Dendrimers as homogeneous transition metal catalysts.
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The photochemically activated preparation of diphenylphosphine-functionalised carbosilane dendrimers: a [2+2] addition or a radical mechanism?

Si(CH₂CH₂CH₂PPh₂)₃ functionalised carbosilane dendrimers have been prepared by a photochemically initiated addition reaction of diphenylphosphine to the olefinic endgroups of the dendrimer. This reaction is believed to proceed via a radical mechanism, in which the primary step is the formation of a PR₂-radical. The possibility of a photochemically activated [2+2] addition mechanism has been investigated experimentally and by using DFT calculations. DFT calculations show that the energy barrier for the reaction proceeding via a cyclic transition state is very low, suggesting that this is a likely pathway. Calculations also give low energy barriers for a radical mechanism. Experimental results point towards a radical mechanism, but a [2+2] addition mechanism cannot be excluded completely.

Introduction

Dendrimers have received considerable attention during the past decade.\(^1\) One of the potential applications of dendrimeric molecules is their use as a homogeneous catalyst support\(^2\) since its size enables recycling by means of nanofiltration.\(^3,4\) In order to use dendrimers as a catalyst support the periphery of the dendrimer can be functionalised with ligands that form catalytically active sites when complexed to transition metals\(^5,6,7\) (see also chapters 2, 3 and 5). The catalytic sites of surface functionalised dendrimers are easily accessible to the substrate in bulk solution.

Because of their inertness in catalysis, we generally use carbosilane dendrimers as a backbone for our catalytic system. When functionalising dendrimers it is important to use relatively simple procedures that give very high yields. Recently, we have reported the functionalisation of carbosilane dendrimers with phosphine ligands for the use in allylic substitution and hydroformylation reactions (see chapters 2 and 3).\(^4,7\) Reaction of lithiated methylidiphenylphosphine with the chlorosilane endgroups of the dendrimer gave dendrimers containing SiCH\(_2\)PPh\(_2\) and Si(CH\(_2\)PPh\(_2\))\(_2\) endgroups. Here we report the synthesis of carbosilane dendrimers with Si(CH\(_2\)CH\(_2\)CH\(_2\)PPh\(_2\))\(_3\) endgroups via an addition reaction of diphenylphosphine to the unsaturated endgroups of the dendrimer. Cole-Hamilton and co-workers used this approach to functionalise silsesquioxane molecules containing carbosilane dendritic wedges.\(^6\) They performed the reaction in presence of azobisisobutyronitrile (AIBN) at 70°C.

The addition reaction of a disubstituted phosphine to an unsaturated compound is known to proceed \emph{via} a radical mechanism, either by photochemical initiation\(^8\) (at room temperature) or initiation by a free radical initiator such as di-t-butyl peroxide\(^8\) or azobisisobutyronitrile (AIBN)\(^9\) at elevated temperatures. The reaction has also been reported using a combination of AIBN and UV irradiation.\(^10\) The primary step of the mechanism is the formation of a PR\(_2\)-radical.\(^8\) Pringle et al. have reported the use of a platinum catalyst for the addition of a disubstituted phosphine to acrylonitrile.\(^11\)

Long reaction times were required for the complete functionalisation of the carbosilane dendrimers with Si(CH\(_2\)CH\(_2\)CH\(_2\)PPh\(_2\))\(_3\)-endgroups. Before optimising the procedure we decided to investigate the mechanism of this reaction. An alternative mechanism, analogous to the [2+2] cycloaddition reaction of two alkenes, was considered. DFT calculations were performed to determine the energy barriers for both a radical mechanism and a photochemically activated [2+2] addition mechanism.
Results & discussion

Synthesis

The allyl terminated zeroth, first and second generation carbosilane dendrimers were reacted with diphenylphosphine under the influence of light (350 nm) and in the presence of AIBN, using the phosphine as the solvent (scheme 1). The reaction was clean and the excess of diphenylphosphine was removed in vacuo yielding colourless wax-like solids. The dendrimers could be functionalised completely, but long reaction times were required. The complete functionalisation of the zeroth generation dendrimer took two weeks, the first generation four weeks and the second generation six weeks. The phosphine functionalised dendrimers were characterised by $^1$H-, $^{31}$P- and $^{13}$C-$^1$H-NMR spectroscopy, MALDI-TOF mass spectrometry and elemental analysis.

