Palladium and Platinum Units Grafted on the Periphery of Carbosilane Dendrimers

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The reaction of a series of phosphanyl-terminated carbosilane dendrimers with palladium and platinum complexes was carried out. The new metallodendrimers containing $PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)$ and $PtCl_2$ or $Pt(C{\equiv}CPh)_2$ as peripheral groups were characterized by ^1H, ^{13}C, ^{29}Si, ^{31}P, and ^{195}Pt NMR spectroscopy, and, in some cases, by mass spectrometry. The $PtCl_2$-containing species of the second-generation carbosilane dendrimer displays only one of the two possible stereoisomers. By comparison with the ^{31}P NMR spectra of the model compounds *cis*-$[PtCl_2(PPh_2CH_2SiMe_3)_2]$ (**4**) and *cis*-$[PtCl_2\{Me_2Si(CH_2PPh_2)_2\}]$ (**5**), it was deduced that the $PtCl_2$ units are bound on the surface of the dendrimer through two phosphorus atoms belonging to the same branch. The palladium dendrimers were tested as catalysts in the hydrovinylation of styrene, and their activity was compared with that of the model catalyst $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_2CH_2SiMe_3)]$. The crystal structures of **4**, **5**, and $[Pt(C{\equiv}CPh)_2\{Me_2Si(CH_2PPh_2)_2\}]$ (**6**) were solved by X-ray diffraction analysis.

Introduction

There is currently an interest in the synthesis of dendrimers and in the development of their chemistry.[1] Carbosilane dendrimers have been widely used in recent years because they are very stable, both kinetically and thermodynamically.[2] Moreover, peripheral groups, such as Si−Cl offer the opportunity of introducing other functions through the appropriate chemistry; such as the synthesis of carbosilane dendrimers containing diphenylphosphane-terminated groups.[3] Recently, we used these species as "dendrimer ligands" to coordinate a number of metal units (e.g., AuCl).[4] These units reacted, in turn, with metal anions to give dendrimers decorated on the surface by transition metal clusters.[5] We now report an extension of our previous efforts to graft palladium and platinum fragments on the periphery of the dendrimers and the study of the reactivity of such types of species, including the use of palladium compounds as catalytic precursors in the hydrovinylation of styrene.

Results and Discussion

The carbosilane dendrimers chosen for this study are listed in Scheme 1. They display different numbers of terminal phosphanyl groups on the surface (**1** and **2**), and the surface congestion on **3** is lower due to the presence of $CH_2-CH_2-SiMe_2$ spacers in the arms. The dendrimers were obtained by a repetitive stepwise synthetic route of hydrosilylation of the vinylic end groups of the dendrimer with chlorosilanes followed by alkenylation with vinylmagnesium chloride.[3] Next, reaction with the tetramethylethylenediamine complex of [(diphenylphosphanyl)methyl]lithium permitted the incorporation of terminal CH_2PPh_2 groups.

Platinum Dendrimers

Generally, the functionalization of the peripheral *P*-branched dendrimers with transition metals is simply achieved by taking advantage of the complexation ability of these species.[6] For example, they have been treated with complexes such as [Rh(acac)(COD)][7] or $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$.[8] Several reports describe peripheral platinum-containing dendrimers, but only one example shows platinum centers bonded to phosphorus atoms.[7]

In this paper we have functionalized the surface of our *P*-branched dendrimers with platinum by reaction with [$PtCl_2$(COD)]. We also synthesised the model compounds $[PtCl_2(PPh_2CH_2SiMe_3)_2]$ (**4**) and $[PtCl_2\{Me_2Si(CH_2PPh_2)_2\}]$ (**5**). Compound **4** was synthesised from $PPh_2CH_2SiMe_3$ (2 equiv.) and [$PtCl_2$(COD)] (1 equiv.), and **5** from [$PtCl_2$(COD)] (1 equiv.) and $Me_2Si(CH_2PPh_2)_2$ (1 equiv) (Scheme 2). Details of spectroscopy data of these compounds are given in the Exp. Sect.

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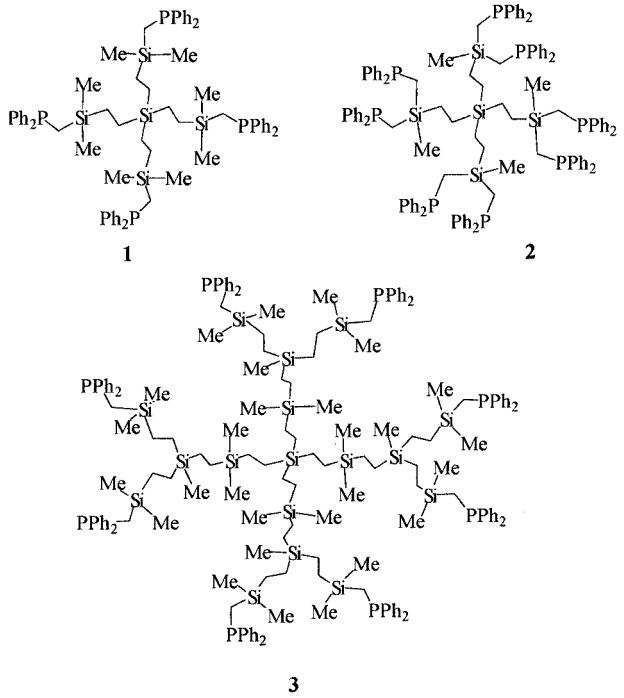
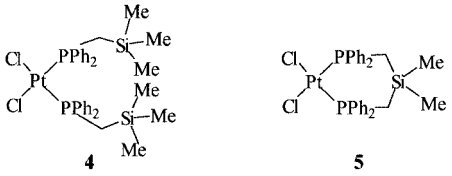


Scheme 1



Scheme 2

X-ray Crystal Structures of 4 and 5

A view of the compound *cis*-[$PtCl_2(PPh_2CH_2SiMe_3)_2$] (**4**) appears in Figure 1, and selected bond lengths and angles are given in Table 1. The platinum atom has a planar coordination with the slight tetrahedral distortion frequently observed for d^8 metal ions with bulky ligands.

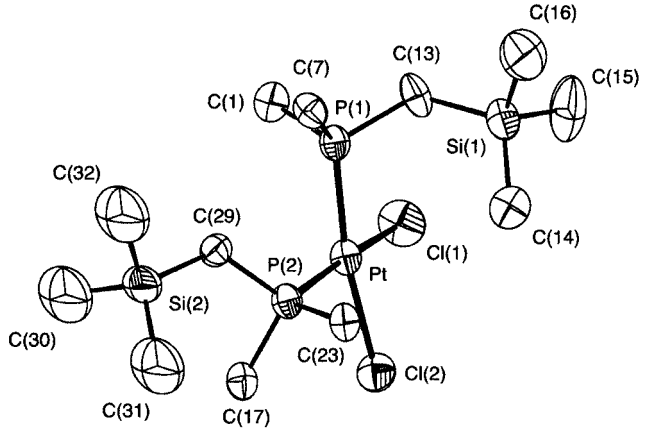


Figure 1. ORTEP drawing of the molecular structure and numbering scheme of **4**

Table 1. Selected bond lengths [Å] and angles [°] for **4**

Pt−P(1)	2.2401(9)	P(2)−C(29)	1.813(3)
Pt−P(2)	2.2545(8)	Si(1)−C(13)	1.892(4)
Pt−Cl(1)	2.3563(8)	Si(2)−C(29)	1.901(3)
Pt−Cl(2)	2.3506(9)	P(1)−C(13)	1.825(3)
P(1)−Pt−P(2)	100.90(3)	P(2)−C(29)−Si(2)	126.43(17)
P(1)−Pt−Cl(2)	169.85(3)	C(17)−P(2)−Pt	110.46(11)
P(2)−Pt−Cl(2)	87.89(3)	C(23)−P(2)−Pt	111.47(10)
P(1)−Pt−Cl(1)	84.92(3)	Cl(2)−Pt−Cl(1)	86.70(3)
P(2)−Pt−Cl(1)	172.88(3)	C(7)−P(1)−Pt	120.23(11)
C(13)−P(1)−Pt	112.61(14)	C(1)−P(1)−Pt	112.43(12)
C(29)−P(2)−Pt	118.06(10)		

The phosphane ligands adopt a *cis* configuration, in spite of the known fact that the bulky phosphane favors the formation of *trans* isomers to minimize ligand interactions. The Pt−Cl bond lengths are in the expected range, and the Pt−P distances are not elongated to any significant extent. The angles around the platinum atom are in the range 84.92(3)° [P(1)−Pt−Cl(1)] to 100.90(3)° [P(1)−Pt−P(2)]. The latter is intermediate between that found for [$PtCl_2(PPh_3)_2$] (97.8°)[9] and [$PtCl_2(PCy_3)_2$] (107.6°).[10] There is a steric tension between C(31) and the phenyl group C(17), which implies an increase in the Si(2)−C(29)−P(2) angle to 126.4°.

