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Albert Soran, Peter M. Chapple, Claire Longuet, Rodolphe Sonnier, Marie Cordier, et al.. Phosphorus-containing polycarbosilazanes: Synthesis via dehydrocoupling catalysis and flame-retardant properties. Dalton Transactions, In press, 10.1039/d4dt03172e . hal-04867110

HAL Id: hal-04867110

<https://hal.science/hal-04867110v1>

Submitted on 6 Jan 2025

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**Phosphorus-containing polycarbosilazanes:
Synthesis via dehydrocoupling catalysis and flame-retardant properties†**

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† Dedicated to Professor Cristian Silvestru, in celebration of his 70th birthday.

‡ These two co-authors have contributed equally to the work and must be considered as first co-authors.

Abstract

The barium complex $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ has been used to catalyse the dehydropolymerisation of the phosphine-functionalised hydrosilane 4-Ph₂P-C₆H₄SiH₃ (**A**) with the α,ω -diamine 1,4-(CH₂NHMe)₂-C₆H₄ (**C**), for the production of $-\text{[Si(4-C}_6\text{H}_4\text{PPh}_2\text{)H-N(Me)CH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{N(Me)]}_n\text{-}$ polycarbosilazanes that contain dangling phosphino groups along the polymer backbone. The comonomers **A** and **C**, specifically prepared for this purpose and comprehensively characterised, lend themselves well to barium-promoted dehydrocoupling catalysis. They allow for the formation of linear, amine-capped polymers with molecular weights in the range 4,000-8,000 g mol⁻¹, as estimated by DOSY and ¹H end-group NMR analyses. The terpolymerisation of **C** with various mixtures of **A** and PhSiH₂R (R = H or Ph) led to the formation of terpolymers featuring various contents of phosphine-functionalised silazane groups, with an overall composition that reflects well the initial feed ratio of the comonomers. Thermal decomposition and flammability were studied at microscale on a series of polycarbosilazanes to assess the effect of molecular groups on thermal stability and heat release. The SiCN backbone containing silazane group significantly contributes to the “charring” of the polymer. By contrast, PPh₂, as other groups bearing a phosphorus atom in a low oxidation state, is not an effective char promoter.

Introduction

Polysilazanes containing alternating silicon and nitrogen atoms (N–Si–)_n can be broadly classified in three major groups.¹ Inorganic, carbon-free perhydropolysilazanes easily undergo hydrolysis of the N–Si bonds to eventually form silica; they are used as precursors to prepare high quality thin-films of silica to protect surfaces against weathering, or also for the synthesis of Si₃N₄ ceramics by pyrolysis at temperatures above 400 °C.²⁻⁴ In organic polysilazanes, the polymer backbone also includes carbon (aka polycarbosilazanes) or, alternatively, can have carbon substituents on the silane or amine moiety as pendent side-arms attached to the (N–Si–)_n main chain. They have desirable mechanical and durability properties compared to inorganic polysilazanes. The third group is made of hybrid polysilazanes, obtained by functionalising organopolysilazanes with, for instance, diisocyanates, epoxy oligomers, or phenolic oligomers. The Merck DURAZANE® coating agents contains all three varieties of polymers.⁵ Polysilazanes offer improved thermal stability and greater hardness compared to most organic polymers.⁶ They have good heat resistance, and retain up to 70 wt-% of their mass residue under nitrogen gas at 1100 °C, placing them among the best polymers by weight retention for non-flame retarded and unfilled polymers.⁷ The major application for polysilazanes is as material coatings, typically in the temperatures between 0-1500 °C.⁸ These coatings can be used for their anti-adherent properties,⁹ and provide protection from corrosion,¹⁰ UV degradation and decreased wettability, useful for the synthesis of superhydrophobic surfaces.¹¹ The optical properties,¹² permeability,¹³⁻¹⁴ antifouling¹⁰ and antibacterial^{10,15} properties of surfaces are modified with polysilazane coatings. Other applications include semiconductors,¹⁶ photonic crystals,¹⁷ LED and organic electronic device materials.¹⁸ One area where polysilazanes have been less exploited is as flame-retardant agents. Compared to other fire-retardant formulations, thermosetting hybrid resin systems based on unsaturated polyesters and polysilazanes were shown to burn with high intensity but fast extinction, resulting in lower total heat and smoke emission.⁷ The fire performances of virgin or formulated polysilazanes were also evaluated, and kinetic profiles for a three-step combustion process were proposed.¹⁹

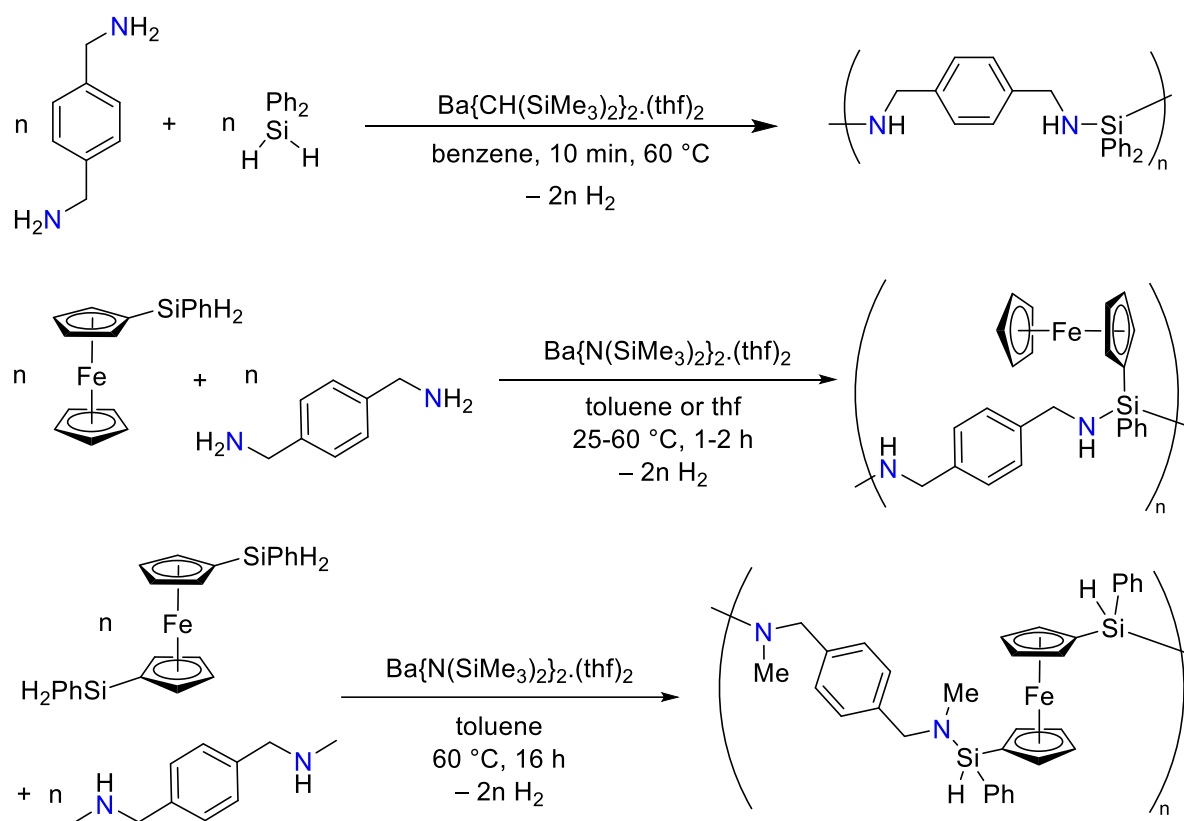
Phosphorus-containing polymers are primarily used for anticorrosion protective coatings, though they are also used for other applications including dental applications, tissue engineering, superhydrophobic surface coatings, optical materials, ion conducting membranes, or to remove metal ions from wastewater.²⁰⁻²⁶ One of their most desirable properties is their high thermal stability, which is one of several reasons they have found applications as flame retardants.²⁷⁻²⁹ Yet, we are not aware of phosphorus-functionalised organopolysilazanes.

The most common method to synthesise polysilazanes is by polycondensation between primary or secondary amines and di/trichlorosilanes in either the gas phase or in solution (aminolysis). This method has a number of drawbacks, making the process of restricted use industrially. Limitations include the generation of HCl gas (which can further protonate the silazane species, as well as significantly reducing functional group tolerance), low atom efficiency and low yields, and the tedious separation of the polysilazane from the ammonium salt coproducts.^{1,30} Metalation of a primary or

secondary amine followed by salt metathesis with chlorosilanes is another common way to generate oligosilazanes; however, this method suffers from many of the same drawbacks.³¹ Catalytic routes to polysilazanes are more desirable due to their increased atom efficiency and avoidance of corrosive chlorosilanes. The catalytic ring-opening of cyclic polysilazanes with alkali reagents has been reported,^{30,32} but it first requires access to cyclic monomers. Dehydrocoupling between primary or secondary amines and hydrosilanes forms Si-N bonds both as oligosilazanes and for polysilazanes. The earliest such example used the bifunctional hydrosilane HSiMe₂NHSiMe₂H with ammonia gas and [Ru₃(CO)₁₂] as a catalyst.³³⁻³⁴ Other rhodium³⁵ or titanium³⁶ catalysts have since been utilised.

