{$H_2C\equiv CHCH_2C(CH_3)(CH_2PPh_2)_2$}$PdCl_2$] (14a) and [{$H_2C\equiv CHCH_2C(CH_3)(CH_2PPh_2)_2$}$PdI_2$] (14b). A solution of 580 mg (2.03 mmol) of [(COD)$PdCl_2$] in 45 ml of CH_2Cl_2 was added at room temperature to a solution of 947 mg (2.03 mmol) of $H_2C=CHCH_2C(CH_3)(CH_2PPh_2)_2$ (**13**) in 8 ml of CH_2Cl_2. The reaction mixture was stirred for another 16 h and the product precipitated by slow addition of *n*-pentane. The solid was isolated, twice washed with pentane and then dried *in vacuo*. The product [{$H_2C=CHCH_2C(CH_3)(CH_2PPh_2)_2$}$PdCl_2$] (**14a**) is obtained as a colourless, microcrystalline solid.



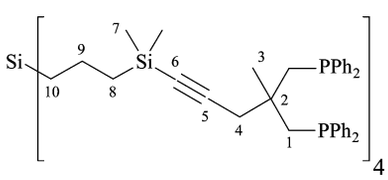
Yield: 1.20 g (1.87 mmol, 92%). M.p.: 228 °C (dec.). ^1H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ 0.32 (s, 3 H, H-3), 1.96–1.99 (m, 2 H, H-4), 2.16–2.50 (m, 4 H, H-1), 4.93 (dd, 1 H, $^3J_{HH}$ = 19.4 Hz, $^2J_{HH}$ = 2.0 Hz, H-6_{trans}), 5.07 (dd,1 H, $^3J_{HH}$ = 10.1 Hz, $^2J_{HH}$ = 2.0 Hz, H-6_{cis}), 5.44–5.58 (m, 1 H, H-5), 7.48–7.72 (m, aromat. H), 8.12–8.18 (m, aromat. H). $\{^1H\}^{13}C$-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ 26.7 (t, CH_3, $^3J_{PC}$ = 5.0 Hz, C-3), 37.6 (m, CH_2, C-1), 38.5 (s, C, C-2), 51.8 (t, CH_2, $^3J_{PC}$ = 10.2 Hz, C-4), 120.6 (s, CH_2, C-6), 128.8–136.0 (m, aromat. C), 132.4 (s, CH, C-5). $\{^1H\}^{31}P$-NMR (121.51 MHz, CD_2Cl_2, 295 K): δ 16.6 (s). IR (film): ν = 3052 (w), 2956 (w), 2883 (w), 1624 (w) 1480 (m), 1435 (s), 1098 (s), 998 (w), 836 (w), 805 (w), 751 (m), 726 (s), 690 (s) cm^{-1}. MS (FAB, CsI): *m/z* = 609.2 $[M-Cl]^+$. $C_{31}H_{32}Cl_2P_2Pd$ (643.87 g mol^{-1}): calcd.: C 57.83 H 5.01; found: C 58.10 H 4.94 %.

A solution of 625 mg (971 μmol) of [{$H_2C=CHCH_2C(CH_3)(CH_2PPh_2)_2$}$PdCl_2$] (**14a**) in 20 ml of CH_2Cl_2 was added to a suspension of 727 mg (4.85 mmol) of NaI in 20 ml of CH_2Cl_2 and then stirred at room temperature for 16 h After work up as described above the pure iodo complex [{$H_2C=CHCH_2C(CH_3)(CH_2PPh_2)_2$}$PdI_2$] (**14b**) was obtained as a colourless solid.