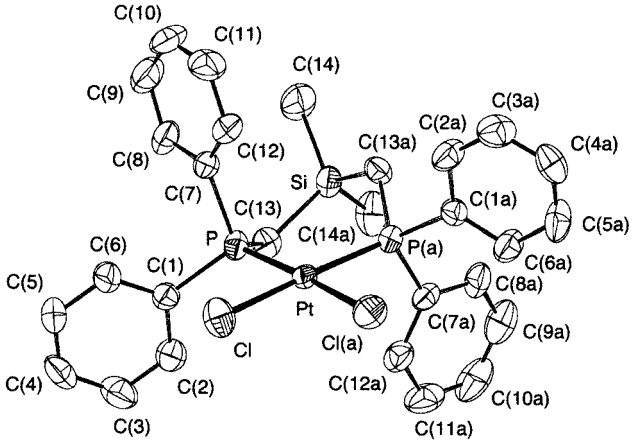


Figure 2. View of the molecular structure of **5** together with the atomic numbering scheme

The molecular structure of **5** is shown in Figure 2. Selected bond lengths and angles are listed in Table 2. Com-

Table 2. Selected bond lengths [Å] and angles [°] for **5**

Pt−P(1)	2.2456(16)	Si(1)−C(14)	1.845(7)
Pt−Cl(1)	2.3440(17)	Si(1)−C(13)	1.872(7)
P(1)−C(1)	1.822(6)	P(1)−C(13)	1.806(7)
P(1)−C(7)	1.810(6)		
P(1)−Pt−Cl(1)	88.59(7)	P(1)−Pt−Cl(1′)	175.98(6)
Cl(1)−Pt−Cl(1′)	87.40(10)	C(14′)−Si−C(13)	105.9(4)
C(14′)−Si−C(14)	109.3(6)	C(13)−Si−C(13′)	107.5(4)
C(14)−Si−C(13)	114.3(4)	C(13)−P−Pt	115.5(2)
C(7)−P−C(1)	105.4(3)	C(7)−P−Pt	113.9(2)
P−C(13)−Si	118.1(4)	C(1)−P−Pt	114.9(2)
P−Pt−P′	95.43(8)		

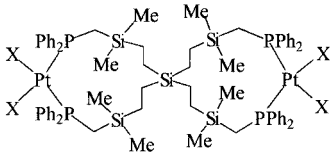
plex **5** contains a four-coordinate distorted square-planar platinum center, with the chlorine ligands displaced by −0.0052(1) Å (Cl) and 0.0052(1) Å [Cl(a)] from the Pt−P−P(a) plane. The ligand PP is bound in a bidentate fashion.

It should be noted that the ligand 2,2-dimethyl-1,3-bis(diphenylphosphanyl)-2-silapropane is an analogue of dppp, although the substitution of the CH_2 unit for $SiMe_2$ in the backbone not only increases complex solubility but also provides an excellent NMR spectroscopic handle. The Pt−P distances compare well with values reported in the compound $[PtCl_2(dppp)]$.[11] The shorter Pt−P bond lengths also suggest that a stronger bond than normal results from the chelate ring formation.

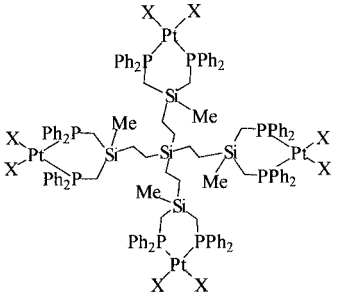
The six-membered chelate ring comprising Pt−P−C−Si−C−P adopts a twisted boat conformation, as found, for example, in $[Ni(NO_3)_2\{Ph_2PCH_2Si(CH_3)_2CH_2PPh_2\}]$.[12] It is noteworthy that the equivalent chelate ring in $[CoBr_2\{Me_2Si(CH_2PPh_2)_2\}]$[13] adopts a chair conformation, presumably due to the tetrahedral metal center. The chelate bite angle in **5** is 95.43(8)° (P1−Pt−P1′), somewhat shorter than that found for **4** and for the tetrahedral metal compounds $[CdCl_2(PP)]$,[14] $[CoCl_2(PP)]$,[13] and $[HgI_2(PP)]$[15] [PP = $Me_2Si(CH_2PPh_2)_2$].

Synthesis

Dendrimers **1** and **2** reacted with $[PtCl_2(COD)]$ in CH_2Cl_2 at room temperature to give, after COD displacement, the soluble, yellow, platinum-containing dendrimers **1a** and **2a**, respectively, within a few minutes (Scheme 3).



1a

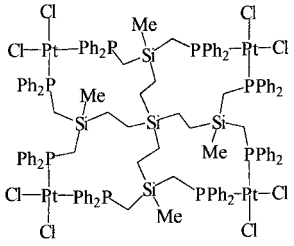


2a X= Cl
2b X= C≡CPh
2c X= $Co_2(CO)_6(C_2Ph)$

Scheme 3

The unique signal in the ^{31}P NMR spectra of their solutions clearly indicate that no mixture of compounds was formed, and reveal the complexation of platinum by the presence of platinum satellites (J_{Pt-P} = 3686 Hz for **1a** and 3558 Hz for **2a**). Two silicon signals are observed for both compounds, namely δ = 8.98 ppm (Si_0) and δ = 4.04 ppm (Si_1) ($CDCl_3$) for **1a**, and δ = 9.54 ppm (Si_0) and δ = 0.49 ppm (Si_1) ($[D_6]$DMSO) for **2a**. The ^{195}Pt NMR spectra showed a triplet at δ = −4320 ppm for **1a** and at δ = −4482 ppm for **2a** indicating the equivalence of the platinum atoms.

It is worth noting that the $PtCl_2$ units can be bound on the surface of the dendrimer through two P atoms belonging to the same branch, or alternatively, to different branches. Accordingly, **2a** can exhibit another stereoisomer, **2a′** (Scheme 4). A third possibility would be the simultaneous interaction of the platinum fragment with two molecules of dendrimer. However, in this case, the solubility of the resulting polymer species would probably be very low.



2a'

Scheme 4

As mentioned earlier, the unique resonance in the ^{31}P NMR spectrum indicates that only one isomer is formed. In order to assign it to **2a** or **2a′**, model compounds **4** and **5** are useful. Thus, for **4**, the angle P−Pt−P is 100.9° and J_{P-Pt} = 3673 Hz (δ = 4.2 ppm), while for **5**, the P−Pt−P angle is 95.43° and J_{P-Pt} = 3560 Hz (δ = 3.48 ppm). Although both values are close, we tentatively propose that the stereoisomer formed is **2a** (J_{P-Pt} = 3558 Hz; δ = 3.23 ppm), based on these data.

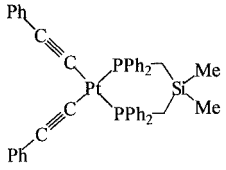
The FAB mass spectrum of **1a** contains two ion peaks at 1665.0 (calcd. 1666) and 815.0 (calcd. 815.4) corresponding to $[M - Cl]^+$ and $[M - 2\ Cl]^{2+}$, respectively. For **2a**, ion peaks at 1450, 954, and 707 were assigned to fragments $[M - 2\ Cl]^{2+}$, $[M - 3\ Cl]^{3+}$, and $[M - 4\ Cl]^{4+}$, respectively.

In contrast with the reported results for **1a** and **2a**, the ^{31}P NMR spectrum of the reaction of **3** with $[PtCl_2(COD)]$ to afford **3a**, shows, along with a sharp signal at δ = 4.4 ppm (t, J_{P-Pt} = 3683 Hz), another broad resonance at δ = 3.7 ppm (J_{P-Pt} = 3545 Hz). This spectrum indicates the presence of a mixture of stereoisomers, which was confirmed by the ^{195}Pt NMR spectrum. However, attempts to separate these isomers were unsuccessful. Electrospray spectrometry showed peaks corresponding to $[M - n\ Cl]^{n+}$ (n = 2, 3, 4, 6).