The development of Si-N-C polycarbosilazanes having carbon atoms *within* the polymer chain has followed a similar route. The aminolysis of dichlorosilanes with diamines was for long the main path to polycarbosilazanes.³⁷⁻⁴¹ In 1999, dehydropolymerisation of 1,4-bis(dimethylsilyl)benzene with ammonia was catalysed by [Pd₂(dba)₃],⁴² while a strategy based on platinum-catalysed hydrosilylation furnished hyperbranched and dendrimeric polycarbosilazanes.⁴³ More recently, we and others have shown that complexes of the inexpensive group 2 metals provided potent molecular catalysts for the dehydropolymerisation of amines and hydrosilanes, yielding oligo- and polycarbosilazanes with molecular weights in the range 1,000-20,000 g mol⁻¹.^{44,45} Barium catalysts, e.g. the straightforward [Ba{CH(SiMe₃)₂}(thf)₂] and its amido congener [Ba{N(SiMe₃)₂}(thf)₂], have proved particularly effective, offering fast reaction rates and high chemoselectivity.^{46,47} The syntheses of linear and cyclic macromolecules were achieved by dehydropolymerisation of *p*-xylylenediamine and Ph₂SiH₂ (Scheme 1).⁴⁴ [CpFe(CpSiPhH₂)] was coupled with *p*-xylylenediamine to give polycarbosilazanes with dangling ferrocenes, whereas hybrid polymers with ferrocene units *within* the main backbone were produced by coupling 1,4-(CH₂NHR)₂C₆H₄ (R = H, Me) with [Fe{Cp(SiPhH₂)₂}]₂ or [Fe{Cp(SiMe₂H)₂}]₂.⁴⁵

As part of our continued interest in barium-mediated dehydrocoupling catalysis, we report here the synthesis of phosphorus-containing polycarbosilazanes. Among several possible strategies to obtain the targeted materials, the attempts focusing on 4-SiH₃-C₆H₄PPh₂ as starting materials are discussed herein. The synthesis of P-functionalised substrates is presented, along with their polymerisation to a range of polymers possessing various contents of P-atoms along the main backbone. An insight into the flame-retardant properties of these materials from pyrolysis combustion flow calorimetry and thermogravimetric analyses is also provided.



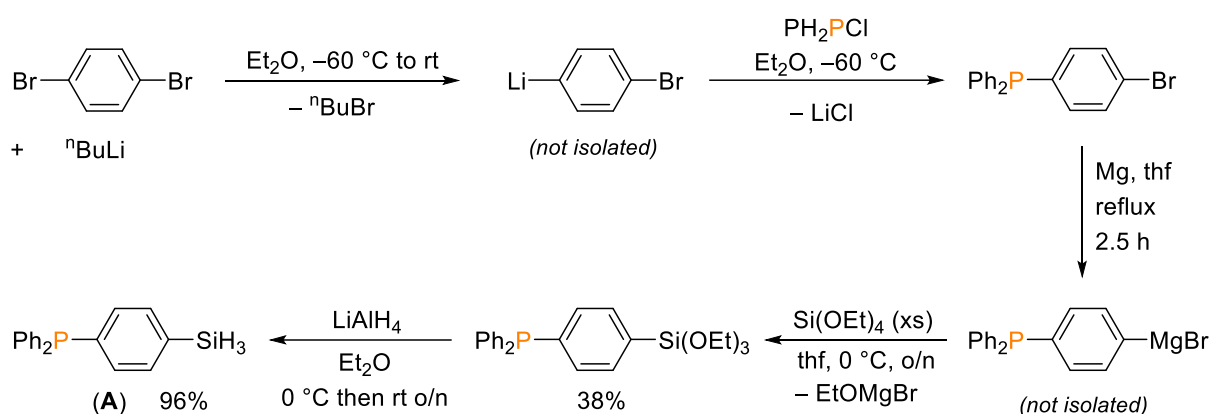
Scheme 1. Barium-catalysed synthesis of polycarbosilazanes.^{44,45}

Results and Discussion

Building on earlier work that demonstrated the ability of barium catalysts to enable the controlled dehydropolymerisation of diphenylsilane and *p*-xylylenediamine,⁴⁴ our chosen synthetic pathway to P-containing polycarbosilazanes focused on the utilisation of two functional substrates, 4-Ph₂P-C₆H₄CH₂NH₂ and, especially, 4-Ph₂P-C₆H₄SiH₃.

Synthesis of starting materials

The primary silane 4-Ph₂P-C₆H₄SiH₃ (**A**) was synthesised in a five-step process (Scheme 2). 1,4-Dibromobenzene was reacted in Et₂O with freshly titrated *n*BuLi. Subsequent reaction with Ph₂PCl at –60 °C proceeded quantitatively to yield 4-Br-C₆H₄PPh₂ (characterised by a sharp singlet at δ_P –6.4 ppm by ³¹P NMR in chloroform-*d*₃) as an off-white solid after work-up.^{48,49} NMR analysis of the crude product showed that the main impurity (ca. 2%) consisted of the P-P reductive coupling product Ph₂P-PPh₂ (δ_P –16.0 ppm).



Scheme 2. Synthesis of 4-Ph₂P-C₆H₄SiH₃ (**A**).

Adapting a protocol for the arylation of tetraalkyl orthosilicates,⁵⁰ 4-Ph₂P-C₆H₄MgBr was prepared and then reacted in situ with excess tetraethyl orthosilicate to yield 4-Ph₂P-C₆H₄Si(OEt)₃. Although not highly selective toward the formation of the desired product, we found that the Grignard route was overall cleaner and more efficient than that involving the corresponding lithium reagent, 4-Ph₂P-C₆H₄Li. A threefold excess of Si(OEt)₄ was found to encourage formation of the monosubstituted product and minimise that of the multiply substituted by-products, (4-Ph₂P-C₆H₄)₂Si(OEt)₂ (mostly; δ_P –5.1 ppm by ³¹P NMR in benzene-*d*₆) and (4-Ph₂P-C₆H₄)₃SiOEt. Yet, the crude product after aqueous workup still consisted of a mixture of the three compounds. The sought 4-Ph₂P-C₆H₄Si(OEt)₃ was separated from the by-products and obtained as a pure, colourless oil by distillation with a Kugelrohr (260–280 °C / 1.1 10^{–3} mbar; 38% isolated yield). The identity of this synthetic intermediate was established by NMR spectroscopy and mass spectrometry, and its purity was further confirmed by combustion analysis. Notable NMR data include a singlet at δ_P –5.2 (with satellites, *J*_{PC} = 19.4 Hz) and a singlet at δ_{Si} –58.8 ppm in the ³¹P and ²⁹Si NMR spectra, respectively.

Compound **A** was eventually obtained by reduction of 4-Ph₂P-C₆H₄Si(OEt)₃ with a fivefold excess of LiAlH₄.⁵¹ It was isolated in 96% yield as a colourless powder, and X-ray quality crystals were grown from slow evaporation of a diethyl ether solution. Compound **A** can also be sublimed under vacuum (10⁻³ mbar / 80 °C). The identity of the compound was established by X-ray diffraction crystallography, NMR spectroscopy and mass spectrometry; bulk purity was corroborated by elemental analysis. The molecular solid-state structure of **A** depicted in Figure 1 shows the phosphorus atom P1 to be in the expected pyramidal environment ($\Sigma_{\theta}(\text{P1}) = 305.9(6)^\circ$), while the geometry about the silicon atom Si1 is tetrahedral (note that the positions of the three silicon-bound hydrogens were not idealised but actually determined from electronic density in the Fourier map). The main NMR data for **A** are displayed in Figure 2. Its ¹H NMR spectrum features a diagnostic singlet at δ_{H} 4.17 ppm (with the corresponding satellites for the coupling to ²⁹Si, $J_{\text{SiH}} = 201$ Hz) integrating for three hydrogen atoms, while a singlet at δ_{P} -5.3 ppm (satellites at $J_{\text{PC}} = 19.4$ Hz) is detected in the ³¹P NMR spectrum. The ²⁹Si NMR spectrum features a single resonance at δ_{Si} -60.4 ppm.