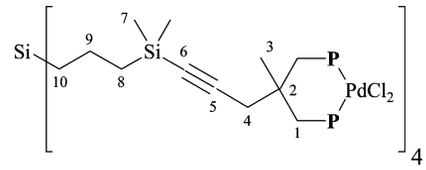
Yield: 722 mg (873 μmol, 90 %). M.p.: 232 °C (dec.). ^{1}H-NMR (300.17 MHz, CD_2Cl_2, 295 K): δ 0.21 (s, 3 H, H-3), 1.86 (d, 2 H, $^3J_{HH}$ = 7.25 Hz, H-4), 2.18–2.44 (m, 4 H, H-1), 4.89 (d, 1 H, $^3J_{HH}$ = 16.9 Hz, H-6$_{trans}$), 5.04 (d, 1 H, $^3J_{HH}$ = 8.5 Hz, H-6$_{cis}$), 7.50–8.15 (m, 20 H, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, CD_2Cl_2, 295 K): δ 26.8 (t, CH_3, $^3J_{PC}$ = 4.9 Hz, C-3), 38.1 (s, C, C-2), 38.3 (m, CH_2, C-1), 52.1 (t, CH_2, $^3J_{PC}$ = 10.5 Hz, C-4), 120.3 (s, CH_2, C-6), 128.5–136.4 (m, aromat. C), 131.2 (s, CH, C-5). {^{1}H}^{31}P-NMR (121.51 MHz, CD_2Cl_2, 295 K): δ 4.7 (s). IR (KBr): ν = 3052 (w), 2956 (w), 2962 (w), 1654 (w), 1478 (m), 1435 (s), 1381 (m), 1098 (s), 1025 (w), 999 (m), 837 (m), 800 (m), 742 (m), 741 (s), 697 (s) cm^{-1}. MS (FAB): *m*/*z* = 698.9 [M–I]$^+$. $C_{31}H_{32}I_2P_2Pd$ (826.77 g mol^{-1}): calcd.: C 45.04 H 3.90; found: C 45.21 H 3.94 %.

G[0]-[C≡CCH$_2$C(CH$_3$)(CH$_2$PPh$_2$)$_2$]$_4$ (15). To a stirred solution of 1.43 g (3.07 mmol) of HC≡CCH$_2$C(CH$_3$)(CH$_2$PPh$_2$)$_2$ (**7**) in 7 ml of THF, which was cooled at −78 °C, 1.92 ml (3.07 mmol) of a 1.6 M solution of LDA in THF were slowly added. The reaction mixture was first stirred for 1 h at −78 °C and then for another hour at room temperature. After cooling again to −78 °C, a solution of 417.8 mg (732 μmol) of G[0]-[Cl]$_4$ in THF was added. The reaction mixture was stirred at room temperature for 17 h, the volatiles removed *in vacuo* and the residue extracted with 50 ml of toluene. After filtration of the extract, the solvent was removed *in vacuo* and washed several times with *n*-pentane and methanol to give G[0]-[C≡CCH$_2$C(CH$_3$)-(CH$_2$PPh$_2$)$_2$]$_4$ (**15**) as a soft, colourless solid.



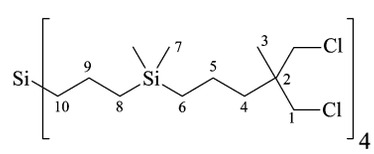
Yield: 1.30 g (571 μmol, 78 %). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.09 (s, 24 H, H-7), 0.32 (s, 12 H, H-3), 0.42–0.60 (m, 16 H, H-8,10), 2.13 (s, 8 H, H-4), 2.36–2.53 (m, 24 H, H-1,9), 7.42–8.20 (m, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ −1.3 (s, CH_3, C-7), 17.5 (s, CH_2, C-8/9/10), 18.8 (s, CH_2, C-8/9/10), 21.5 (s, CH_2, C-8/9/10), 26.0 (t, CH_3, $^3J_{PC}$ = 7.4 Hz, C-3), 36.7 (m, CH_2, C-1), 38.6 (s, C, C-2), 38.9 (t, CH_2, $^3J_{PC}$ = 14.6 Hz, C-4), 89.4 (s, C, C-6), 102.7 (s, C, C-5), 128.8–136.0 (m, aromat. C). {^{1}H}^{31}P-NMR (121.51 MHz, CD_2Cl_2, 295 K): −26.4 (s). {^{1}H}^{29}Si-NMR (79.49 MHz, CD_2Cl_2, 295 K): −17.9 (s, Si≡C), 0.5 (s, Si). IR (film): ν = 3052 (w), 2947 (m), 2911 (m), 2863 (m), 2168 (m), 1482 (w), 1435 (s), 1248 (m), 1098 (s), 1026 (m), 998 (m), 838 (m), 745 (m), 725 (m), 689 (s) cm^{-1}. MS (FAB): *m*/*z* = 2282.6 [M]$^+$. $C_{144}H_{164}P_8Si_5$ (2283.10 g mol^{-1}): calcd.: C 75.76 H 7.24; found: C 75.37 H 7.11 %.