Following the same methodology for **1a**, **2a**, and **3a**, novel organometallic dendrimers containing platinum acetylide units were prepared. This class of derivatives has been actively investigated in the design of polymeric transition-metal complexes containing σ-bonded acetylide units because of their potential use in catalytic processes and as

precursors to cluster-containing dendrimers.[16] Two examples of organometallic dendrimers with a backbone composed of platinum acetylide units have been recently reported.[17]

We grafted $Pt(C{\equiv}CPh)_2$ fragments onto the surface of dendrimers **1** and **2** by treating them with $[Pt(C{\equiv}CPh)_2(COD)]$. According to the methodology followed in this paper, the model compound **6** was firstly synthesised from $Me_2Si(CH_2PPh_2)_2$ and $[Pt(C{\equiv}CPh)_2(COD)]$. (Scheme 5).



6

Scheme 5

The $^{195}Pt\{^1H\}$ NMR spectrum of **6** shows a resonance at $\delta = -3813$ ppm ($J_{P-Pt} = 2266$ Hz) and the ^1H NMR spectrum reveales the coupling of the CH_2 protons of the CH_2P fragment with the P and Pt nucleus ($J_{H-P} = 11.2$ Hz and $^3J_{H-Pt} = 32.95$ Hz). In accordance with its structure, the C_α acetylene carbon resonances appear in the $^{13}C\{^1H\}$ NMR spectrum at $\delta = 104.9$ ppm as a first-order doublet of doublets ($^2J_{C\alpha-Pcis} = 20.1$ Hz; $^2J_{C\alpha-Ptrans} = 150.2$ Hz), while the C_β signal is found at $\delta = 109.67$ ppm as the typical A part of a second-order AXX′ system [$^3J_{C\beta-Pcis} + {}^3J_{C\beta-Ptrans} = 35.5$ Hz)]. These values are very close to those reported by Forniés et al. in a series of *cis*-bis(alkynyl)platinum complexes.[18]

Crystal Structure of 6

The molecular structure of **6** was determined by X-ray structure analysis (Figure 3). Selected bond lengths and angles are collected in Table 3. Compound **6** is a nearly square-planar 16e$^-$ platinum complex formed by a diphosphane ligand and two mutually *cis*-oriented acetylide groups. The six atoms that form the chelate ring adopt a boat conformation with no appreciable twist distortion compared with that of **5**. The Pt−C and Pt−P distances are within the range of values quoted in the literature for *cis*-acetylide complexes. Bond lengths and angles in the two independent acetylide ligands are normal and the Pt−C≡C−C systems do not deviate significantly from linearity (see Table 3).[18,19]

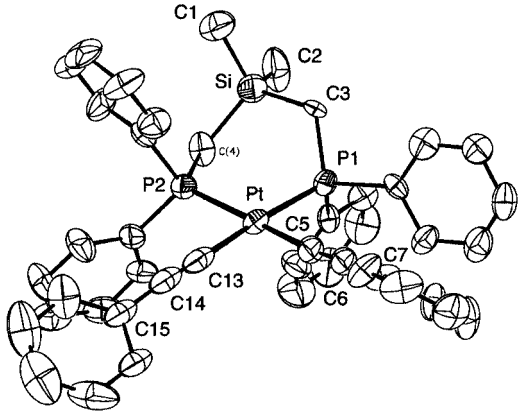


Figure 3. ORTEP drawing of the molecular structure and numbering scheme of **6**

Table 3. Selected bond lengths [Å] and angles [°] for **6**

Pt−C(13)	1.945(9)	Pt−P(1)	2.294(2)
Pt−C(5)	1.993(8)	Pt−P(2)	2.299(2)
P(1)−C(3)	1.799(6)	P(2)−C(4)	1.819(6)
Si−C(2)	1.859(7)	Si−C(4)	1.867(7)
Si−C(1)	1.870(8)	Si−C(3)	1.916(7)
C(5)−C(6)	1.209(9)	C(6)−C(7)	1.461(10)
C(13)−C(14)	1.148(10)	C(14)−C(15)	1.530(11)
C(13)−Pt−C(5)	87.3(3)	C(13)−Pt−P(1)	175.8(2)
C(5)−Pt−P(1)	91.7(2)	C(13)−Pt−P(2)	86.2(2)
C(5)−Pt−P(2)	171.2(2)	P(1)−Pt−P(2)	95.21(8)
C(3)−P(1)−Pt	112.9(2)	C(4)−P(2)−Pt	117.4(2)
C(4)−Si−C(3)	110.0(3)	P(1)−C(3)−Si	117.4(3)
P(2)−C(4)−Si	118.5(4)	C(6)−C(5)−Pt	173.1(7)
C(5)−C(6)−C(7)	177.7(8)	C(14)−C(13)−Pt	175.2(8)
C(13)−C(14)−C(15)	172.1(9)		

The reaction of **2** with the platinum acetylide complex in a 1:4 molar ratio gave **2b** in a high yield. The analytical and spectroscopic (IR and ^1H, ^{13}C, ^{31}P, ^{29}Si, ^{195}Pt NMR) data are in agreement with the formula proposed for the new complex. The most remarkable feature of the IR spectrum is the presence of an absorption at 2117 cm^{-1} attributed to the $\nu_{C\equiv C}$ stretching vibration, which is considerably shifted to lower wavenumbers compared to that of the σ-alkynyl precursor. The C_α alkynyl carbon resonance in the $^{13}C\{^1H\}$ NMR spectrum appears at $\delta = 104.4$ ppm ($^2J_{C\alpha-Pcis} = 20.0$ Hz; $^2J_{C\alpha-Ptrans} = 150.3$ Hz); that of C_β appears at $\delta = 109.97$ ppm [$^3J_{C\beta-Pcis} + {}^3J_{C\beta-Ptrans} = 32.0$ Hz)]. The ^{195}Pt NMR spectrum shows a triplet with a coupling constant ($J_{Pt-P} = 2255$ Hz), very similar to that found for **6**, which, along with the NMR spectroscopic data discussed above, confirms the proposed structure for **2b**.

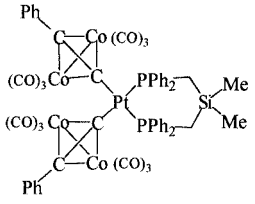
As expected, the attachment of the acetylide group increased its solubility considerably compared with that of **2a**. In contrast, the reaction of the platinum acetylide compound with **1** gave a mixture of species. These species were not analyzed because of their complexity. It seems that the bite angle P−Pt−P displayed in **1**, as compared with **2**, is higher than that required for the complexation of the $Pt(C{\equiv}CPh)_2$ fragment.

Reaction with $Co_2(CO)_8$

Alkyne systems easily react with $Co_2(CO)_8$ to afford $C_2[Co(CO)_3]_2$ tetrahedrane clusters that can be used as a part of the backbone dendritic connectivity or as peripheral groups. This is a facile method for the introduction of mul-

tiple metal clusters, but it has found little use in metallodendrimer chemistry,[20] although it is well known in the area of heterometallic stars.[21]

This strategy was thus applied to our dendrimers, in an attempt to form multiple $\{C_2Co_2(CO)_6\}$ cluster sites. A previous reaction between the model compound **6** and $Co_2(CO)_8$ gave $[Pt\{C_2PhCo_2(CO)_6\}_2\{Me_2Si(CH_2PPh_2)_2\}]$ (**7**) (Scheme 6), the spectroscopic data of which are listed in the Exp. Sect., thus permitting optimization of the reaction conditions.



7

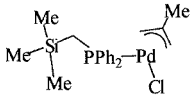
Scheme 6

Compound **2b** was treated in dichloromethane at room temperature with the octacarbonyldicobalt compound, and the new species **2c** was obtained in moderate yields after 2 h.