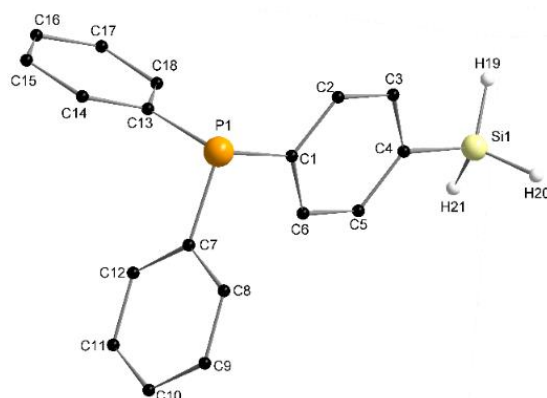


Figure 1. Representation of the molecular solid-state structure of 4-Ph₂P-C₆H₄SiH₃ (**A**). H atoms except those bounded to Si omitted for clarity. Selected interatomic distances (Å) and angles (°): P1-C1 = 1.8267(8), P1-C7 = 1.8254(9), P1-C13 = 1.8275(8), Si1-C4 = 1.8654(8); C1-P1-C7 = 101.99(3), C1-P1-C13 = 101.60(3), C7-P1-C13 = 102.32(4).

We also set out to prepare a phosphine-containing amine substrate. Hence, the primary amine 4-Ph₂P-C₆H₄CH₂NH₂ (**B**) was synthesised in high yield following known procedures.⁵² Starting from 4-bromobenzonitrile, lithiation through halo-metal exchange followed by reaction with Ph₂PCl generated 4-Ph₂P-C₆H₄CN, and then reduction of the nitrile by LiAlH₄ to give **B** with yields in excess of 90%.

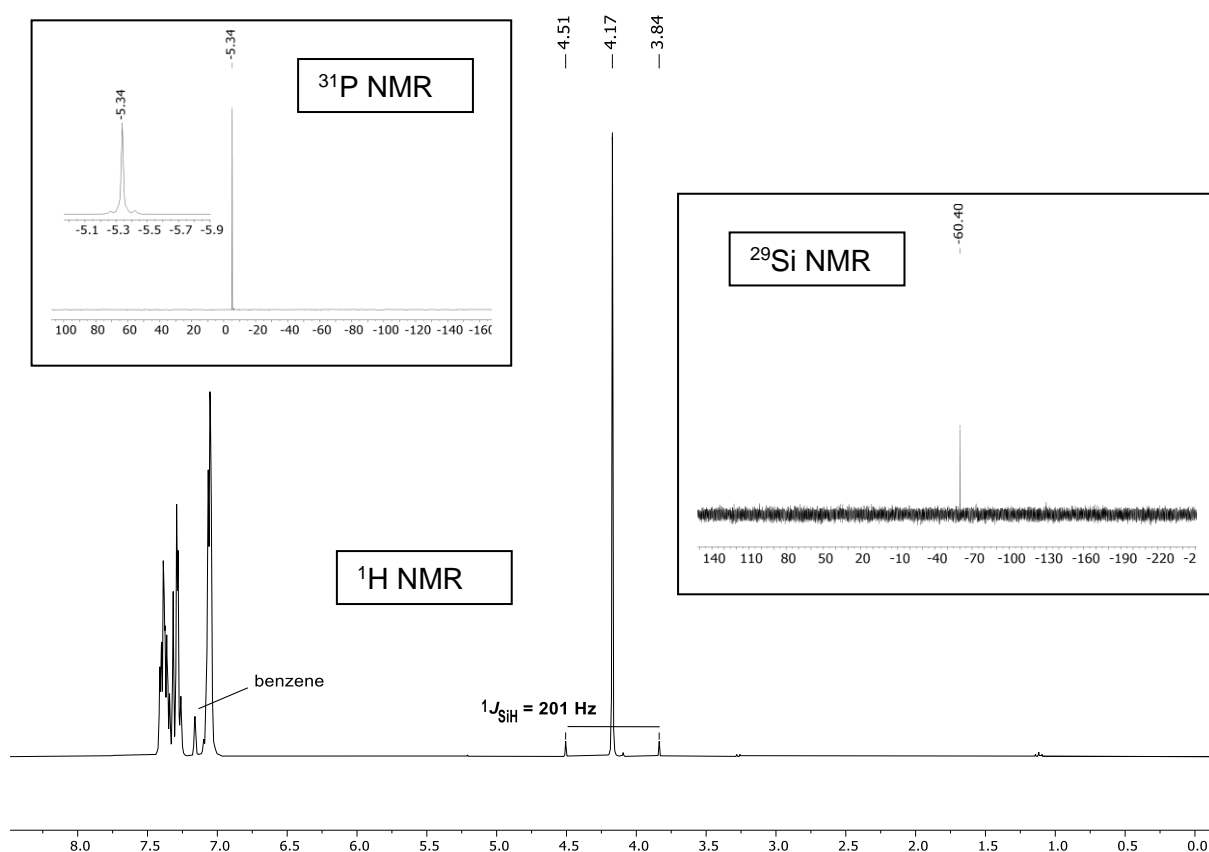


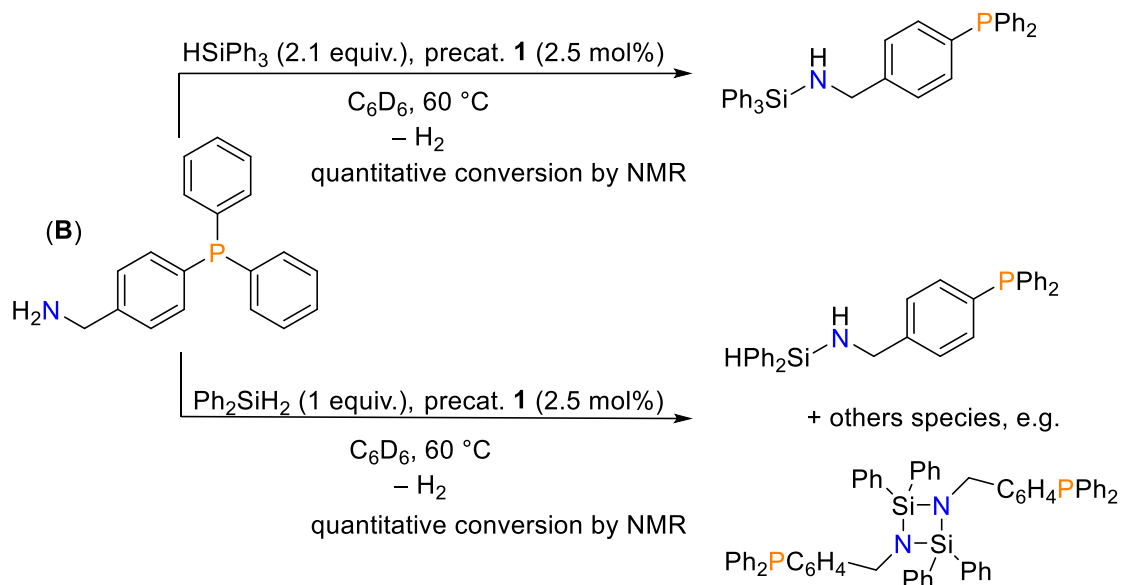
Figure 2. Representative ^1H (300.1 MHz), ^{31}P (121.5 MHz, left insert) and ^{29}Si (79.5 MHz, right insert) NMR data for 4- $\text{Ph}_2\text{P-C}_6\text{H}_4\text{SiH}_3$ (**A**). Data recorded at 26 °C in C_6D_6 .