G[0]-[C≡CCH$_2$C(CH$_3$)(CH$_2$PPh$_2$)$_2$PdCl$_2$]$_4$ (16). A solution of 653 mg (286 μmol) of G[0]-[C≡CCH$_2$C(CH$_3$)(CH$_2$PPh$_2$)$_2$]$_4$ (**15**) in 15 ml of CH_2Cl_2 was added to a solution of 327 mg (1.14 mmol) of [(COD)PdCl$_2$] in 10 ml of CH_2Cl_2. The reaction mixture was stirred at room temperature for 15 h and the colourless solution then concentrated to 10 ml. The product G[0]-[C≡CCH$_2$C(CH$_3$)(CH$_2$PPh$_2$)$_2$PdCl$_2$]$_4$ (**16**) was precipitated by slow addition of pentane and, after drying *in vacuo*, compound **16** was isolated as a colourless solid.



Yield: 805 mg (269 μmol, 94 %). M.p.: 233 °C (dec.). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ 0.09 (s, 24 H, H-7), 0.32 (s, 12 H, H-3), 0.42–0.60 (m, 16 H, H-8,10), 2.13 (s, 8 H, H-4), 2.36–2.53 (m, 24 H, H-1,9), 7.42–8.20 (m, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ −1.3 (s, CH_3, C-7), 17.5 (s, CH_2, C-8/9/10), 18.8 (s, CH_2, C-8/9/10), 21.5 (s, CH_2, C-8/9/10), 26.0 (t, CH_3, $^3J_{PC}$ = 7.4 Hz, C-3), 36.7 (m, CH_2, C-1), 38.6 (s, C, C-2), 38.9 (t, CH_2, $^3J_{PC}$ = 14.6 Hz, C-4), 89.4 (s, C, C-6), 102.7 (s, C, C-5), 128.8–136.0 (m, aromat. C). {^{1}H}^{31}P-NMR (121.51 MHz, CD_2Cl_2, 295 K): δ 17.3 (s). {^{1}H}^{29}Si-NMR (79.49 MHz, CD_2Cl_2, 295 K): δ −17.9 (s, Si≡C), 0.5 (s, Si). IR (film): ν = 3052 (w), 2947 (m), 2911 (m), 2863 (m), 2168 (m), 1482 (w), 1435 (s), 1248 (m), 1098 (s), 1026 (m), 998 (m), 838 (m), 745 (m), 725 (m), 689 (s) cm^{-1}. MS (FAB): *m*/*z* = 2955.9 [M–Cl]$^+$. $C_{144}H_{164}Cl_8P_8Pd_4Si_5$ (2992.4 g mol^{-1}): calcd.: C 57.80 H 5.52; found: C 57.37 H 5.40 %.

