Catalysis in the core of a carbosilane dendrimer

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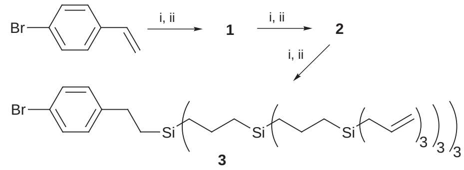
The synthesis of a series of diphosphine ligands having phosphorus donor atoms in the core of a carbosilane dendrimer and their use in palladium catalysed allylic alkylation is described.

Dendrimers are fascinating molecules owing to their unique physical and chemical properties.[1] From the beginning catalysis has been recognised as one of their main potential applications, but so far only a few examples have appeared in the literature.[2–5] Two general strategies for the construction of dendritic catalysts can be applied: (1) multiple catalytic sites at the periphery of the dendrimer and (2) one (or more) catalytic site(s) in the core of the dendrimer.

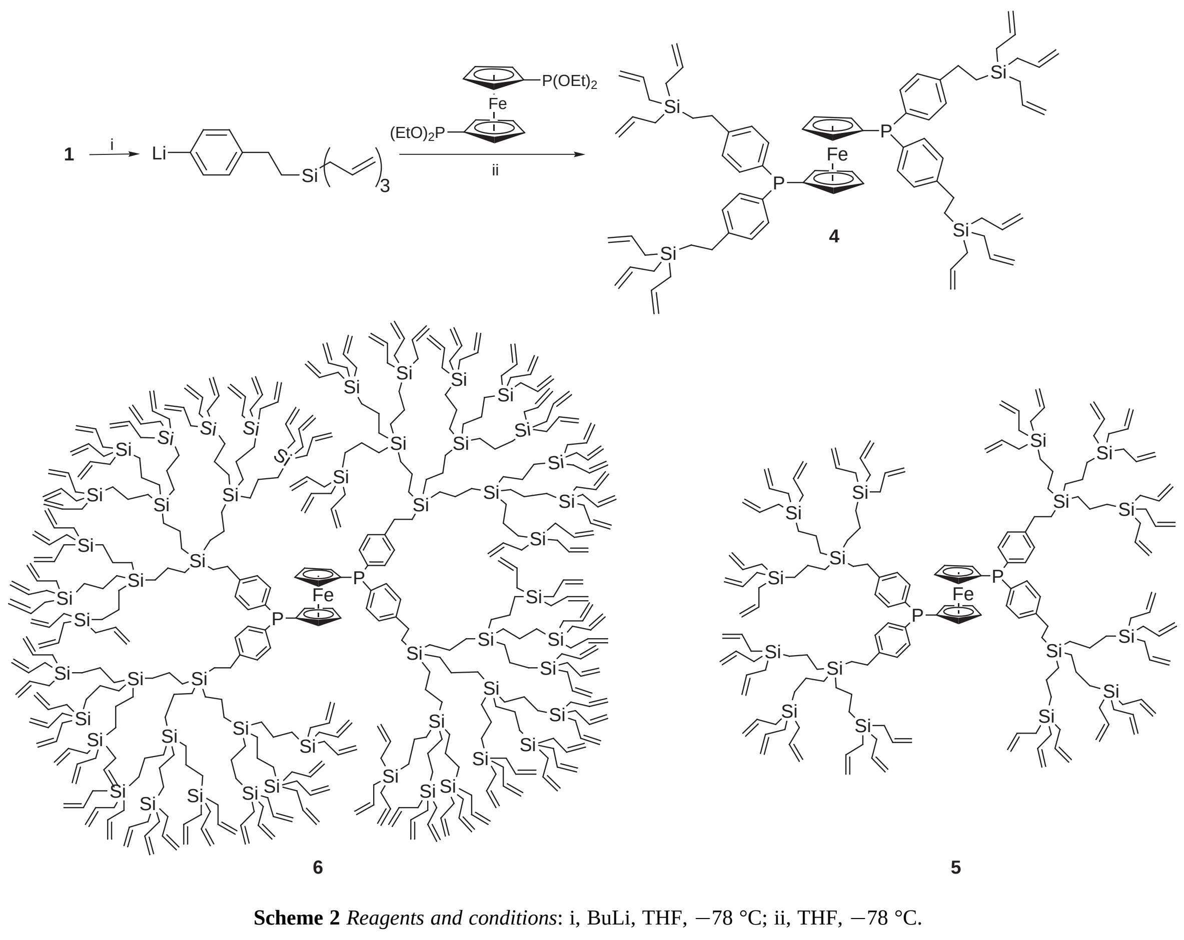
Previously, we and others have reported examples of the periphery strategy.[2,3] This approach has the major advantage that the catalyst can be removed from the product mixture *via* nanofiltration and reused.[3,4]