Scheme 1. Synthesis of diphenylphosphine-functionalised carbosilane dendrimers using AIBN.

Mechanistic studies

The addition reaction of a disubstituted phosphine to an unsaturated compound is known to proceed via a radical mechanism, in which the primary step is the formation of a PR$_2$-radical. To the best of our knowledge a photochemically activated [2+2] addition mechanism has not been investigated. The possibility of a concerted [2σ+2π] addition mechanism has been investigated for the addition of thiophenol (PhSH) to the double bond.
of methylenecyclopropane derivatives by De Meijere and co-workers. However, they concluded that the reaction proceeds via a radical mechanism and not via a concerted [2+2] addition mechanism, based on the products that were formed.

In order to study the mechanism of the addition of diphenylphosphine to the unsaturated endgroups of the dendrimer, we performed some test experiments under various conditions using the zeroth generation dendrimer, diphenylphosphine and toluene as a solvent (table 1). These reactions were all carried out in NMR tubes and we studied the effect of different additives, such as a radical initiator, a triplet sensitizer and a radical scavenger. In the absence of any additives a slow but clean conversion was observed. In the presence of 10 mol% of the radical initiator AIBN the conversion after 2 hours was nearly four times as high (7.8% conversion versus 2.0%). The presence of AIBN also resulted in the formation of tetraphenylbiphosphine in addition to the alkene addition product. Ph$_2$P-PPh$_2$ can be formed by a radical reaction between two Ph$_3$P-radicals. Thus the formation of Ph$_3$P-PPh$_2$ clearly supports the presence of phosphine radicals. The fact that the reaction is also faster in the presence of AIBN strongly suggests that under these conditions the reaction proceeds via a radical mechanism. The difference in conversion between the reactions with and without AIBN after 22.5 hours is less pronounced than that after 2 hours: in the absence of AIBN 22% and in the presence of AIBN 33% conversion was observed. The reaction without AIBN shows the formation of only very small amounts of tetraphenylbiphosphine. This suggests that under these conditions less diphenylphosphine radicals are present.

The possibility of a photochemical [2+2] addition mechanism was investigated by performing an experiment in the presence of a triplet sensitizer. The presence of 10 mol% of the triplet sensitizer p-methoxyacetophenone accelerated the reaction compared to the reaction without additives (6.5% conversion after 2 hours versus 2.0%). However, again the formation of tetraphenylbiphosphine was observed. The triplet sensitizer facilitates the formation of diphenylphosphine in the triplet excited state. Subsequently, the reaction can take place via the concerted [2+2] addition mechanism or the diphenylphosphine can decompose to form radicals. The formation of tetraphenylbiphosphine suggests that a substantial amount of phosphine radicals is formed.
One way to verify the presence of radicals is to use a radical scavenger.\textsuperscript{14} When 10 mol\% galvinoxyl\textsuperscript{15} free radical scavenger was present in the reaction mixture, initially no addition to the alkenes was observed. After a reaction time of 2 hours only the formation of tetraphenylbiphosphine and a new side product (a signal at 0.5 ppm in the $^{31}$P-$^1$H-NMR spectrum) were observed. The new compound might be the product of the reaction of a diphenylphosphine radical with one of the carbon atoms of the galvinoxyl radical scavenger.\textsuperscript{15} The presence of these products, which are formed by a reaction of phosphine radicals, suggests that galvinoxyl also behaves as a radical initiator. When the reaction had proceeded for 22.5 hours, Ph$_2$P-PPh$_2$ as well as the alkene addition product were obtained. The amount of radical scavenger (0.1 equiv.) is probably too low to scavenge all the radicals that are formed, which can be inferred from the decolouration of the reaction mixture.