The incorporation of the carbonylmetal units was confirmed by the appearance of strong absorptions in the IR spectrum at 2081, 2060, and 2016 cm^{-1}, typical of $[Co_2(CO)_6(RCCR)]$ clusters. Strong evidence of cluster formation could not be inferred from the ^{13}C NMR spectrum, given the poor solubility of **2c**. A single signal at $\delta = 210$ ppm was assigned to the carbonyl carbon atoms. In the ^1H NMR spectrum the broad signal at $\delta = 1.65$ ppm is in agreement with the diastereotopic and therefore nonequivalent nature of the CH_2−P protons. This fact was observed analogously in the spectra of **2a** and **2b**. The ^{31}P NMR spectrum shows only one signal at $\delta = 12.6$ ppm flanked by platinum satellites. The $Co_2(CO)_6$ coordination caused an increase of the coupling constant J_{P-Pt} from 2254 Hz of **2b** to 3496 Hz. We are currently extending the chemical and structural aspects of these novel high-nuclearity species.

Palladium Dendrimers

Before the synthesis of the Pd-containing dendrimers, we prepared the model compound $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_2CH_2SiMe_3)]$ (**8**) by treating $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ with $PPh_2CH_2SiMe_3$ (Scheme 7).

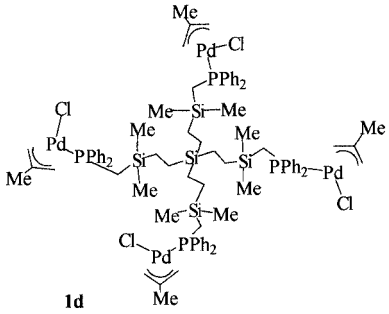


8

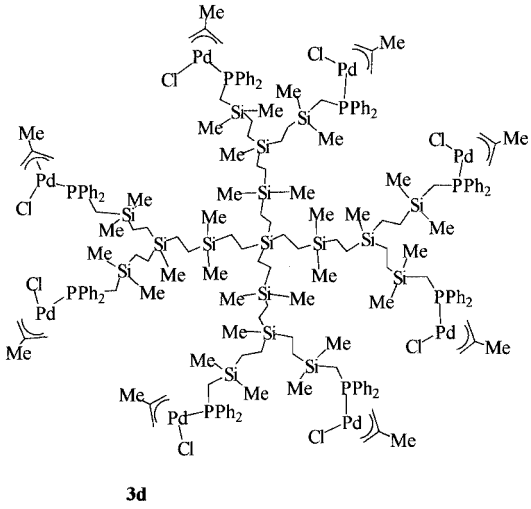
Scheme 7

The ^{31}P NMR spectrum of **8** shows only one signal at $\delta = 17.8$ ppm and the ^{29}Si NMR spectrum, another one at $\delta = 0.8$ ppm. The ^1H and ^{13}C NMR spectra evidence the presence of the allyl and the dendrimer ligands.

The grafting of the palladium fragments $Pd(\eta^3\text{-}2\text{-}MeC_3H_4)Cl$ on the surface of our dendrimers was achieved in good yields by treating **1** and **3** with the dinuclear allyl complex $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$ in THF at room temperature (Scheme 8).



1d



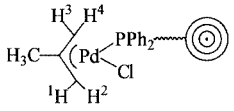
3d

Scheme 8

The synthesis of the new palladodendrimers **1d** and **3d** was monitored by ^{31}P NMR spectroscopy. In both cases, the complete disappearance of the signal at $\delta = -23$ ppm along with the emergence of a new one at $\delta \approx 17$ ppm confirmed that the reaction occurred quantitatively. The yellow compounds obtained were pure within the limits of the NMR spectroscopic detection. They were soluble in the most common organic solvents, and were characterized by elemental analyses, ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR, as well as by fast atom bombardment (FAB) or electrospray mass spectrometry.

The ^1H NMR spectra for **1d** and **3d** showed the resonances for the methyl, methylene, and ethylene protons with chemical shifts in the corresponding regions of the spectrum in the expected integrated ratio. The coordination of the palladium fragment to the dendrimer gives rise to the coupling of the H^1 and H^2 with the phosphorus nucleus

($^3J_{H-P}$ = 6.5 and 10 Hz) and the high-field shifts of the H^3 and H^4 resonances (Scheme 9).

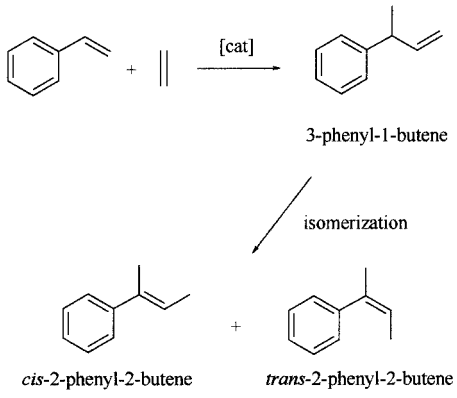


Scheme 9

The ^{13}C NMR spectra confirmed the presence of the above-mentioned groups. The ^{29}Si NMR spectra display clearly separated signals (two for **1d** and four for **3d**) for the different types of silicon atoms in the molecules. These signals can be easily assigned on the basis of the chemical shifts and the peak intensities. The presence of only one signal in the ^{31}P NMR spectra indicates that no mixture of products is formed in the reaction.A solution of sodium chloride in THF was added to the samples **1d** and **3d** in order to improve the peak resolution in mass spectrometry. Thus, FABMS showed the $[M - Cl]^+$ peak at m/z = 1923.6 for **1d** (calcd. 1920.5), and the MS/ES, the peak $[M - 3\{Pd(2\text{-}CH_3\text{-}C_3H_4)Cl\} - 3\ Cl]^{3+}$ at m/z = 1272.2 for **3d** (calcd. 1273.1) in accordance with the proposed formula. Other fragments were also assigned (see Exp. Sect.).

Catalytic Studies

One of the main applications of dendrimers is in catalysis. The well-defined structure and the possibility of attaching a large number of active sites makes them especially interesting for catalyst immobilization and catalyst recycling.[22] Recently, some palladium-containing carbosilane dendrimers have been used as catalysts in allylic alkylation reactions[8] and in the selective hydrovinylation of styrene performed in a continuous flow membrane reactor.[23] Here, the palladium dendrimers **1d** and **3d** were tested as catalysts in the hydrovinylation of styrene (Scheme 10), and their activity was compared with that of the mononuclear model complex $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)(PPh_2CH_2SiMe_3)]$ (**8**). Interestingly, hydrovinylation of styrene produced 3-phenyl-1-butene as a main product, this process being a model reaction for the synthesis of compounds with pharmacological activity.



Scheme 10

The fact that **8**, **1d**, and **3d** have an $RCH_2Si(CH_3)_2\text{-}CH_2PPh_2$ moiety in common permits the evaluation of the steric effects caused only by changes in the dendrimeric structure.

It is well known that active catalysts in hydrovinylation reactions are cationic species, so we synthesised the cationic species of our dendrimers in situ by adding $Ag[BF_4]$ to their dichloromethane solutions and removing the silver chloride by filtration. Otherwise, the cationic complexes stabilized with CH_3CN ligands were isolated as solids and their activity compared with that exhibited by the species prepared in situ. In order to differentiate between the two types of species, we will refer to the cationic dendrimers obtained in situ as **1d**$^+$, **3d**$^+$, and **8**$^+$, and the salts stabilized with CH_3CN as **1d***, **3d***, and **8***.

The catalytic data obtained in the hydrovinylation of styrene using the described compounds are shown in Table 4.

Table 4. Hydrovinylation of styrene by palladium compounds

Entry[a]	Precursor	T [°C]	t [h]	Conversion[b]	Selectivity[c]	TOF/h[d]
1	**8**$^+$	15	2	94.2	80.3	465
2	**8**$^+$	25	0.5	86.8	85.7	1710
3	**8**$^+$	25	0.33	57.5	95.9	1695
4	**1d**$^+$	25	2	88.6	85.9	440
5	**1d**$^+$	25	1	55.4	96.0	550
6	**3d**$^+$	25	1	63.0	94.4	620
7	**8***	25	0.75	78.5	91.6	1040
8	**8***	15	2	71.5	94.4	355
9	**1d***	15	2	29.6	100	145
10	**1d***	25	2	74.2	92.1	368
11[e]	**1d***	25	2	3.5	100	18
12	**3d***	25	1	43.0	97.6	425
13	**3d***	25	1.5	57.4	94.9	380

[a] Initial ethylene pressure, 15 bar; solvent: CH_2Cl_2; ratio styrene/Pd 1000:1. [b] Conversion of starting styrene. [c] Selectivity:% of 3-phenyl-1-butene respect to the total amount of arylbutenes formed. [d] TOF/h calculated as the total amount of arylbutenes formed. [e] In THF.