Recently, a number of groups reported core-functionalised dendrimers as examples of the second strategy.[5] Some of these so-called 'dendrizymes' showed that the substrate selectivity of the catalytic reaction changed with increasing generations.[6]



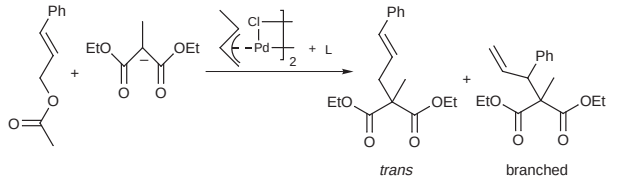
Scheme 1 *Reagents and conditions*: i, $HSiCl_3$, [Pt], rt, 2 h, 100%; ii, $BrMgCH_2CH{=}CH_2$, Et_2O, rt, 100%.

Here we describe the synthesis of carbosilane dendritic wedges using *p*-bromostyrene as starting compound. The bromide can be used to construct a new type of ligand embedded in the apolar dendrimer. The dendritic analogues of dppf [bis(diphenylphosphino)ferrocene] were synthesised as examples of such core-functionalised dendrimers. Initial experiments show that palladium complexes of these dendrimers are active catalysts in allylic alkylation reactions and a significant change in the product selectivity is observed for the largest dendrimer.



Scheme 2 *Reagents and conditions*: i, BuLi, THF, −78 °C; ii, THF, −78 °C.

Table 1 Activity and selectivity in the allylic alkylation of 3-phenylallyl acetate with diethyl 2-sodio-2-methylmalonate after 60 min[a]



L	Conversion (%)[b]	*trans* product (%)[c]
—	8	96 (±1.0)
dppf	72	90 (±0.7)
4	76	88 (±1.2)
5	58	87 (±0.8)
6	17	79 (±0.4)

[a] Conditions: 0.25 μmol $[crotyl\text{-}PdCl]_2$, 0.5 μmol **L**, 6.0 ml THF, 0.5 mmol 3-phenylallyl acetate, 1.0 mmol malonate, 0.05 mmol decane, rt. [b] All catalytic reactions reached full conversion in 24 h. [c] The selectivity of the reaction was independent of the conversion.

The carbosilane wedges **1**–**3** (Scheme 1) were prepared in a divergent manner starting from *p*-bromostyrene, using a two-step methodology.[7] These steps involve a platinum-catalysed hydrosilylation with $SiHCl_3$ followed by reaction with an excess of allylmagnesium bromide yielding wedges **1** to **3**. Under optimised reaction conditions the wedges were obtained quantitatively, purified by flash chromatography and characterised by ^1H and ^{13}C NMR spectroscopy, elemental analysis, and FAB and MALDI-TOF mass spectrometry. The bromobenzene moiety can be used to synthesise a core-functionalised dendrimer in a convergent way. After lithiation using BuLi at −78 °C, these wedges were made to react with tetraethyl ferrocene-1,1′-diylbis(phosphonite)[8] yielding the bidentate ligands **4**–**6** with molecular weights up to 8567 (Scheme 2). These compounds were purified by column chromatography and analysed by ^1H and ^{31}P NMR spectroscopy, MALDI-TOF mass spectrometry and elemental analysis.†

Palladium dichloride complexes were prepared by stirring the ligand with $Pd(MeCN)_2Cl_2$ in CH_2Cl_2 for 60 min during which the solution turned red. ^{31}P NMR spectroscopy confirmed complete complexation of the ligand in a bidentate *cis* fashion. The signal of the free ligand around δ −18 was completely replaced by a singlet around δ +32.