**Table 1.** Results of the reaction of diphenylphosphine with tetraallylsilane under various conditions.\textsuperscript{a}

<table>
<thead>
<tr>
<th>additive</th>
<th>time (h)</th>
<th>conversion ($%$)</th>
<th>SiCH$_2$CH$_2$CH$_2$PPh$_2$ ($%$)</th>
<th>Ph$_2$P-PPh$_2$ ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>2.0</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>22</td>
<td>99</td>
<td>1</td>
</tr>
<tr>
<td>AIBN\textsuperscript{b}</td>
<td>2</td>
<td>7.8</td>
<td>84</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>33</td>
<td>91</td>
<td>9</td>
</tr>
<tr>
<td>$p$-methoxyacetophenone\textsuperscript{c}</td>
<td>2</td>
<td>6.5</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>39</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>galvinoxyl\textsuperscript{d}</td>
<td>2</td>
<td>6.1</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>22.5</td>
<td>26</td>
<td>61</td>
<td>39</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Room temperature, solvent: toluene, 350 nm, [HPPh$_2$] = 2.0 M, [tetraallylsilane] = 0.5 M; \textsuperscript{b}[AIBN] = 0.2 M; \textsuperscript{c}[$p$-methoxyacetophenone] = 0.2 M; \textsuperscript{d}[galvinoxyl] = 0.2 M.

To study the effect of stoichiometric amounts of radical scavenger we decreased the concentrations of the starting materials. In the presence of the galvinoxyl free radical scavenger (0.5, 1 and 2 equiv.) the phosphine starting material (HPPh$_2$) was converted, but no alkene addition product was formed. The formation of tetraphenylobiphosphine was
observed as well as the formation of several other side products. Apparently the radical scavenger can accelerate the formation of diphenylphosphine radicals, since no diphenylphosphine starting material was left after overnight reaction using two equivalents of radical scavenger.

The UV-Vis spectrum of diphenylphosphine showed a strong absorption due to the phenyl groups at <300 nm with a shoulder between 300-350 nm. The latter band may belong to an electronic transition of the lone pair on the phosphorus atom to the LUMO of the diphenylphosphine localised on the phenyl-ring and likely also on the P-H bond. Since 350 nm is at the very edge of the spectrum, the photochemically activated [2+2] addition might be favoured when using a slightly lower wavelength. The reactions were performed without solvent at higher concentrations of starting material resulting in lower amounts of tetraphenylibiphosphine. Irradiation of the reaction mixture at 350 nm in the presence of 10 mol% of the triplet sensitiser p-methoxyacetophenone gave a conversion after 1 hour that was nearly 2.5 times as high as that of the reaction without additives (12% conversion versus 5%). When irradiating at 334 nm a similar acceleration was observed (5% and 2% conversion with and without triplet sensitiser, respectively). In all cases only 1-2% tetraphenylibiphosphine was obtained. Unfortunately, the experiments performed using the light source of 350 nm and those using the light source of 334 nm cannot be compared, because of the difference in light intensity of the sources. It is clear, however, that the triplet sensitiser causes a similar acceleration. Since only very small amounts of tetraphenylibiphosphine were observed, it is likely that under these conditions either the steady state concentrations of radicals are very low or the reaction proceeds via a photochemically activated [2+2] addition mechanism.

Since the experimental results were inconclusive about the mechanism, we decided to compare the two routes discussed above using DFT calculations. For these calculations we used the model compounds propene and dimethylphosphine (similar reactions using dimethylphosphine are known). In the photochemically activated [2+2] addition mechanism the HOMO of the excited state of the phosphine should react with the LUMO of the alkene. The DFT calculations were performed to study the mechanism in the gas phase (see experimental section for details).
Figure 1 shows the reactants: dimethylphosphine in the singlet ground state ($S=1$), propene, and dimethylphosphine in the triplet excited state ($S=3$). When dimethylphosphine is excited to the triplet state, an elongation of the P–H bond is observed (from 1.438 Å to 1.580 Å). The molecular orbitals of the compounds are visualised in figure 1 and it is clear that the overlap between the LUMO of propene and the HOMO of HPMe$_2$ in the triplet excited state is far superior to the overlap of the LUMO of propene and the HOMO of HPMe$_2$ in the singlet ground state. Calculations of the energy levels show that the HOMO of HPMe$_2$ in the triplet excited state and the LUMO of propene are closer together in energy (the difference is 3.1 kcal/mol) than the energy level of the HOMO of HPMe$_2$ in the singlet ground state and the LUMO of propene (the difference is 4.9 kcal/mol). (It should be noted that the structure of HPMe$_2$ in the singlet ground state is tetrahedral, while the structure of HPMe$_2$ in the triplet excited state is square planar.) Hence, the excitation of dimethylphosphine to the triplet state facilitates a [2+2] addition mechanism with propene.