As can be seen from Table 4, activity is lower for the cationic dendritic precursors **1d**$^+$ (or **1d***) and **3d**$^+$ (or **3d***), compared with the mononuclear precursor **8**. The same effect was observed by Vogt and van Koten in similar hemilabile PO-stabilized dendritic precursors.[24] Probably, the dendrimers block some of the space that olefins can use in their approach to the palladium atoms, the active sites. However, it is remarkable that the activity of the biggest system **3d** is higher or similar to that of **1d** (Entries 5 and 6) in spite of the fact that the first shows 8 PPh_2 groups in comparison with the 4 PPh_2 ligands displayed by the second. This interesting effect can be explained by the fact that **3d** has one methyl group over the neighboring Si while bulkier ligands are attached to the neighboring Si in **1d**. This can be seen by comparing Entries 2, 5, 6, with 7, 10, 13. Moreover, Table 4 shows that the catalysts obtained in situ in dichloromethane are better than those previously isolated, due to the ineffective coordinating ability of the

solvent. When a solvent of greater coordination ability, like THF, was used, an impressive decrease in activity was observed (Entries 10 and 11). Formation of oligomers or higher co-oligomers is not significant. In conclusion, it is clear from our data that the catalytic activity is affected by "surface congestion".

The isomerization of the chiral product 3-phenyl-1-butene to achiral (*E*) and (*Z*) internal olefins (Scheme 10) is related to the conversion of the process. Thus, at high conversions the consecutive isomerization reaction becomes important and consequently an increase of the internal olefins is obtained (Table 4). It is well known that the isomerization occurs through the previous coordination of the 3-phenyl-1-butene to the catalyst. Thus, the coordination ability of other molecules present in the reaction media determines the selectivity. Obviously, in our case, the solvent can compete with the 3-phenyl-1-butene. For example, Entries 1−3 and 8 indicate that the presence of stoichiometric amounts of acetonitrile competes successfully with 3-phenyl-1-butene and avoids its attachment to the catalyst, thus improving the selectivity of the process. In conclusion, in order to improve the selectivity of the process, a major goal would be to find a ligand or a hemilabile bidentate ligand with a coordinating ability towards the metallic system intermediate between styrene and 3-phenyl-1-butene.

From Table 4 we can observe in all cases a decrease of the activity in increasing the reaction times, as a consequence of the deactivation of the catalytic species. This effect is more important for the dendrimers. The deactivation of the catalyst is clearly observed when runs at different reaction times are compared − Entries 4 and 5 or 12 and 13. This is evidenced by a decrease in the TOF number upon increasing the reaction time, in the significant range of conversions. The model compound **8** showed higher stability, but shorter reaction times − Entries 2 and 3. Our preliminary results showed similar loss of activity of **1d** and **3d** precursors. Interestingly, no precipitation of palladium black was observed before total conversion. In order to obtain more conclusive results about the relative stability of these dendritic systems as a function of their size we would need to test the activity of catalyst based on higher generations.

In summary, the dendrimers studied in this paper are active for the hydrovinylation of styrene, but their activity is lower than that shown by the mononuclear model **8** and other related palladium complexes containing different phosphane ligands.[25] However, polynuclear complexes **1d** and **3d** are more active compared with other dendritic catalysts containing 8 and 12 terminal bidentate PO coordinating atoms on the surface.[24] Moreover, the good selectivity of our dendrimers towards 3-phenyl-1-butene is remarkable.

Experimental Section

General: All reactions were carried out under dry nitrogen using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl (THF and Et_2O), $CaCl_2$ and stored over molecular sieves (acetone) or dried with $CaCl_2$ and distilled from CaH_2 (CH_2Cl_2) under N_2 prior to use. Elemental analyses (C, H) were performed at the Servicio de Microanálisis del Centro de Investigación y Desarrollo del Consejo Superior de Investigaciones Científicas (CSIC). ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded at 25 °C with a Bruker 250 spectrometer. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for ^1H, ^{13}C and ^{29}Si, 85% H_3PO_4 for ^{31}P and H_2PtCl_6 for ^{195}Pt) and coupling constants are given in Hz. Infrared spectra were recorded with FT-IR 520 Nicolet or Impact 400 Nicolet spectrometers in the 4000−400 cm^{-1} range as KBr pellets. MS (FAB and ES) spectra were recorded with a Fisons VGQuattro spectrometer using NBA (3-nitrobenzyl alcohol) as a matrix for FAB spectra. MALDI-TOF spectra were recorded with a Voyager DE-RP (Perspective Biosystems) spectrometer using DHB (2,5-dihydrobenzoic acid) as a matrix. The starting materials $Me_2Si(CH_2PPh_2)_2$,[26] $[Pd(\mu\text{-}Cl)(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)]_2$,[27] $[PtCl_2(COD)]$,[28] and $[Pt(C{\equiv}CPh)_2(COD)]$[29] were prepared according to published procedures. Other reagents were purchased from commercial suppliers and used as received.

Synthesis of Diphenyl[(trimethylsilyl)methyl]phosphane ($PPh_2CH_2SiMe_3$): This phosphane, described in the literature,[30] was synthesised by a different method here. To a suspension of the Grignard reagent (slight excess) of (chloromethyl)trimethylsilane, prepared from 1.77 g (14.4 mmol) of (chloromethyl)trimethylsilane and 0.45 g (18.5 mmol) of magnesium in THF (50 mL), was slowly added chlorodiphenylphosphane (2.95 g, 13.4 mmol); the resulting mixture was stirred at room temperature for 30 min and hydrolysed with an aqueous solution of NH_4Cl (10%). The organic layer was washed twice with water and dried with Na_2SO_4. Concentration of this solution to dryness gave the desired phosphane as a colorless oil (2.92 g, yield 80%). ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.25 (s, 9 H, CH_3), 1.34 (s, 2 H, CH_2), 7.28−7.34 (m, 6 H, C_6H_5), 7.45−7.50 (m, 4 H, C_6H_5) ppm. ^{31}P NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = −22.05 (s) ppm. ^{29}Si NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 1.26 (d, J = 14.7 Hz) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = −0.2 (d, J = 4.7 Hz, CH_3), 14.6 (d, J = 29.0 Hz, CH_2), 128.1−141.2 (m, C_6H_5) ppm.

Synthesis of $[PtCl_2(Me_3SiCH_2PPh_2)_2]$ (4): $[PtCl_2(COD)]$ (0.08 g, 0.21 mmol) was dissolved in CH_2Cl_2 (10 mL) and a solution of $PPh_2CH_2Si(Me_2)CH_2PPh_2$ (0.12 g, 0.43 mmol) in CH_2Cl_2 (10 mL) was added. The solution was stirred overnight and then concentrated to dryness. The solid was recrystallized from CH_2Cl_2/Et_2O and dried under vacuum. Yield: 172 mg, 50%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.18 (s, 18 H, CH_3), 1.72 (d, $^2J_{H-P}$ = 15.7, $^3J_{H-Pt}$ = 32 Hz, 4 H, CH_2P), 7.24−7.57 (m, 20 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = 0.9 (s, CH_3), 18.3 (m, CH_2P), 128.1−133.2 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 Hz, $CDCl_3$, 25 °C): δ = 0.11 ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 4.2 (s, $^1J_{P-Pt}$ = 3673.2 Hz) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 MHz, $CDCl_3$, 25 °C): δ = −4318.0 (t) ppm. $ESMS^+$ (CH_2Cl_2): m/z = 775.7 $[M - Cl]^+$. $MSFAB^+$ (THF): m/z = 810.2 $[M]^+$, 775.3 $[M - Cl]^+$. $C_{32}H_{42}Cl_2P_2PtSi_2$ (810.80): calcd. C 47.36, H 5.22; found C 48.26, H 5.43.