Model dehydrocoupling reactions

Prior to dehydropolymerisation studies, a set of model reactions were first carried out using **A** and **B** to assess their behaviour in bi- or trimolecular barium-catalysed dehydrocouplings, even if we were confident that introduction of the Ph_2P substituent would not alter significantly the overall behaviour of hydrosilanes and amines.^{46,47} Our catalyst of choice was $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**1**), on account of its ease of access and demonstrated efficiency in amine-hydrosilane dehydrocoupling reactions.⁴⁴⁻⁴⁷

The reaction between **B** and excess triphenylsilane (2.1 equiv; metal loading 2.5 mol-%) in benzene- d_6 at 60 °C proceeded smoothly within 1 h to give the monocoupled silazane 4- $\text{Ph}_2\text{P-C}_6\text{H}_4\text{CH}_2\text{NHSiPh}_3$ as the main product (Scheme 3). The ^1H NMR spectrum of the product displays a number of low field aromatic resonances between 7.7–7.0 ppm, along with a doublet for the methylene CH_2 resonance at δ_{H} 3.95 ppm, downfield shifted from the amine precursor, and a broad triplet amine NH resonance at δ_{H} 1.25 ppm. Single crystals were grown and analysed by X-ray diffraction crystallography, and the structure of the compound was established (Figure 3). It is unsurprising that only one molecule of HSiPh_3 reacted with the primary amine **B**, as similar dehydrocoupling reactions between benzylamine and triphenylsilane have previously shown identical chemoselectivity.^{46,47} Similarly, the equimolar reaction of **B** with the difunctional Ph_2SiH_2 afforded the monocoupled silazane 4- $\text{Ph}_2\text{P-C}_6\text{H}_4\text{CH}_2\text{NHSiPh}_2\text{H}$, which was characterised by NMR and HR-MS; no sign of the dicoupled

product $\{4\text{-Ph}_2\text{P-C}_6\text{H}_4\text{CH}_2\text{NH}\}_2\text{SiPh}_2$ was detected in the course of the reaction. However, the appearance of at least one other unidentified species could be seen, and its concentration increased with time. It is worth noting that the barium-mediated formation of cyclic disilazanes with $[\text{N}_2\text{Si}_2]$ cores has been observed before in related reactions; it is thermodynamically favoured over chain propagation, and could not be overcome to afford oligocarbosilazanes.⁵³ The production of cyclic disilazane is a nuisance when high molecular weight polymers are sought, as it may affect both the stoichiometry of the catalysed dehydropolymerisation and the microstructure of the resulting materials.



Scheme 3. Synthesis of $4\text{-Ph}_2\text{P-C}_6\text{H}_4\text{CH}_2\text{NHSiPh}_2\text{R}$ ($\text{R} = \text{Ph}$, top; H , bottom) from the primary amine **B** catalysed by $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**1**).

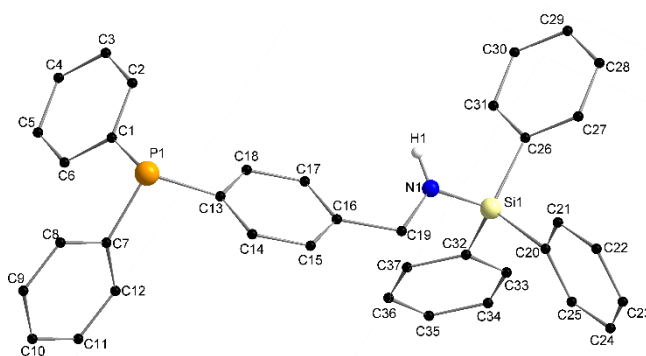
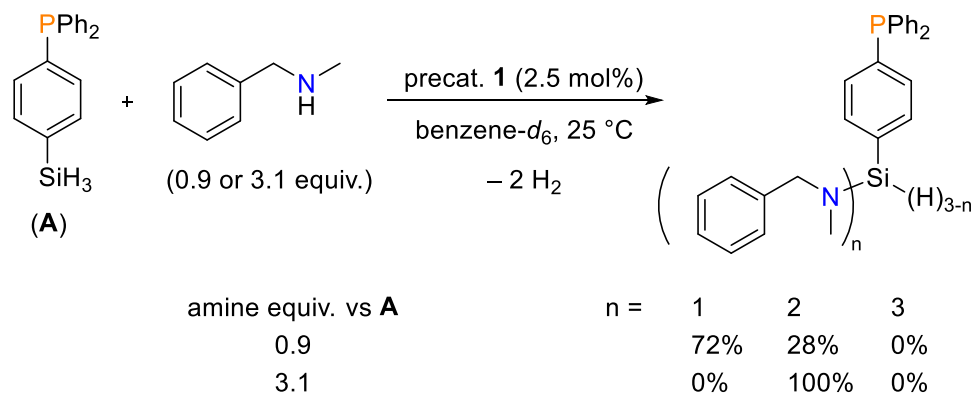


Figure 3. Representation of the molecular solid-state structure of $4\text{-Ph}_2\text{P-C}_6\text{H}_4\text{CH}_2\text{NHSiPh}_3$. Only one of the two independent molecules in the asymmetric unit is depicted. H atoms except those bounded to Si omitted for clarity. Selected interatomic distances (\AA) and angles ($^\circ$): $\text{P1-C1} = 1.855(5)$, $\text{P1-C7} = 1.840(4)$, $\text{P1-C13} = 1.866(4)$, $\text{Si1-N1} = 1.720(8)$, $\text{Si1-C20} = 1.900(4)$, $\text{Si1-C26} = 1.903(4)$, $\text{Si1-C32} = 1.904(4)$, $\text{N1-C19} = 1.468(11)$; $\text{C1-P1-C7} = 102.1(3)$, $\text{C1-P1-C13} = 104.3(3)$, $\text{C7-P1-C13} = 103.5(3)$,

N1-Si1-C20 = 110.1(3), N1-Si1-C26 = 106.4(3), N1-Si1-C32 = 109.1(3), C20-Si1-C26 = 109.3(3), C20-Si1-C32 = 112.0(3), C26-Si1-C32 = 109.7(3), C19-N1-Si1 = 120.5(6).

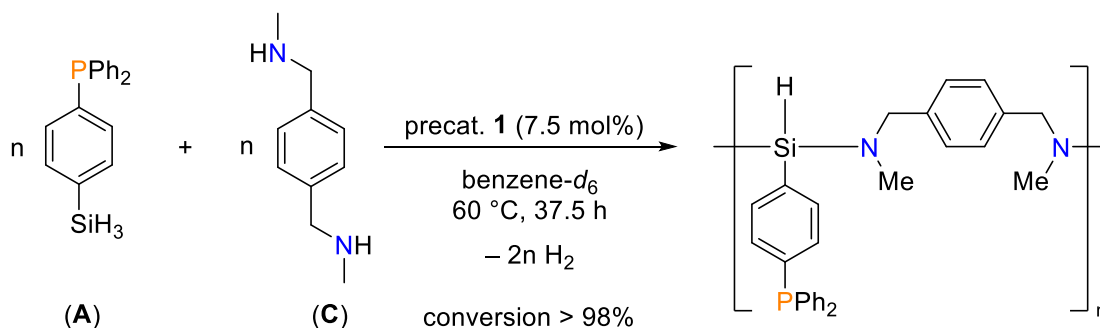
Finally, even after 150 h at 60 °C, the reaction between **B** and 0.5 equivalent of diphenylsilane was incomplete. It yielded an unclear mixture containing the expected dicoupled product $\{4\text{-Ph}_2\text{P-C}_6\text{H}_4\text{CH}_2\text{NH}\}_2\text{SiPh}_2$ along with substantial amounts of the starting materials and several other species, perhaps resulting from decomposition due to the long reaction time, that could not be identified. Hence, taken collectively, these data suggest that the reactions involving **B** are not selective nor easy to drive to completion; both observations constitute serious limitations to the use of **B** for the production of silazanes.

The reaction of trihydrosilane **A** with a threefold excess of *N*-methylbenzylamine catalysed by **1** (2.5 mol-% vs. **A**) at 25 °C in benzene-*d*₆ is chemoselective and generates the product of double dehydrocoupling, 4-PPh₂-C₆H₄SiH{N(Me)CH₂Ph}₂ (Scheme 4). This disilazane, a colourless oil, was characterised by combustion analyses and NMR spectroscopy. A resonance at $\delta_{\text{P}} -5.2$ ppm is visible in its ³¹P NMR spectra, while the diagnostic triplet ($^1J_{\text{Si-H}} = 219$ Hz) for the SiH hydrogen appears at $\delta_{\text{H}} 5.32$ ppm in the ¹H NMR spectrum. The formation of the mono- and tricoupled products, i.e. 4-PPh₂-C₆H₄SiH₂N(Me)CH₂Ph and 4-PPh₂-C₆H₄Si{N(Me)CH₂Ph}₃, was not detected. On the other hand, when the analogous reaction was carried out with only 0.9 equiv. of *N*-methylbenzylamine vs. **A** to assess whether 4-PPh₂-C₆H₄SiH₂N(Me)CH₂Ph could be formed selectively, only a 72:28 mixture of the mono- and di-coupled products was obtained along unreacted **A**, indicating that the rate constant for the second SiH/HN coupling is competitive with that of the first one. Even at -78 °C in toluene-*d*₈, a mixture of the two compounds is formed in a 87:13 ratio. Finally, the catalysed dehydropolymerisation of **A** with benzylamine under identical conditions is not selective nor controlled, and generates very quickly a solid insoluble in the reaction solvent. The NMR data in thf-*d*₈ of the isolated material showed the presence of multiple products whose identity could not be precisely ascertained, but which presumably consisted of various cyclic and/or cross-linked (macro)molecules.