**Figure 1.** Calculated structures of the reactants in the gas phase of the model [2+2] addition reaction of dimethylphosphine and propene: HPMe$_2$ in the singlet ground state ($S=1$) (left), propene (middle) and HPMe$_2$ in the triplet excited state ($S=3$) (right).
**Chapter 4**

**Figure 2.** Calculated structures of the intermediates of the [2+2] addition of dimethylphosphine with propene.

Table 2. Selected bond lengths (Å) and atomic charges\(^a\) (e) of the reactants, intermediates and product.

<table>
<thead>
<tr>
<th>bond or atom</th>
<th>propene</th>
<th>HPMe(_2) ((S=1))</th>
<th>HPMe(_2) ((S=3))</th>
<th>I ((S=3))</th>
<th>II ((S=3))(^b)</th>
<th>III ((S=3))</th>
<th>IV ((S=1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P–H</td>
<td>1.438</td>
<td>1.580</td>
<td>1.547</td>
<td>1.626</td>
<td>2.957</td>
<td>2.927</td>
<td></td>
</tr>
<tr>
<td>P–Cl</td>
<td></td>
<td></td>
<td>1.922</td>
<td>2.112</td>
<td>2.077</td>
<td>1.879</td>
<td></td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.333</td>
<td></td>
<td>1.469</td>
<td>1.495</td>
<td>1.518</td>
<td>1.537</td>
<td></td>
</tr>
<tr>
<td>C2–H</td>
<td></td>
<td></td>
<td>2.699</td>
<td>1.611</td>
<td>1.102</td>
<td>1.102</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>+0.056</td>
<td>+0.145</td>
<td>+0.169</td>
<td>+0.115</td>
<td>+0.126</td>
<td>+0.062</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>−0.033</td>
<td>−0.104</td>
<td>−0.076</td>
<td>−0.013</td>
<td>+0.043</td>
<td>+0.052</td>
<td></td>
</tr>
<tr>
<td>C (1)</td>
<td>−0.099</td>
<td></td>
<td>−0.120</td>
<td>−0.108</td>
<td>−0.110</td>
<td>−0.125</td>
<td></td>
</tr>
<tr>
<td>C (2)</td>
<td>−0.050</td>
<td></td>
<td>−0.046</td>
<td>−0.056</td>
<td>−0.078</td>
<td>−0.071</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{\(^a\)Computed with the VDD method; \(^b\)Transition state.}\)

Several intermediate structures of the [2+2] addition mechanism were calculated. In figure 2 the different intermediates, including a transition state, are shown and in table 1 relevant bond lengths and Voronoi deformation density (VDD)\(^{16,17}\) charges are given. The calculations show that HPMe\(_2\) \((S=3)\) and propene form an intermediate (I) with a net
stabilisation of 11.1 kcal/mol with respect to the isolated reactants (figure 3). The relative charges on the carbon atoms of propene (table 2) show that C1 has a larger affinity for the positively charged P-atom of the triplet state of dimethylphosphine than C2 (see relative charges in table 2), resulting in a preference for the linear product. The transition state (TS) shows a concerted [2+2] addition and a hydrogen is transferred to the C2 carbon. From the molecular orbitals of structure (II) (bottom of figure 2) it is clear that the LUMO of propene mixes into the HOMO of the triplet excited state of dimethylphosphine. The bond lengths between the atoms of the four membered ring of the transition state are all in between those of the reactants and the product. The transition state structure shows that the reaction proceeds via a concerted mechanism and the extremely low energy barrier (4.8 kcal/mol) indicates that the reaction can take place at room temperature. Finally, in two consecutive steps via intermediate (III), the singlet ground state of the product (IV) is formed.

**Figure 3.** Energy level diagram of the [2+2] addition reaction of dimethylphosphine with propene.

The low activation energy ($E_a$) of the transition state with respect to the isolated reactants (+4.8 kcal/mol, see figure 3) and the highly reactive intermediates (high relative energies) suggest that the reaction can proceed directly via the concerted transition state (II). Therefore, we believe that the reaction does not necessarily take place via intermediate (I), although the calculations indicate that (I) is stable on the potential energy surface. In
conclusion, these DFT calculations indicate that the reaction can proceed via a photochemically activated [2+2] addition mechanism.

**Figure 4.** Calculated structures of the reactants in the gas phase of the model radical addition reaction of dimethylphosphine and propene: the dimethylphosphine radical (left) and propene (right).