After it was shown that these novel core-functionalised dendrimers formed similar Pd complexes as dppf, the catalytic activity of the compounds was tested in palladium catalysed allylic alkylation. In a typical experiment, crotylpalladium chloride dimer was added to a THF solution of the ligand and the mixture was incubated for 1 h at room temperature. 3-Phenylallyl acetate, decane (internal standard) and diethyl 2-sodio-2-methylmalonate were added.‡ The reactions were followed by GC analysis of samples taken from the reaction mixture. All the Pd complexes of the dendritic phosphines were catalytically active (see Table 1), producing mainly the linear *trans* product. The *cis* product was not observed. As indicated by the similar conversion for dppf and **4**, the allyl end groups do not interfere in the catalytic reaction. As expected, the rate of the reaction decreased using the higher generation catalysts. This effect, also found by others,[5,9] is due to more difficult mass transport with increasing steric bulk of the dendritic wedges, and is most pronounced when going from generation 2 to 3.

Remarkably, the size of the dendrimers determined also the selectivity of the allylic alkylation reaction; Pd–**6** yielded significantly more of the branched product. This change in selectivity might be due to the increasing steric bulk of the dendrimer hindering the attack of the nucleophile on the Pd–allyl. The apolar microenvironment created by the carbosilane wedges could also be the reason for this observed selectivity effect. Current research is aiming at a detailed insight in the nature of the dendritic effect and extending the synthetic approach to other core functionalities.

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Notes and references

† *Selected data* for **4**: $\delta_H(CDCl_3)$ 0.94 (m, 8H, $SiCH_2CH_2Ph$), 1.62 (d, 24H, $SiCH_2CH$), 2.64 (m, 8H, $SiCH_2CH_2Ph$), 4.02 (d, 4H, H_{Fc}), 4.09 (d, 4H, H_{Fc}), 4.87 (d, 12H, $CHCH_2$), 4.92 (dd, 12H, $CHCH_2$), 5.79 (m, 12H, $CHCH_2$), 7.12 (d, 8H, H_{ar}), 7.22 (d, 8H, H_{ar}); $\delta_P(CDCl_3)$ −18.39. For **5**: $\delta_H(CDCl_3)$ 0.61 (t, 24H, $SiCH_2CH_2CH_2Si$), 0.67 (t, 24H, $SiCH_2CH_2Si$), 0.84 (m, 8H, $SiCH_2CH_2Ph$), 1.38 (m, 24H, $SiCH_2CH_2CH_2Si$), 1.59 (d, 72H, $SiCH_2CH$), 2.56 (m, 8H, $SiCH_2CH_2Ph$), 4.06 (d, 4H, H_{Fc}), 4.15 (d, 4H, H_{Fc}), 4.85 (d, 36H, $CHCH_2$), 4.90 (dd, 36H, $CHCH_2$), 5.78 (m, 36H, $CHCH_2$), 7.11 (d, 8H, H_{ar}), 7.26 (dd, 8H, H_{ar}); $\delta_P(CDCl_3)$ − 18.53. For **6**: $\delta_H(CDCl_3)$ 0.54 (t, 96H, $SiCH_2CH_2CH_2Si$), 0.66 (t, 96H, $SiCH_2CH_2CH_2Si$), 0.82 (m, 8H, $SiCH_2CH_2Ph_2$), 1.29 (m, 96H, $SiCH_2CH_2CH_2Si$), 1.56 (d, 216H, $SiCH_2CH$), 2.54 (m, 8H, $SiCH_2CH_2Ph$), 4.04 (br s, 4H, H_{Fc}), 4.14 (br s, 4H, H_{Fc}), 4.83 (d, 108H, $CHCH_2$), 4.88 (dd, 108H, $CHCH_2$), 5.75 (m, 108H, $CHCH_2$), 7.11 (d, 8H, H_{ar}), 7.23 (brs, 8H, H_{ar}); $\delta_P(CDCl_3)$ − 17.9; *m/z* (MALDI-TOF) 8679 [M + Ag].

‡ In catalysis isolated complexes gave similar results as *in situ* complexes.

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