Synthesis of $[PtCl_2\{Me_2Si(CH_2PPh_2)_2\}]$ (5): Experimental conditions and workup were identical to those for the preparation of **4**. Yield: 218 mg, 90%. ^1H NMR (250 MHz, CD_2Cl_2, 25 °C): δ = −0.34 (s, 6 H, CH_3), 1.77 (d, 4 H, $^2J_{P-H}$ = 12.3, $^3J_{H-Pt}$ = 62.3 Hz, CH_2P), 7.4−7.8 (m, 20 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, CD_2Cl_2, 25 °C): δ = −0.1 (t, $^3J_{C-P}$ = 3.4 Hz, CH_3), 12.2 (m, CH_2P), 128.2−133.5 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, CD_2Cl_2, 25 °C): δ = −0.96 ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, CD_2Cl_2, 25 °C): δ = 3.5 (s, $^1J_{P-Pt}$ = 3559.8 Hz,

PPh_2) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 MHz, CD_2Cl_2, 25 °C): δ = −4491.7 (t) ppm. MSFAB$^+$ (CH_2Cl_2): *m/z* = 687.2 [M − Cl]$^+$. $C_{28}H_{30}Cl_2P_2PtSi$ (722.58): calcd. C 46.54, H 4.19; found C 45.60, H 4.23.

Synthesis of 1a: Experimental conditions and workup were identical to those for the preparation of **4**. Yield: 145 mg, 71%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.06 (br. s, 24 H, CH_3), 0.75−1.44 (br. s, 16 H, CH_2), 1.92 (d, $^2J_{H-P}$ = 15.8 Hz, 8 H, CH_2P), 7.00−7.70 (m, 40 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = −0.6 (s, C^1H_3), 4.7 (s, $-CH_2-$), 10.3 (s, $-CH_2-$), 16.2 (m, CH_2P), 127.7−132.4, (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 4.04 (s, Si_1), 8.98 (s, Si_0) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 4.4 (s, $^1J_{P-Pt}$ = 3686.4 Hz, PPh_2) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 MHz, $CDCl_3$, 25 °C): δ = −4322.0 (t) ppm. ESMS$^+$ (THF): *m/z* = 1665.0 [M − Cl]$^+$, 815.0 [M − 2 Cl]$^{2+}$. $C_{68}H_{88}Cl_4P_4Pt_2Si_5$ (1701.77): calcd. C 47.99, H 5.21; found C 47.70, H 5.27.

Synthesis of 2a: Experimental conditions and workup were identical to those for the preparation of **4** Yield: 170 mg, 50%. ^1H NMR (250 MHz, [D$_6$]DMSO, 25 °C): δ = −(0.64−0.52) (s, 12 H + 16 H, $-CH_3$; $-CH_2-$), 1.66−1.93 (m, 16 H, CH_2P); 7.30−7.76 (m, 40 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, [D$_6$]DMSO, 25 °C): δ = −2.8 (s, CH_3-), 0.6 (s, $-CH_2-$), 7.6 (s, $-CH_2-$), 10.2 (m, CH_2P), 128.3−133.8 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, [D$_6$]DMSO, 25 °C): δ = 0.49 (s, Si_1), 9.54 (s, Si_0) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, [D$_6$]DMSO, 25 °C): δ = 4.1 (s, $^1J_{P-Pt}$ = 3558.4 Hz, PPh_2) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 Hz, [D$_6$]DMSO, 25 °C): δ = −4482.0 (s). ESMS$^+$ (CH_2Cl_2): *m/z* = 1450.0 [M − 2 Cl]$^{2+}$, 954.0 [M − 3 Cl]$^{3+}$, 707.0 [M − 4 Cl]$^{4+}$. $C_{116}H_{124}Cl_8P_8Pt_4Si_5$ (2970.47): calcd. C 46.90, H 4.21; found C 46.60, H 4.27.

Synthesis of 3a: Experimental conditions and workup were identical to those for the preparation of **4**. Yield: 220 mg, 65%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.22−0.00 (m, 84 H, CH_3), 0.29 (br. s, 64 H, $-CH_2-$), 1.59−1.64 (m, 16 H, CH_2P), 7.29−7.59 (m, 80 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = −6.6 (s, CH_3), −4.2 (s, CH_3), −1.6 (s, CH_3), 2.8 (s, $-CH_2-$), 4.5 (s, $-CH_2-$), 6.7 (s, $-CH_2-$), 9.4 (s, $-CH_2-$), 10.3 (s, $-CH_2-$), 16.3 (sbr, CH_2P), 128.0−133.0 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 3.80 (s, Si_3), 5.71 (s, Si_1), 7.84 (s, Si_2), 9.32 (s, Si_0) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 3.7 (s, $^1J_{P-Pt}$ = 3545 Hz, PPh_2), 4.4 (s, $^1J_{P-Pt}$ = 3683 Hz, PPh_2) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 MHz, $CDCl_3$, 25 °C): δ = −4311.0 (t, major isomer), −4325.2 (t, minor isomer). ESMS$^+$ (CH_2Cl_2): *m/z* = 1968.3 [M − 2 Cl]$^{2+}$, 1298.6 [M − 3 Cl]$^{3+}$, 965.6 [M − 4 Cl]$^{4+}$, 631.0 [M − 6 Cl]$^{6+}$. $C_{164}H_{244}Cl_8P_8Pt_4Si_{17}$ (4004.99): calcd. C 49.18, H 6.14; found C 48.89, H 6.25.

Synthesis of [Pt(C≡CPh)$_2${Me$_2$Si(CH$_2$PPh$_2$)$_2$}] (6): [Pt(C≡CPh)$_2$(COD)] (0.16 g, 0.31 mmol) was suspended in acetone (10 mL) and a solution of $Me_2Si(CH_2PPh_2)_2$ (0.14 g, 0.31 mmol) in acetone (10 mL) was added; resulting in a quick dissolution. The resulting yellow solution was stirred at room temperature for 2 h and then concentrated to dryness, washed with diethyl ether and dried under vacuum. Crystals suitable for X-ray analysis were collected from a CH_2Cl_2/Et_2O mixture at −20 °C. Yield: 194 mg, 73%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.30 (s, 6 H, CH_3), 1.70 (d, $^2J_{H-P}$ = 11.2, $^3J_{H-Pt}$ = 32.95 Hz, 4 H, CH_2P), 6.80−7.70 (m, 30 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = 0.8 (t, $^3J_{C-P}$ = 3.4 Hz, CH_3), 11.7 (m, CH_2P), 105.0 (dd, $^2J_{C\alpha-Pcis}$ = 20.1, $^2J_{C\alpha-Ptrans}$ = 150.2 Hz, C_α), 109.7 (AXX′, $^3J_{C\beta-Pcis}$ + $^3J_{C\beta-Ptrans}$ = 35.5 Hz, C_β), 124.7−133.6 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 0.0 ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 1.6 (s, $^1J_{P-Pt}$ = 2258.1 Hz, CH_2P) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 MHz, $CDCl_3$, 25 °C): δ = −3813.0 (t) ppm. IR (KBr, cm^{-1}): ν(C≡C) = 2120. ESMS$^+$ (CH_2Cl_2): *m/z* = 854.1 [M]$^+$. $C_{44}H_{40}P_2PtSi$ (853.93): calcd. C 61.89, H 4.72; found C 61.75, H 4.67.

Synthesis of 2b: Experimental conditions and workup were identical to those for the preparation of **6**. Yield: 222 mg, 84%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −(0.38−0.16) (m, 12 H + 16 H, CH_3, $-CH_2-$), 1.60 (m, 16 H, $-CH_2P$), 6.8−7.8 (m, 120 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = −1.7 (s, CH_3-), 1.1 (s, $-CH_2-$), 8.4 (s, $-CH_2-$), 10.1 (m, $-CH_2P$), 104.4 (dd, $^2J_{C\alpha-Pcis}$ = 20, $^2J_{C\alpha-Ptrans}$ = 150.3 Hz, C_α), 109.97 (AXX′, $^3J_{C\beta-Ptrans}$ + $^3J_{C\beta-Pcis}$ = 32.0 Hz, C_β), 124.8−135.7 (m, C_6H_5). $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 2.85 (s, Si_1), 9.66 (s, Si_0) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 1.4 (s, $^1J_{P-Pt}$ = 2254.4 Hz, PPh_2) ppm. $^{195}Pt\{^1H\}$ NMR (53.54 MHz, $CDCl_3$, 25 °C): δ = −4802.4 (t) ppm. IR (KBr, cm^{-1}): ν(C≡C) 2117. $C_{180}H_{164}P_8Pt_4Si_5$ (3495.87): calcd. C 61.84, H 4.73; found C 60.14, H 4.81.