The radical pathway has also been studied using DFT calculations. Figure 4 shows the reactants: the diphenylphosphine radical and propene. Most of the electron density of the unpaired spin of the Me₂P-radical is located on the P-atom. Figure 5 shows the calculated structures and the molecular orbitals of the reaction intermediates and in table 3 the relevant bond lengths are given. The HOMO of the Me₂P-radical reacts with the LUMO of propene to give structure (V). A transition state has not been calculated for this step, but the energy barrier is expected to be very low. Structure (VI) results when a diphenylphosphine molecule is in close proximity to (V) giving a net stabilisation of 1.3 kcal/mol (figure 6). Subsequently, the hydrogen of diphenylphosphine is transferred to (V) via a transition state (VII) giving a diphenylphosphine radical and the product (VIII). From the molecular orbitals of structure (VII) (bottom of figure 5) it is clear that the radical is localised on the P2-atom and on the C2 of propene. Table 3 shows that the
distance between the P-atom and the H-atom in the transition state (VII) (1.508 Å) is in between that of structure (VI) (1.448 Å) and (VIII) (2.675 Å). Also the C2-H distance of the transition state (1.785 Å) has a value in between those of the preceding and following structures (2.262 Å and 1.102 Å, respectively). The energy barrier of the transition state is only 13.9 kcal/mol (figure 6), which indicates that the radical mechanism can also occur at room temperature.

**Figure 5.** Calculated structures of the intermediates of the radical addition of dimethylphosphine to propene.

![Calculation structures](image)

**Table 3.** Selected bond lengths (Å) and atomic charges\(^a\) (e) of the intermediates and product of the radical mechanism.

<table>
<thead>
<tr>
<th>bond or atom</th>
<th>V (S=2)</th>
<th>VI (S=2)</th>
<th>VII (S=2) (^b)</th>
<th>VIII (S=2)</th>
</tr>
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<tbody>
<tr>
<td>P2–H</td>
<td></td>
<td>1.448</td>
<td>1.508</td>
<td>2.675</td>
</tr>
<tr>
<td>P2–C1</td>
<td>1.922</td>
<td>1.915</td>
<td>1.918</td>
<td>1.878</td>
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<tr>
<td>C1–C2</td>
<td>1.472</td>
<td>1.476</td>
<td>1.482</td>
<td>1.533</td>
</tr>
<tr>
<td>C2–H</td>
<td>2.262</td>
<td>1.785</td>
<td>1.102</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Computed with the VDD method; \(^b\)Transition state.
Figure 6. Energy level diagram of the radical addition reaction of dimethylphosphine with propene.

\[
\Delta E \quad (\text{kcal/mol})
\]

DFT calculations have shown that this reaction can proceed via a photochemically activated [2+2] addition mechanism and via a radical mechanism at room temperature. Experimental results show that a radical reaction is taking place. So far we have not obtained conclusive experimental evidence to either prove or exclude that the reaction also occurs via a [2+2] addition mechanism. Probably the conditions determine the mechanism that dominates.

In order to optimise the synthetic procedure for the complete functionalisation of carbosilane dendrimers with Si(CH$_2$CH$_2$CH$_2$PPh$_2$)$_3$ endgroups via a photochemically activated addition of diphenylphosphine to the olefinic endgroups of the dendrimer, we found that it is important to use high concentrations of starting material to avoid the formation of side products. The presence of a triplet sensitisser or a radical initiator accelerates the reaction. These additives do not disturb the easy purification of the product, since both additives can be removed in vacuo (p-methoxyacetophenone has a boiling point of 152-154°C/26mmHg, AIBN decomposes to give isobutyronitrile (bp. = 107-108°C)).

Conclusions
Three generations of carbosilane dendrimers with Si(CH$_2$CH$_2$CH$_2$PPh$_2$)$_3$ endgroups have been prepared by reaction of diphenylphosphine with the unsaturated endgroups of the dendrimers. Long reaction times were required for the complete functionalisation of the dendrimers. We investigated the mechanism of this reaction by performing several test experiments using a radical initiator (AIBN), a triplet sensitisser (p-methoxyacetophenone)
and a radical scavenger (galvinoxyl). Experimental results show that a radical reaction is taking place, but cannot exclude that a [2+2] addition mechanism might also be present. DFT calculations have been performed to study both the photochemically activated [2+2] addition mechanism and the radical mechanism using the model compounds dimethylphosphine and propene. A cyclic transition state has been found for the [2+2] addition mechanism with a very low energy barrier (+4.8 kcal/mol). For the radical mechanism also a transition state with a low energy barrier was found (13.9 kcal/mol). Therefore, both reaction mechanisms are likely to occur at room temperature and might co-exist.