Scheme 4. Selectivity in the coupling of 4-Ph₂P-C₆H₄SiH₃ (**A**) with *N*-methylbenzylamine catalysed by [Ba{N(SiMe₃)₂]₂ (**1**).

precatalyst was used, whereas only partial conversion (ca. 43%) of the substrates was observed with a 2.5 mol-% loading in **1**. The NMR data of the crude product (aka **co-PhPZ-0**) recorded at the end of the reaction (no work-up) are given in Figures 4 and 5. The ^{31}P and ^{29}Si NMR spectra each feature a single, sharp resonance at $\delta_{\text{P}} -5.3$ ppm and $\delta_{\text{Si}} -15.2$ ppm. The latter chemical shift is in line with that reported above for the model coupling of *N*-methylbenzylamine and **A**, but substantially deshielded compared to that observed in polycarbosilazanes obtained from Ph_2SiH_2 and *p*-xylylenediamine, ca. -24.0 ppm.⁴⁴ The ^1H NMR spectrum contains characteristic resonances at δ_{H} 5.37 (triplet with $^1J_{\text{Si-H}} = 219$ Hz), 4.03 (singlet) and 2.46 (singlet) ppm for the SiH , ArCH_2N and NCH_3 hydrogen atoms, respectively. The absence of clearly detectable $-\text{MeNH}$ or $-\text{SiH}_2(\text{Ar})$ end-groups suggests again the creation of a cyclic oligo- or polycarbosilazane; no attempt at molecular weight determination was made at this point (see below). The resonances for free $\text{HN}(\text{SiMe}_3)_2$, dihydrogen and a Ba-amide species are also visible.



Scheme 6. Dehydropolymerisation between **A** and **C** catalysed by $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**1**). The absence of detectable end-groups by NMR spectroscopy is consistent with a cyclic structure.

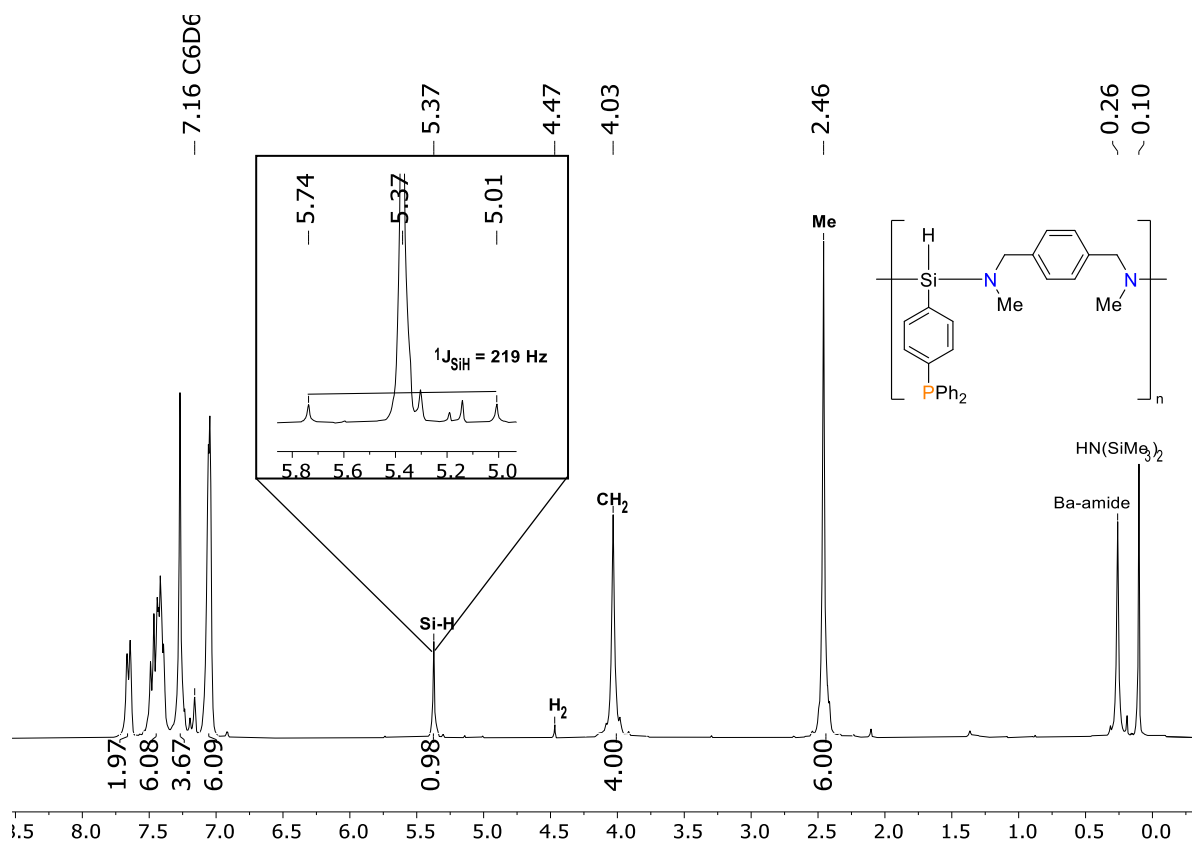


Figure 4. ^1H NMR spectrum (300.1 MHz, 25 °C) of the crude material (**co-PhPZ-0**) resulting from the Si-H/H-N dehydrocoupling between **A** and **C** catalysed by $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**1**) in C_6D_6 .

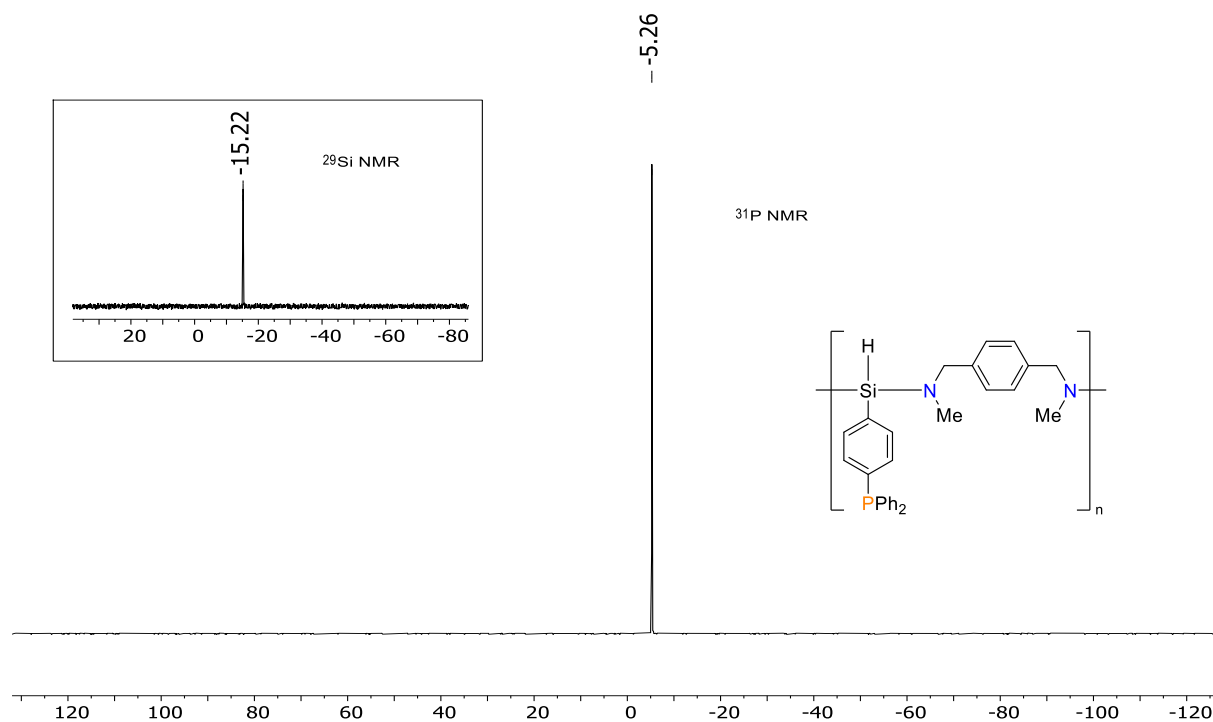
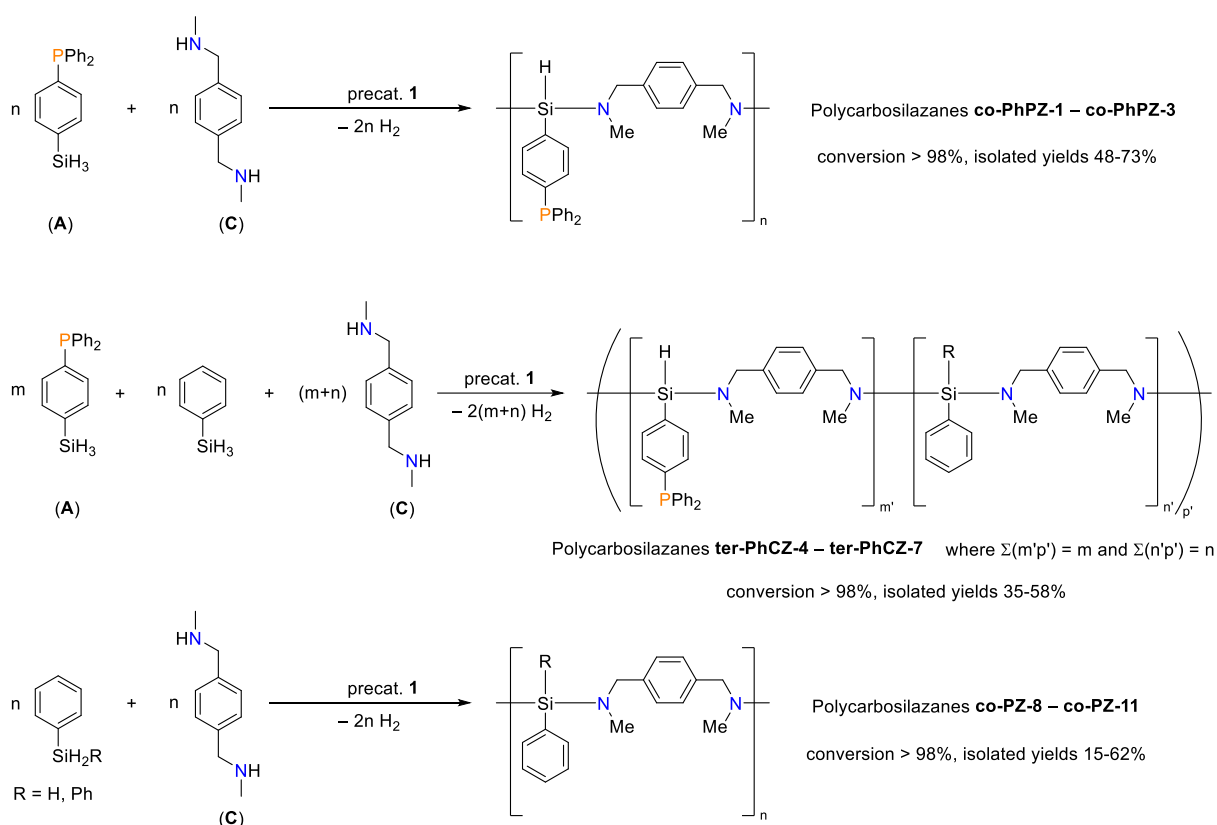