Synthesis of [Pt{C$_2$PhCo$_2$(CO)$_6$}$_2${Me$_2$Si(CH$_2$PPh$_2$)$_2$}] (7): Compound **6** (0.09 g, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL) and $Co_2(CO)_8$ (0.10 g, 0.29 mmol) was added as a solid. The mixture was stirred at room temperature for 2 h. The resulting brown solution was concentrated to half the original volume and filtered through a small column of alumina. The solution obtained was concentrated to dryness. Yield: 74 mg, 49%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.61 (s, 6 H, CH_3), 1.73 (d, $^2J_{H-P}$ = 10.6, $^3J_{H-Pt}$ = 48.8 Hz, 4 H, CH_2P), 7.46−7.81 (m, 30 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = 0.2 (s, CH_3), 14.1 (m, CH_2P), 128.2−137.6 (m, C_6H_5), 209.7 (s, CO) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 13.2 (s, $^1J_{P-Pt}$ = 3498.9 Hz, CH_2P) ppm. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2095 w, 2081 w, 2055 vs, 2014 vs, 1950 s. ESMS$^+$ (CH_2Cl_2): *m/z* = 994.4 [M − $Co_3(CO)_9$]$^+$, 967.5 [M − $Co_3(CO)_{10}$]$^+$, 853.4 [M − $Co_4(CO)_{12}$]$^+$. $C_{56}H_{40}Co_4O_{12}P_2PtSi$ (1425.78): calcd. C 47.18, H 2.83; found C 47.01, H 2.85.

Synthesis of 2c: Experimental conditions and workup were identical to those for the preparation of **7**. Yield: 194 mg, 79%. ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −(0.74−0.32) (s, 12 H + 16 H, CH_3-, $-CH_2-$), 1.65 (br. m, 16 H, CH_2P), 6.8−7.6 (m, C_6H_5) ppm. ^{31}P NMR (101.26 MHz, CD_2Cl_2, 25 °C): δ = 12.68 (s, $^1J_{P-Pt}$ = 3496.0 Hz, PPh_2) ppm. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2100 w, 2081 s, 2060 vs, 2016 vs, 1989 ssh, 1890 w. $C_{228}H_{164}Co_{16}O_{48}P_8Pt_4Si_5$ (5783.28): calcd. C 47.35, H 2.86; found C 47.09, H 2.94.

Synthesis of [PdCl(η^3-2-MeC$_3$H$_4$)(PPh$_2$CH$_2$SiMe$_3$)] (8): To a solution of [Pd(η^3-C_4H_7)(μ-Cl)]$_2$ (0.62 g, 1.57 mmol) in CH_2Cl_2 (30 mL), was added $Me_3SiCH_2PPh_2$ (0.86 g, 3.14 mmol) and the reaction mixture stirred for 30 min at room temperature. The solvent was evaporated to dryness and the solid was washed with diethyl ether and dried under vacuum. Yield: 1.18 g (80%). ^1H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.04 (s, 9 H, CH_3), 1.90 (s, 3 H, CH_3), 1.97 (d, $^2J_{H-P}$ = 14.3 Hz, 2 H, CH_2P), 2.63 (s, 1 H, H^4), 3.33 (br. s, 1 H, H^3), 3.46 (d, $^3J_{H-P}$ = 10.1 Hz, 1 H, H^2), 4.44 (dd, $^3J_{H-P}$ = 6.9 Hz, J_{H-H} = 2.8 Hz, 1 H, H^1), 7.30−7.65 (m, 10 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 0.4 (d, $^3J_{C-P}$ = 3.8 Hz, CH_3), 14.4 (d, $^1J_{C-P}$ = 11.4 Hz, CH_2P), 23.2 (s, CH_3), 57.8 (s, C_{cis}), 76.9 (d, $^2J_{C-P}$ = 33.2 Hz, C_{trans}), 128.3−136.2 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 0.82 (s) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 17.8 (s). $C_{20}H_{28}ClPPdSi$ (469.36): C 51.18, H 6.01; found C 51.13, H 6.11.

Synthesis of 1d: Experimental conditions and workup were identical to those for the preparation of **8**. Yield 380 mg, 85%. ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): δ = −0.03, −0.07 (s, 24 H, CH_3), 0.15 (s, 16 H, $-CH_2-$), 1.96 (s, 12 H, CH_3), 2.05 (d, $^2J_{H-P}$ = 15.0 Hz, 8 H, CH_2P), 2.70 (s, 4 H, H^4), 3.31 (s, 4 H, H^3), 3.42 (d, $^3J_{H-P}$ = 9.8 Hz, 4 H, H^2), 4.39 (d, $^3J_{H-P}$ = 6.2 Hz, 4 H, H^1), 7.44−7.66 (m, 40 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = − 2.0 (s, CH_3), 2.5 (s, $-CH_2-$), 9.1 (d, $^3J_{C-P}$ = 4.8 Hz, $-CH_2-$), 12.8 (d, $^1J_{C-P}$ = 11.0 Hz, CH_2P), 23.3 (s, CH_3), 58.0 (s, C_{cis}), 76.7 (d, $^2J_{C-P}$ = 32.0 Hz, C_{trans}), 128.3−136.3 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 3.0 (s, Si_1), 18.5 (s, Si_0) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 17.4 (s, PPh_2) ppm. MSFAB$^+$: *m/z*: 1923.6 [M$^+$ − Cl]. $C_{84}H_{116}Cl_4P_4Pd_4Si_5$ (1956.03): calcd. C 51.53, H 5.93; found C 52.07, H 6.17.

Synthesis of 3d: Experimental conditions and workup were identical to those for the preparation of **8**. Yield: 430 mg, 82%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = −0.26 (s, 12 H, C^2H_3), −0.13 (s, 24 H, C^1H_3), −0.09, −0.05 (s, 48 H, C^3H_3, $C^{3'}H_3$), 0.16−0.20 (m, 64 H, $-CH_2-$), 1.86 (s, 24 H, C^4H_3), 1.90 (d, $^2J_{H-P}$ = 11.0 Hz, CH_2P), 1.90 (d, $^2J_{H-P}$ = 10.5 Hz, CH'_2P), 2.61 (s, 8 H, H^4), 3.30 (s, 8 H, H^3), 3.41 (d, $^3J_{H-P}$ = 10.0 Hz, 8 H, H^2), 4.37 (d, $^3J_{H-P}$ = 4.6 Hz, 8 H, H^1), 7.32−7.55 (m, 80 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (62.86 MHz, $CDCl_3$, 25 °C): δ = −6.7 (s, C^2H_3), −4.5 (C^1H_3), −2.1 (s, C^3H_3, $C^{3'}H_3$), 4.2 (s, $-C^1H_2-$, $-C^2H_2-$), 4.5 (s, $-C^3H_2-$), 6.5 (d, $-C^5H_2-$), 8.9 (d, $^3J_{C-P}$ = 3.7 Hz, $-C^6H_2-$), 12.6 (d, $^1J_{C-P}$ = 11.0 Hz, CH_2P), 23.1 (s, C^4H_3), 57.8 (s, C_{cis}), 76.4 (d, $^2J_{C-P}$ = 32.9 Hz, C_{trans}), 128.2−136.1 (m, C_6H_5) ppm. $^{29}Si\{^1H\}$ NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 3.14 (s, Si_3), 5.72 (s, Si_1), 8.04 (s, Si_2), 9.43 (s, Si_0) ppm. $^{31}P\{^1H\}$ NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 17.7 (s, PPh_2). ESMS$^+$ (acetonitrile): *m/z* = 2122.8 [M − {Pd(2-CH_3−C_3H_4)Cl} − 2 Cl]$^{2+}$, 2026.2 [M − 2 {Pd(2-CH_3-C_3H_4)Cl} − 2 Cl]$^{2+}$, 1339.4 [M − 2 {Pd(2-CH_3-C_3H_4)Cl} − 3 Cl]$^{3+}$, 1274.1 [M − 3 {Pd(2-CH_3-C_3H_4)Cl} − 3 Cl]$^{3+}$. $C_{196}H_{300}Cl_8P_8Pd_8Si_{17}$ (4516.62): calcd. C 52.12, H 6.70; found C 52.34, H 7.13.