Under different conditions a different mechanism might dominate.

When optimised the reaction proceeds without the formation of side products, which makes it a convenient way to functionalise dendrimers.

**Experimental**

**General data.** All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Toluene was distilled under N2 from sodium prior to use. Chemicals were purchased from Aldrich Chemical Co. and Acros Chimica and were used without further purification. ¹H- and ³¹P-¹H-NMR spectra were recorded on a Varian Mercury 300 and the ¹³C-¹H-NMR spectra were measured on a Varian Inova 500. The chemical shifts are given in ppm relative to TMS for ¹H- and ¹³C-NMR and relative to H₃PO₄ for ³¹P-NMR. Matrix Assisted Laser Desorption Ionisation (MALDI) Time-of-Flight (TOF) mass spectrometry was performed using a Perkin Elmer/PerSeptive Biosystems Voyager-DE-RP MALDI-TOF mass spectrometer (PerSeptive Biosystems, Inc., Framingham, MA, USA) equipped with delayed extraction. A 337nm UV Nitrogen laser producing 3ns pulses was used and the mass spectra were obtained in the linear and reflectron mode. Samples were prepared in an Atmosbag (Aldrich) filled with argon by mixing 10 µl of dichloromethane solution of the sample with 30 µl of a solution of 3 mg/L 2,5-dihydroxybenzoic acid (DHB) or Dithranol (DIT) in dichloromethane. One µl of the solution was loaded on a gold-sample plate, the solvent was removed in warm air and the sample transferred to the vacuum of the mass spectrometer for analysis. Elemental analyses were measured on an Elementar Vario EL apparatus.
Typical procedure for preparation of the diphenylphosphine functionalised dendrimers:

**Si(CH_2CH_2CH_2PPh_2)_4:**

1: A solution of 169.0 mg tetraallylsilane (0.88 mmol) and 100 mg AIBN (0.60 mmol) in 800 mg diphenylphosphine (4.30 mmol) was irradiated with a UV-light (350 nm) for 10 days. The excess of diphenylphosphine was removed *in vacuo* (3.5-10^-6 mbar, 80°C). Product 1 was obtained as a colourless solid in 68% yield (562.8 mg, 0.60 mmol). ^1^H-NMR (300 MHz, CDCl_3): δ 7.8-7.3 (m, 40H, ArH), 2.05 (m, 8H, SiCH_2CH_2CH_2P), 1.4 (m, 8H, SiCH_2CH_2CH_2P), 0.8 (m, 8H, SiCH_2CH_2CH_2P). ^3^P-{^1^H}-NMR (121.5 MHz, CDCl_3): δ 138.9 (d, ipso-PhP, J_{CP} = 13.2 Hz), 132.6 (d, o-PhP, J_{CP} = 18.6 Hz), 128.6 (s, m-PhP, J_{CP} = 6.7 Hz), 122.3 (d, SiCH_2CH_2CH_2P, J_{CP} = 11.8 Hz), 20.5 (d, SiCH_2CH_2CH_2P, J_{CP} = 17.0 Hz), 14.2 (d, SiCH_2CH_2CH_2P, J_{CP} = 11.3 Hz). MALDI-TOF-MS: m/z 938 (M^+) (calcd. 397.2), 954 (monooxide), 970 (dioxide), 986 (trioxide), 1002 (tetraoxide). Anal. calcd. for C_60H_60SiP_4: C 76.90; H 6.88. Found: C 76.15; H 6.90.