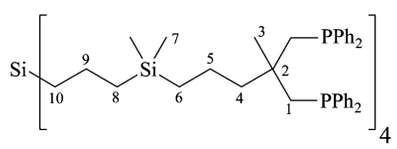
G[0]-[CH$_2$CH$_2$CH$_2$C(CH$_3$)(CH$_2$Cl)$_2$]$_4$ (17) and its conversion to G[0]-[CH$_2$CH$_2$CH$_2$C(CH$_3$)(CH$_2$PPh$_2$)$_2$]$_4$ (18). To a solution of 936 mg (5.61 mmol) of H$_2$C=CHCH$_2$C(CH$_3$)(CH$_2$Cl)$_2$ (**12**) and 404 mg (932 μmol) of Si[CH$_2$CH$_2$CH$_2$Si(CH$_3$)$_2$H]$_4$ in 8 ml of benzene were added a few drops of a 2.1–2.4 % solution of Karstedt's catalyst in xylene. The reaction mixture was stirred at 70 °C for 24 h. After removal of the volatiles *in vacuo* the residue was purified by column chromatography on silica gel yielding G[0]-[CH$_2$CH$_2$CH$_2$C(CH$_3$)(CH$_2$Cl)$_2$]$_4$ (**17**) as a colourless oil.



Yield: 915 mg (830 μmol, 89%). R_f (kieselgel, EtOAc–*n*-hexane = 1:9) = 0.43. ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = −0.04 (s, 6 H, H-7), 0.44–0.57 (m, 6 H, H-6,8,10), 1.01 (s, 3 H, H-3), 1.23–1.41 (m, 6 H, H-4,5,9), 3.41–3.49 (m, 4 H, H-1). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = −3.2 (s, CH_3, C-7), 16.1 (s, CH_2, C-4/5/6/8/9/10), 17.5 (s, CH_2, C-4/5/6/8/9/10), 17.7 (s, CH_2, C-4/5/6/8/9/10), 18.6 (s, CH_2, C-4/5/6/8/9/10), 20.3 (s, CH_2, C-4/5/6/8/9/10), 20.6 (s, CH_3, C-3), 39.7 (s, CH_2, C-4/5/6/8/9/10), 39.8 (s, C, C-2), 50.5 (s, CH_2, C-1). {^{1}H}^{29}Si-NMR (79.49 MHz, $CDCl_3$, 295 K): δ = 0.4 (s, Si), 1.4 (s, SiMe$_2$). IR (Film): ν = 2913 (s), 2872 (s), 2793 (w), 1458 (m), 1438 (m), 1411 (m), 1378 (m), 1332 (m), 1294 (s), 1276 (m), 1247 (m), 1168 (m), 1141 (m), 1078 (m), 1021 (m), 908 (m), 883 (m), 837 (s), 740 (m) cm^{-1}. MS (FAB): *m*/*z* = 1123.5 [M+Na]$^+$. $C_{48}H_{100}Cl_8Si_5$ (1101.37 g/mol): calcd.: C 52.35 H 9.15; found: C 52.01 H 9.11. To a stirred solution of 1.10 g (5.92 mmol) of HPPh$_2$ in 5 ml of DME, which was cooled at −30 °C were added 3.7 ml of a solution of *n*-BuLi in hexane (1.6 M, 5.92 mmol) and the resulting deep red solution stirred for 30 mins at room temperature. After complete metallation of the phosphine, 642 mg (592 μmol) of G[0]-[CH$_2$CH$_2$CH$_2$C(CH$_3$)(CH$_2$Cl)$_2$]$_4$ (**17**) in 5 ml of DME were added and the reaction mixture stirred at ambient temperature for 24 h. After removal of the volatiles in vacuo the residue was extracted with 20 ml of toluene, the extract washed twice with water and then dried over anhydrous Na$_2$SO$_4$. After evaporation of the solvent, the residue was washed with methanol and then dried in vacuo to yield G[0]-[CH$_2$CH$_2$CH$_2$C-(CH$_3$)-(CH$_2$PPh$_2$)$_2$]$_4$ (**18**) as a soft, colourless solid.