Synthesis of the Cationic Complexes 1d*, 3d* and 8*: To a solution of **1d**, **3d**, or **8** (2.24 mmol) in CH_2Cl_2 (40 mL) were added a few drops of acetonitrile and $AgBF_4$ (0.45 g, 2.78 mmol). The mixture was stirred for 1 h in the dark, and the AgCl formed was removed by filtration through Celite. The resulting solution was concentrated and the addition of ether caused the precipitation of a white solid as a resin, which was washed twice with ether and dried. Yield: 60−70%. **1d***: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = −0.132 (s, 24 H, Me), 0.352 (s, 16 H, CH_2), 1.914 (s, 12 H, Me), 2.310 (s, 12 H, $NCCH_3$), 2.739 (s, 4 H, H^4), 3.335 (s, 4 H, H^3), 3.617 (s, 4 H, H^2), 4.764 (s, 4 H, H^1), 7.20−7.60 (m, 40 H, C_6H_5) ppm. ^{13}C NMR (62.90 MHz, $CDCl_3$, 25 °C): δ = −2.4 (s, 8 C, Me), 1.0 (s, 8 C, CH_2), 3.0 (s, $NCCH_3$), 12.9 (s, 4 C, CH_2P), 23.1 (s, 4 C, Me), 58.9 (s, 4 C, C_{cis}), 79.8 (d, *J* = 27.12 Hz, 4 C, C_{trans}), 129.0−136.6 (m, C_6H_5) ppm. ^{29}Si NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 3.35 (s, 4Si) ppm, the core signal was not observed. ^{31}P NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 15.76 (s) ppm. **3d***: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): Spectrum similar to that of **1d*** but with very broad signals. ^{31}P NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 14.5 (br. s) ppm. **8***: ^{31}P NMR (101.26 MHz, $CDCl_3$, 25 °C): δ = 14.26 (s) ppm. ^{29}Si NMR (49.66 MHz, $CDCl_3$, 25 °C): δ = 1.31 (s) ppm. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = −0.01 (s, 9 H, CH_3), 1.85 (d, *J* = 14.39 Hz, 2 H, CH_2), 1.97 (s, 3 H, CH_3), 2.32 (s, 3 H, $NCCH_3$), 2.72 (s, 1 H, H^4), 3.28 (s, 1 H, H^3), 3.70 (d, *J* = 9.24 Hz, 1 H, H^2), 4.93 (br. s, 1 H, H^1), 7.30−7.60 (m, 10 H, C_6H_5) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$, 25 °C): δ = 0.3 (d, *J* = 3.5 Hz, CH_3), 2.8 (s, $NCCH_3$), 14.9 (d, *J* = 11.4 Hz, CH_2), 23.1 (s, CH_3), 58.6 (s, $CH_{2,cis}$), 80.7 (d, *J* = 26.7 Hz, $CH_{2,trans}$).

Catalytic Reactions: Hydrovinylation reactions were performed in a stainless-steel autoclave fitted with an external jacket connected to a thermostatically controlled isobutyl alcohol bath maintained

Table 5. Crystal data and structure refinement for **4**, **5**, and **6**

Compound	**4**	**5**	**6**
Empirical formula	$C_{32}H_{42}Cl_2P_2PtSi_2{\cdot}0.5H_2O$	$C_{28}H_{30}Cl_2P_2PtSi$	$C_{44}H_{40}P_2PtSi$
Formula mass	819.77	722.54	853.88
Temperature	293(2) K	293(2) K	293(2) K
Wavelength	0.71069 Å	0.71069 Å	0.71069 Å
Crystal system, space group	monoclinic, $P2_1/n$	orthorhombic, *Pcnb*	monoclinic, $P2_1/c$
Unit cell dimensions	*a* = 9.9960(10) Å *b* = 18.9050(10) Å, β = 91.2250(10)° *c* = 19.5690(10) Å	*a* = 11.2090(10) Å *b* = 14.7280(10) Å *c* = 16.6540(10) Å	*a* = 18.108(5) Å *b* = 10.773(12) Å, β = 90.60(3)° *c* = 19.687(11) Å
Volume	3697.2(5) Å^3	2749.3(3) Å^3	3840(5) Å^3
Z	4	4	4
Calculated density	1.473 Mg/m^3	1.746 Mg/m^3	1.477 Mg/m^3
Absorption coefficient	4.112 mm^{-1}	5.474 mm^{-1}	3.798 mm^{-1}
F(000)	1636	1416	1704
Crystal size	0.1 × 0.1 × 0.2 mm	0.1 × 0.1 × 0.2 mm	0.1 × 0.1 × 0.3 mm
Θ range for data collection	2.27−28.89°	2.81−24.96°	2.34−29.95°
Index ranges	$-11 \le h \le 10$, $0 \le k \le 25$, $0 \le l \le 26$	$0 \le h \le 12$, $0 \le k \le 16$, $0 \le l \le 19$	$-25 \le h \le 25$, $0 \le k \le 15$, $0 \le l \le 27$
Reflections collected/unique	22007/8165 [*R*(int) = 0.0462]	11504/2402 [*R*(int) = 0.00309]	11092/11092 [*R*(int) = 0.0926]
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/parameters	8165/364	2402/206	11092/433
Goodness-of-fit on F^2	0.899	1.101	0.756
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0261, *wR*2 = 0.0518	*R*1 = 0.0329, *wR*2 = 0.0728	*R*1 = 0.0431, *wR*2 = 0.0568
R indices (all data)	*R*1 = 0.0608, *wR*2 = 0.0557	*R*1 = 0.0480, *wR*2 = 0.0789	*R*1 = 0.2656, *wR*2 = 0.0899
Largest diff. peak and hole (e Å^{-3})	0.619 and −0.600	0.551 and −0.470	0.420 and −0.365

to ± 0.5 °C. The internal temperature was monitored by means of a thermocouple. Internal temperature and pressure as a function of time were registered with a Linseis L-200 Recorder. Gas chromatography was run using an HP 5890 series two chromatograph.

Hydrovinylation Reactions

a) 1d$^+$, 3d$^+$, and 8$^+$ as Catalysts: A mixture of 4.0×10^{-5} mol of the neutral palladium complex, **1d**, **3d**, or **8**, $AgBF_4$ (in a 1:4, 1:8, and 1:1 molar ratio, respectively) and styrene (0.04 mol) in 10 mL of freshly distilled CH_2Cl_2 was stirred for 5 min in the dark under nitrogen. After filtering off the AgCl formed, the solution was placed in a thermostatically controlled autoclave, which had previously been purged with successive applications of vacuum and argon. The autoclave was then pressurized with ethylene to 15 bar. After the desired time, the autoclave was slowly depressurized and 10% HCl (10 mL) was added. The mixture was stirred for 10 min in order to quench the catalyst. The CH_2Cl_2 layer was decanted and dried with Na_2SO_4. The quantitative distribution of products fractions was determined by GC analysis.

b) 1d*, 3d*, and 8* as Catalysts: A solution of 4.0×10^{-5} mol of the cationic palladium complexes, **1***, **3***, or **8***, and styrene (0.0400 mol) in freshly distilled CH_2Cl_2 (10 mL) was prepared under an inert gas. The solution was transferred via syringe under argon into the autoclave, which had previously been purged with successive applications of vacuum and argon. Ethylene was admitted until the initial pressure of 15 bar was reached. The workup procedure was as already described.

X-ray Structure Determination of 4, 5 and 6: Block crystals of compounds **4** and **5** were selected and mounted on a MAR345 diffractometer with image plate detector. A crystal of **6** was mounted on an Enraf−Nonius CAD4 four-circle diffractometer. Crystallographic and experimental details of both compounds are summarized in Table 5. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the usual manner. The structures were solved by Direct Methods, using SHELXS computer program and refined by full-matrix least-squares methods with SHELX97 computer program.[31] The function minimized was $\Sigma w||F_o|^2 - |F_c|^2|^2$, where $w = [\sigma^2(I) + (0.0774 P)^2]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$; f, f' and f'' were taken from International Tables of X-ray Crystallography .[32] All H atoms were computed and refined with an overall isotropic temperature factor equal to 1.2 times the equivalent isotropic temperature factor of the atoms, which were linked using a riding model. The supplementary crystallographic data for this paper can be found in publications CCDC-181768 (**4**), -181770 (**5**), and -181769 (**6**.) These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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