**Si(CH_2CH_2CH_2Si(CH_2CH_2CH_2PPh_2)_3)_3:**

2: This compound was prepared from the first generation carbosilane dendrimer (248.7 mg, 0.31 mmol) and AIBN (100 mg, 0.60 mmol) in diphenylphosphine (1.0 mL, 0.60 mmol) using the same procedure as for 1, yielding a colourless wax-like solid (894.3 mg, 0.28 mmol, 90%). The reaction mixture was irradiated for 30 days. ^1^H-NMR (300 MHz, CDCl_3) δ 7.5-7.2 (m, 120H, ArH), 1.95 (m, 24H, SiCH_2CH_2CH_2P), 1.25 (m, 24H, SiCH_2CH_2CH_2P), 1.05 (m, 8H, SiCH_2CH_2CH_2Si) 0.6 (m, 24H, SiCH_2CH_2CH_2P), 0.4 (m, 16H, SiCH_2CH_2CH_2Si) ^3^P-{^1^H}-NMR (121.5 MHz, CDCl_3): δ 138.9 (d, ipso-PhP, J_{CP} = 12.0 Hz), 132.6 (d, o-PhP, J_{CP} = 18.0 Hz), 128.6 (s, m-PhP, J_{CP} = 6.5 Hz), 128.6 (s, m-PhP, J_{CP} = 11.1 Hz), 20.6 (d, SiCH_2CH_2CH_2P, J_{CP} = 17.0 Hz), 14.4 (d, SiCH_2CH_2CH_2P, J_{CP} = 11.4 Hz), 18.4 (s, CH_2 of SiCH_2CH_2CH_2Si), 17.6 (s, CH_2 of SiCH_2CH_2CH_2Si). Anal. calcd. for C_92H_163Si_2P_3: C 75.96; H 7.17. Found: C 75.86; H 7.17.

**Si(CH_2CH_2CH_2Si(CH_2CH_2CH_2PPh_2)_3)_3:**

3: This compound was prepared from the second generation carbosilane dendrimer (161.8 mg, 0.0614 mmol) and AIBN (100 mg, 0.60 mmol) in diphenylphosphine (1.5 mL, 0.90 mmol) using the same procedure as for 1, yielding a colourless wax-like solid (509.1 mg, 0.0546 mmol, 89%). The reaction mixture was irradiated for 45 days. ^1^H-NMR (300 MHz, CDCl_3) δ
7.8-7.3 (m, 360H, ArH), 2.18 (m, 72H, SiCH₂CH₂CH₂P), 1.4 and 0.8 and 0.7 (m, 240H, other CH₂'s). ³¹P-¹H-NMR (121.5 MHz, CDCl₃) δ-16.9.

**DFT calculations**

The electronic structure calculations were computed within the Kohn-Sham formulation of density functional theory (DFT) using gradient-corrected local functionals. Using the ADF package¹⁸ we performed geometry optimisations and a transition state (TS) search on the different intermediates in the gas phase with the PW91 functional. The TS was optimised with a Hessian possessing one negative Eigen value. Here PW91 refers to the LDA functional using the Vosko-Wilk-Nusair¹⁹ parameterisation of the electron gas data of Ceperley and Alder,²⁰ complemented with a gradient correction for exchange and correlation proposed by Perdew and Wang.²¹ If necessary, an excited triplet state was computed by doing an unrestricted calculation on the intermediate in question. In this case, spin-α and spin-β molecular orbitals may be spatially different and may have different occupation numbers. The molecular orbitals were expanded in an uncontracted triple-ζ Slater-type basis set, augmented with 2p and 3d polarisation functions for hydrogen, and 3d and 4f for carbon and phosphorus. Cores were kept frozen. Excitation energies were computed by time dependent DFT techniques implemented in the ADF code.²²

**Experiments concerning the mechanism**

The experiments concerning the mechanism were performed in an NMR-tube.

A stock solution containing 0.2392 g tetraallylsilane (1.24 mmol) and 0.87 mL diphenylphosphine (5.0 mmol) in 1.5 mL toluene was prepared (to give a total volume of ~2.5 mL). Subsequently, 0.5 mL of this solution was added to either of the following additives: 0.0153 g AIBN (0.093 mmol), 0.0412 g galvinoxyl (0.098 mmol) or 0.0148 g p-methoxyacetophenone (0.099 mmol).

The NMR-samples were irradiated at 350 nm for the desired period of time and the conversion was determined using ³¹P-¹H-NMR spectroscopy.
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(13) Relative reaction rates were determined using $^{31}$P-$^{1}$H-NMR spectroscopy.


A photochemically activated [2+2] addition or a radical mechanism?

(16) This method defines a Voronoi cell around each atom (i.e. the region that is closer to that atom than to any other atom) and looks at the charge flow by comparing the electron density before and after the SCF (Self Consistent Field) calculation in each cell.