Figure 5. $^{31}\text{P}\{^1\text{H}\}$ (main spectrum; 121.5 MHz, 25 °C) and $^{29}\text{Si}\{^1\text{H}\}$ (insert; 79.5 MHz, 25 °C) NMR spectra of the crude material (**co-PhPZ-0**) resulting from the Si-H/H-N dehydrocoupling between **A** and **C** catalysed by $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**1**) in benzene- d_6 .

Following this first NMR-scale reaction, all subsequent dehydropolymerisations were carried on larger scales in Schlenk vessels, allowing the isolation of greater amounts of materials, in particular for more comprehensive characterisation. A suite of phosphorus-containing carbosilazane copolymers (aka **co-PhPZ-X**) and terpolymers (aka **ter-PhCZ-X**), as well as a range of phosphorus-free copolymers (aka **co-PZ-X**), made respectively by Si-H/H-N dehydropolymerisation of various ratios of **A+C**, **A+PhSiH₃+C** and **PhSiH₃+C**, was synthesised (Scheme 7). The specificities of each sample can be found in Table 1; experimental details are provided in the Supporting Information. The reactions were run to complete conversion of the substrates in benzene (or, in rare cases, toluene) with a concentration of 0.34 mol L⁻¹ in the limiting substrate. Isolated yields were often significantly lower than observed conversions measured by NMR, due to the loss of material during work-up. Note that, unless otherwise stated, the polymers were assumed to be end-capped with amine groups with diagnostic NMR resonances (see below for amine end-groups), while no evidence of terminal silane groups was observed in their ¹H NMR spectra. This suggests that, despite our best efforts, slight excesses of diamine **C** vs. trisilyl silane **A** were actually used although a 1:1 stoichiometry was aimed for (*vide infra*). In the case of copolymerisation with both **A** and PhSiH₃ silanes, the contents of the two incorporated silanes in the final bulk materials reflected precisely the initial feed ratio, as all comonomers were fully consumed.



Scheme 7. Polycarbosilazane synthesis by Si-H/H-N dehydrocoupling between **A+C**, **A+PhSiH₃+C** and **PhSiH₃+C**, using precatalyst [Ba{N(SiMe₃)₂]₂ (**1**).

Table 1. Polymers prepared by Si-H/H-N dehydrocoupling between **A**+**C**, **A**+PhSiH₃+**C** and PhSiH₃+**C** using precatalyst [Ba{N(SiMe₃)₂]₂ (**1**).^a

Sample	Substrate contents				solvent	temperature (°C)	time (h)	conversion : yield ^b (%)	M _n end-group (g mol ⁻¹)	X _{n,end-group} ^c	M _n DOSY ^d (g mol ⁻¹)
	A	PhSiH ₃	C	1							
co-PhPZ-1	100	0	100	10	Benzene	60	16	> 98 : 58	4600	18	5500
co-PhPZ-2	100	0	80	10	Toluene	60	16	> 98 : 73	- ^e	- ^e	5600
co-PhPZ-3	95	0	100	10 ^f	Benzene	25	32 ^f	> 98 : 48	7800	33	8500
ter-PhCZ-4^f	50	50	95	10	Benzene	25	16	> 98 : 58	18,600	50	20,500
ter-PhCZ-5^f	20	80	95	10	Benzene	25	16	> 98 : 35	20,500	66	24,500
ter-PhCZ-6^f	5	95	95	10	Benzene	25	16	> 98 : 50	30,500	108	31,500
ter-PhCZ-7	1	99	100	10	Benzene	25	16	> 98 : 56	- ^e	- ^e	34,000
co-PZ-8	0	100	100	10	Benzene	25	16	> 98 : 55	31,500	116	36,500
co-PZ-9	0	100	80	1	Benzene	25	16	> 98 : 56	- ^e	- ^e	21,500
co-PZ-10	0	80	100	1	Benzene	25	16	> 98 : 15	1700	6	5500
co-PZ-11	0	100 ^g	100	10	Benzene	25	16	> 98 : 62	31,500	91	24,000
co-PZ-12	0	100	100 ^h	10	Benzene	25	16	> 98 : 96	- ⁱ	- ⁱ	- ⁱ
co-PZ-13	0	100 ^g	100 ^h	10	Benzene	25	16	> 98 : 94	- ⁱ	- ⁱ	- ⁱ

^a Reactions carried out with [Ba{N(SiMe₃)₂]₂ (**1**), with a concentration of 0.34 mol L⁻¹ in the limiting substrate. Reactions were run to complete conversion of the substrates (> 98%).

^b Percentages of conversion (determined by NMR spectroscopy) and isolated yield after work-up.

^c The degree of polymerisation is defined as monomeric units in the polymer, opposed to the repeating silazane unit, calculated by ¹H NMR spectroscopy.

^d Number-average molecular weight estimated by ¹H DOSY NMR spectroscopy.

^e End-groups could not be identified by ¹H NMR spectroscopy.

^f The catalyst was introduced in two portions: 5 mol-% at the beginning and an extra 5 mol-% after 16 h.

^g Ph₂SiH₂ was used instead of PhSiH₃. For individual diffusion coefficients, see the experimental section.

^h The diamine used was *p*-xylylenediamine instead of **C**.

ⁱ Insoluble materials.