Table 1 X-Ray experimental data of compounds **8**, **9** and **14b**

	8	**9**	**14b**
Formula	$C_{34}H_{38}Cl_2P_2PdSi\cdot 2CHCl_3$	$C_{34}H_{38}Cl_2P_2PtSi\cdot 2CH_2Cl_2$	$C_{31}H_{32}I_2P_2Pd$
Molecular weight	952.78	972.58	826.76
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P\,2_1/c$	$P\,2_1/c$	$P\,2_1/n$
a/Å	16.6775(4)	16.4406(3)	12.9006(2)
b/Å	18.0163(5)	17.8845(5)	18.1476(4)
c/Å	14.0010(5)	13.8996(5)	14.2538(4)
β/deg	92.175(5)	90.946(5)	112.264(5)
V/Å^3	4203.8(2)	4086.4(2)	3088.3(1)
Z	4	4	4
Crystal dim./mm	0.18(0.12(0.06	0.14(0.12(0.10	0.20(0.16(0.06
D_{calc}/g cm^{-3}	1.51	1.58	1.78
*F*000	1928	1928	1600
μ/mm^{-1}	1.080	3.958	2.722
Temperature/K	173	173	173
Wavelength/Å	0.71073	0.71073	0.71073
Radiation	MoKa	MoKa	MoKa
hkl limits	−18,18/−21,23/−21,21	−18,18/−23,18/−21,21	−16,16/−23,21/−18,18
Theta limits/deg	2.5/27.49	2.5/27.47	2.5/27.48
No. of data meas.	16279	16896	11822
No; of data with $I > 3\sigma(I)$	5302	5880	4346
No. of variables	433	415	325
R	0.049	0.038	0.029
Rw	0.072	0.050	0.031
GOF	1.181	1.045	0.917
Largest peak in final difference (e Å^{-3})	1.094	0.753	0.735



Yield: 462.8 mg (0.201 mmol, 34 %). ^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ −0.13 (s, 24 H, H-7), 0.15–0.20 (m, 8 H, H-6/8/10), 0.45–0.57 (m, 16 H, H-6/8/10), 0.93 (s, 12 H, H-3), 1.09–1.65 (m, 24 H, H-4,5,9), 2.28–2.40 (m, 16 H, H-1), 7.27–7.49 (m, aromat. H). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ −3.0 (s, CH_3, C-7), 16.2 (s, CH_2, C-5/6/8/9/10), 18.0 (s, CH_2, C-5/6/8/9/10), 18.6 (s, CH_2, C-5/6/8/9/10), 19.0 (s, CH_2, C-5/6/8/9/10), 20.8 (s, CH_2, C-5/6/8/9/10), 28.4 (t, CH_3, $^3J_{PC}$ = 9.7 Hz, C-3), 38.3 (t, CH_2, $^2J_{PC}$ = 13.4 Hz, C-2), 41.9 (dd, CH_2, $^3J_{PC}$ = 17.0 Hz, $^1J_{PC}$ = 9.7 Hz, C-1), 46.6 (t, CH_2, $^3J_{PC}$ = 9.1 Hz, C-4), 127.7–140.8 (m, aromat. C). {^{1}H}^{31}P-NMR (161.9 MHz, CD_2Cl_2, 295 K): δ −25.6 (s). {^{1}H}^{29}Si-NMR (79.49 MHz, $CDCl_3$, 295 K): δ 0.3 (s, Si), 1.4 (s, $SiMe_2$). MS (FAB): *m*/*z* = 2298.8 [M]$^+$. $C_{144}H_{180}P_8Si_5$ (2299.23 g mol^{-1}): calcd.: C 75.22 H 7.89; found: C 74.91 H 7.62 %.

X-Ray crystallographic study of 8, 9 and 14b

Suitable crystals of the complexes **8**, **9** and **14b** were obtained by layering concentrated solutions of the compounds in dichloromethane or chloroform with hexanes and allowing slow diffusion at room temperature. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transfered to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[20] The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C–H: 0.95 Å) and isotropic temperature factors (B(H) = 1.3 B_{eqv}(C) Å^2) but not refined. The hydrogen atoms of the solvents were not refined. Full least-square refinements were carried out on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from ref. 21. Crystal data and experimental details for the crystals of **8**, **9** and **14b** are given in Table 1.

CCDC reference numbers 190881–190883.

See http://www.rsc.org/suppdata/dt/b2/b207051k/ for crystallographic data in CIF or other electronic format.

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