The first phosphorus-containing polycarbosilazane (**co-PhPZ-1**) was synthesised using equimolar amounts of **A** and **C**, with a 10 mol-% loading of precatalyst **1**. The reaction was left at 60 °C for 16 h to ensure full conversion. The polymer was isolated as a white solid and was dried to constant weight, and it was characterised by multinuclear NMR spectroscopy and elemental analysis. ¹H NMR of the crude material indicated full consumption of all substrates, with overall equal incorporation of **A** and 4-PPh₂-PhSiH₃ in the polymer chains; 2D ROESY NMR was used to show clear coupling between the hydrosilane and the *N*-methyl group hydrogens. The ¹H NMR spectrum of polymer **co-PhPZ-1** (Figures S29 and S43 in the Supporting Information) resembles that depicted in Figure 4 for **co-PhPZ-0**. Yet, in addition to the resonances for typical main chain repeat units (at δ_{H} 5.37 (SiH), 4.03 (CH₂) and 2.46 (NCH₃) ppm), it also featured additional resonances attributed to terminal amino end-groups, that is, 4-polymeryl-C₆H₄-CH₂NHMe, at δ_{H} 3.55 (CH₂), 2.22 (NCH₃) and 0.62 (NH) ppm. The presence of these end-capping units indicates the formation of linear polymer chains, as opposed to cyclic ones in the case of **co-PhPZ-0**. An approximate molecular weight of 4600 g mol⁻¹ was estimated by end-group analysis, corresponding to an average degree of polymerisation of 18. There is a broad resonance in the ²⁹Si{INEPT} NMR spectrum of **co-PhPZ-1** at δ_{Si} -15.2 ppm, identical to that obtained previously for **co-PhPZ-0**; the ³¹P NMR data for the two materials also match very well (δ_{P} -5.2 vs. -5.3 ppm). Barium-mediated silazane dehydropolymerisations have been shown to give exclusively cyclic products previously when a (near) perfect 1:1 stoichiometry of comonomers is achieved.⁴⁴ Polymer **co-PhPZ-1** appears instead to be linear based on the presence of terminal amines, which suggests, as aforementioned, that a slight excess of amine must have been unwittingly used, possibly as the result of slight contamination of **A** by an undetected impurity. Despite repeated attempts under identical reaction conditions, we did not manage to produce a polymer devoid of these amino end-groups. Attempts to analyse **co-PhPZ-1** using gel-permeation chromatography (GPC) failed, most likely due to the high hydrolytic sensitivity of the N-Si bond resulting in decomposition during analysis. More generally, the polymers prepared herein were too sensitive and not soluble enough for characterisation by size exclusion chromatography. Therefore, to gain another indication of the polymers molecular weight (*M_n*), the polymer was analysed by DOSY NMR. Following the protocol described by Grubbs and co-workers,⁵⁴ a series of monodisperse commercial polystyrene standards of known molecular weights were prepared and the diffusion coefficients (*D*) measured for 7 standards between 580 g mol⁻¹ and 70,500 g mol⁻¹. This method has been used before in our laboratory and in others to estimate the molecular weights of a variety of polycarbosilazanes.^{44,45} The molecular weight of **co-PhPZ-1** as measured by DOSY was estimated to be 5500 g mol⁻¹, slightly higher than the estimation by end-group analysis (4600 g mol⁻¹; Figure 6).

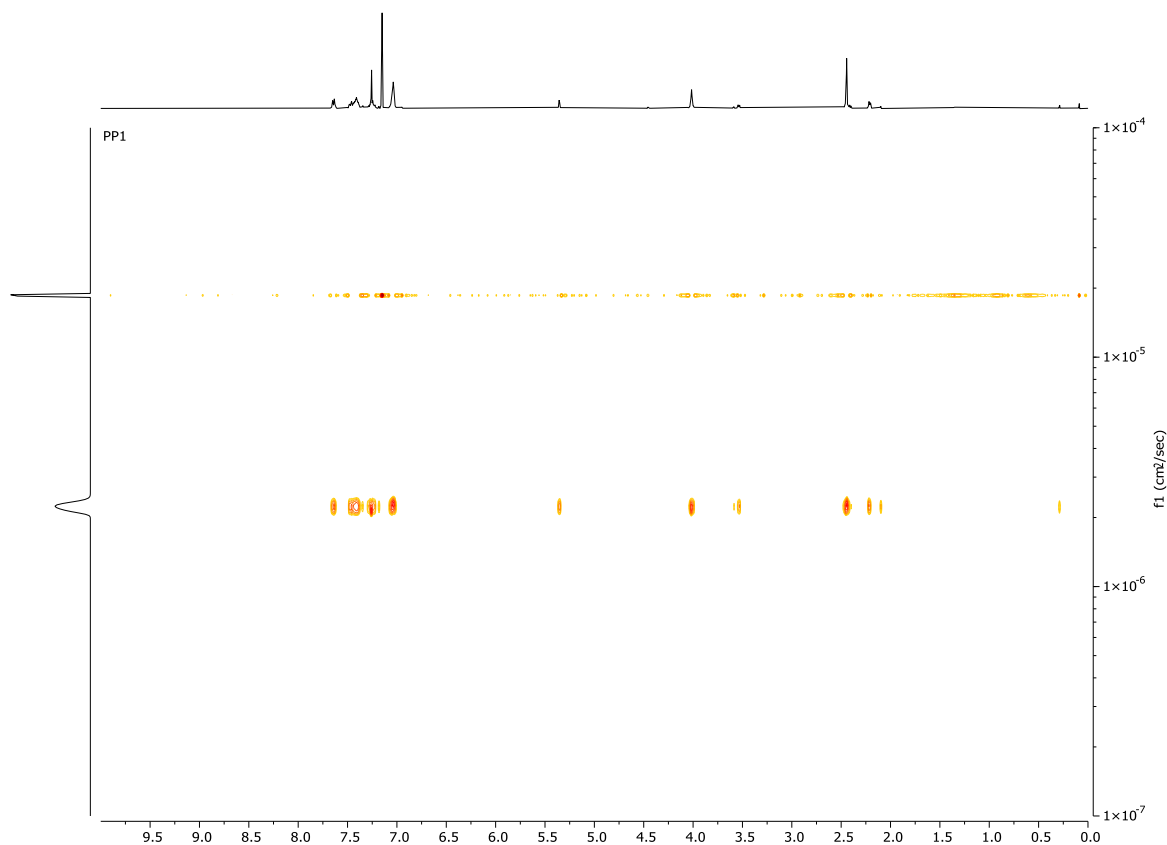


Figure 6. ^1H DOSY NMR spectrum (400.1 MHz, benzene- d_6 , concentration = 1.0 mg mL $^{-1}$, 302 K) of the phosphorus-containing polymer **co-PhPZ-1**.

The polymers **co-PhPZ-2** and **co-PhPZ-3** were synthesised in a similar manner with mild variation of conditions from the synthesis of **co-PhPZ-1** (Table 1). **co-PhPZ-2** was prepared by carrying out the dehydrocoupling reaction using a 20 mol-% default of the amine vs. silane **A**. The ^1H NMR spectrum indicated a less well-defined polymer and end-groups could not be eventually identified; yet, the molecular weight of the material as estimated by DOSY was similar to that of **co-PhPZ-1**. Dropping the catalyst loading to 5.0 mol-% and the reaction temperature to 25 °C resulted in incomplete conversion after 16 h (**co-PhPZ-3**, oligomeric species with both silane and amine chain-ends). However, addition of another 5.0 mol-% of catalyst and another 16 h reaction time allowed complete monomer conversion, and the recovery of a final material with slightly larger molecular weights (7800 g mol $^{-1}$ by end-group analysis, 8500 g mol $^{-1}$ by DOSY). The observation of higher molecular weights at lower reaction temperature agrees with the results obtained by Hill and co-workers.⁴⁵

As we were interested in investigating the effect of having different phosphorus loadings would have on the molecular weight, physical properties and potential flame retardancy (as well as maximising the amount of P-containing polymer we could generate for a given quantity of the silane **A**), a series of terpolymers were synthesised using varying amounts of PhSiH $_3$ in partial substitution of the silane-containing monomer **A**. The four polymers **ter-PhCZ-4** – **ter-PhCZ-7** were obtained from a 50:50, 20:80, 5:95 and 1:99 feed ratio of **A** to PhSiH $_3$, respectively, using otherwise identical conditions (see

Scheme 7). Unexpectedly, these terpolymers had significantly larger molecular weights when measured using both end-group NMR analysis and DOSY measurements compared to **co-PhPZ-1** – **co-PhPZ-3**. Also, there is an apparent clear correlation between higher percentage of PhSiH₃ (vs. **A**) and higher overall molecular weight. We surmised these discrepancies resulted from the fact that, unlike commercial PhSiH₃, the home-made monomer **A** may have contained undetected impurities that led to uncertainty about exact comonomer contents and, by corollary, degree of polymerisation and identity of the endgroup. Yet, bulk comonomers of the best possible purity were used for these polymerisation studies. Another hypothesis would be partial catalyst decomposition, leading to comonomer-to-metal ratios greater than the expected values, with the same consequences. Again, the DOSY estimated molecular weights are slightly higher than those done by end-group analysis, but are generally in reasonable agreement. These terpolymers were poorly soluble in aromatic solvents relative to the lighter molecular weight **co-PhPZ-1** – **co-PhPZ-3**. The samples used for DOSY measurements (~ 1 mg mL⁻¹) required heating and sonication to dissolve the small amount of solid. As such, is it not impossible that during the DOSY measurements, some solid precipitated out of solution. As this was likely the heaviest molecular weight polymer, it is actually possible that the average molecular weight of the polymer is larger than that given in Table 1.

Polycarbosilazane **co-PZ-8**, which does not contain any phosphorus, was synthesised as a reference in order to both investigate the relative molecular weights, as well as to be able to compare effect of phosphorus incorporation on the physical properties of the polymers (Scheme 7). Using the same synthetic conditions as for the previous polymers, **co-PZ-8** featured the highest molecular weight recorded thus far (31,500 g mol⁻¹ by end-group, 36,500 g mol⁻¹ by DOSY). This is in direct line with the already mentioned apparent trend between molecular weight and PhSiH₃ content. The ¹H NMR spectrum of **co-PZ-8** recorded in benzene-*d*₆ is shown in Figure S37 (SI). It features extremely well-defined chemical environments of the polymer. Polymers **co-PZ-9** and **co-PZ-10** were synthesised in the same manner as **co-PZ-8**, though using a molar excess of PhSiH₃ and **C**, respectively. As expected, the molecular weights were significantly lower than in **co-PZ-8**, which once again highlights the importance of molar equivalence in step-growth condensation polymerisations. Interestingly, **co-PZ-9** (which used an excess of phenylsilane) has a significantly higher calculated *M*_n by DOSY measurement (21,500 g mol⁻¹) compared to **co-PZ-10**, which used an excess of the diamine (1700 g mol⁻¹ by end-group, 5500 g mol⁻¹ by DOSY).

The catalytic dehydrocoupling between Ph₂SiH₂ and **C** generated the polycarbosilazane **co-PZ-11** (Scheme 7). Polymer **co-PZ-11** varied from the previous polymers in that its calculated molecular weight based on its diffusion coefficient by DOSY NMR (24,000 g mol⁻¹) was significantly smaller than its molecular weight based off end-group analysis (31,500 g mol⁻¹). It has been proposed that poor correlation between DOSY measurements and end-group analysis for the fully decoupled diphenylsilane-based polycarbosilazanes could be due to the relatively low flexibility of the polymer (arising from its relatively high steric hindrance caused by high effective steric bulk), resulting in a

larger hydrodynamic radii, and hence larger diffusion coefficient.⁴⁵ Yet, that explanation seems unlikely in this case, since the end-group analysis suggests a larger molecular weight than the diffusion coefficient. Instead, we suggest here that the lower molecular weight calculated from the DOSY measurement is due to the relatively low solubility of the compound in benzene, resulting in partial precipitation of the higher weight distribution of the polymer. It may also be that the sample contains cyclic polymers, which would not contain end-groups identifiable by ¹H NMR spectroscopy. Yet, we are at this stage unable to provide evidence to support these hypotheses.

Analysis of Table 1 suggests a few trends. Terpolymers **ter-PhCZ-4** – **ter-PhCZ-7** show a clear correlation between lower loading of **A** and higher degree of polymerisation. Changing the reaction stoichiometry of the silane and amine comonomers away from 1:1 leads to a significantly reduced molecular weight, as is expected for a step-growth polycondensation reaction. For copolymers **co-PhPZ-1** – **co-PhPZ-3**, it is likely that the relatively low molecular weights must be attributed to imperfect reaction stoichiometry. Evidence of this is that the molecular weight increases when slightly less than one equiv. of **A** is used (relative to the amine). There may also be other contributing reasons for the differences in molecular weights of the polymers synthesised with **A** or PhSiH₃, e.g. steric effects, different diffusion rates in solution, different solubilities. The molecular weights estimated from diffusion coefficients in DOSY NMR spectroscopy are generally in good agreement with the molecular weights calculated by end-group analysis. Decreasing the reaction temperature from 60 °C to 25 °C strongly correlates with an increase in molecular weights, perhaps indicating a low ceiling temperature for the polymer. The relative distribution of the P-containing monomer **A** within terpolymers **ter-PhCZ-4** – **ter-PhCZ-7** has not yet been investigated. As such, it is not known whether these are block copolymers or if the phosphorus moiety is more randomly distributed throughout the polymer backbone. One way to investigate this distribution would be through using the P(III) atom as a dative ligand for a mid to late transition metal such as Cu, Ru or Au. Casting of the coordinated metallopolymer could allow imaging of the P distribution using transmission electron microscopy or scanning transmission electron microscopy via energy dispersive X-ray spectroscopy. This will be the topic of a forthcoming investigation.

Preliminary flammability and flame retardancy testing

The materials **co-PhPZ-1**, **ter-PhCZ-5**, **ter-PhCZ-6**, **co-PZ-8** and **co-PZ-11** were subjected to pyrolysis combustion flow calorimetry (PCFC) and thermo-gravimetric analysis (TGA) measurements to investigate their potential as flame retardants. The series of tests also included two additional regular polycarbosilazanes made by dehydropolymerisation of PhSiH₃ with *p*-xylylenediamine (aka **co-PZ-12**) for the first, and of Ph₂SiH₂ with *p*-xylylenediamine (aka **co-PZ-13**) for the other (Figure 7; see Table 1 for details). These latter materials were isolated as colourless solids in near-quantitative yields, insoluble in all common solvents, even at high temperature, presumably as a result of extensive cross-linking.

This precluded NMR characterisation, and molecular weight by NMR techniques or GPC also proved impossible.

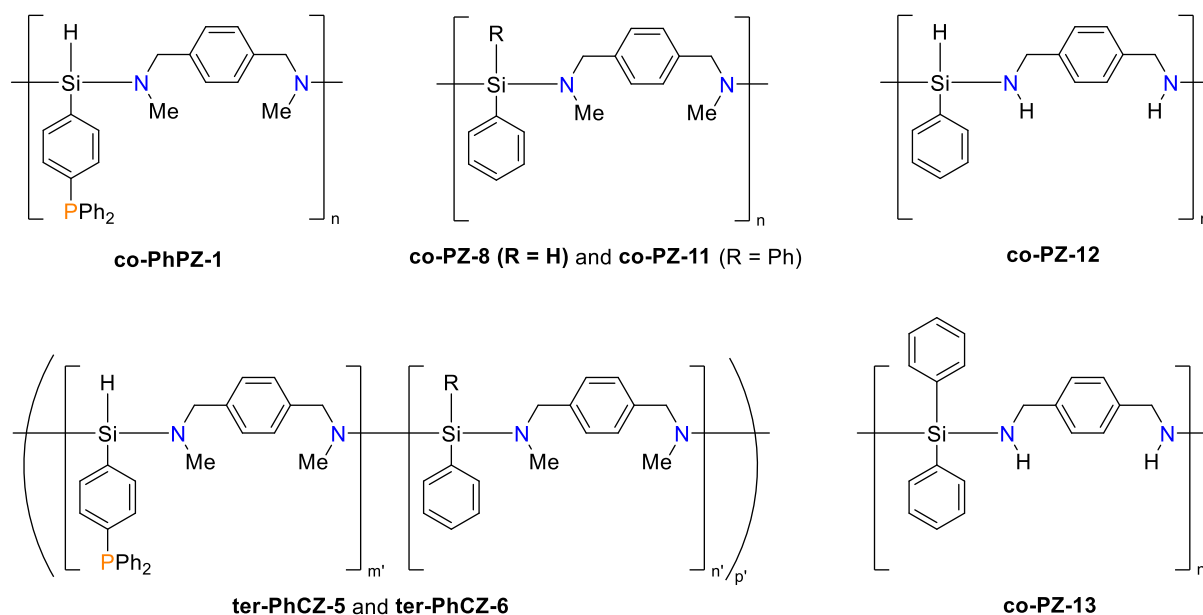


Figure 7. Materials tested for preliminary studies as flame retardants. See Table 1 for details.

TGA and differential thermogravimetric (DTG) curves for the different samples are collated in Figure 8. Note that a small peak is sometimes observed at very low temperature (ca. 100 °C) and may be related to the presence of residual solvent or monomers. Excluding this early mass loss, the decomposition of **co-PZ-12** and **co-PZ-13** starts at low temperature and continues over a large temperature range (around 200-700 °C), but it is important to highlight this decomposition occurs at a low mass loss rate. On the contrary, when nitrogen atoms are substituted by methyl groups as in **co-PZ-8** and **co-PZ-11**, main decomposition begins at higher temperature (> 300 °C) but is faster, with an intense peak of mass loss rate. The decomposition ends at ca. 600 °C. Residue yield is high in all cases (40-60%) due to the polymer backbone comprising an aromatic ring as well as silazane groups. It tends to decrease when additional methyl, phenyl or *p*-PPh₂-C₆H₄ groups are introduced on nitrogen and silicon atoms.

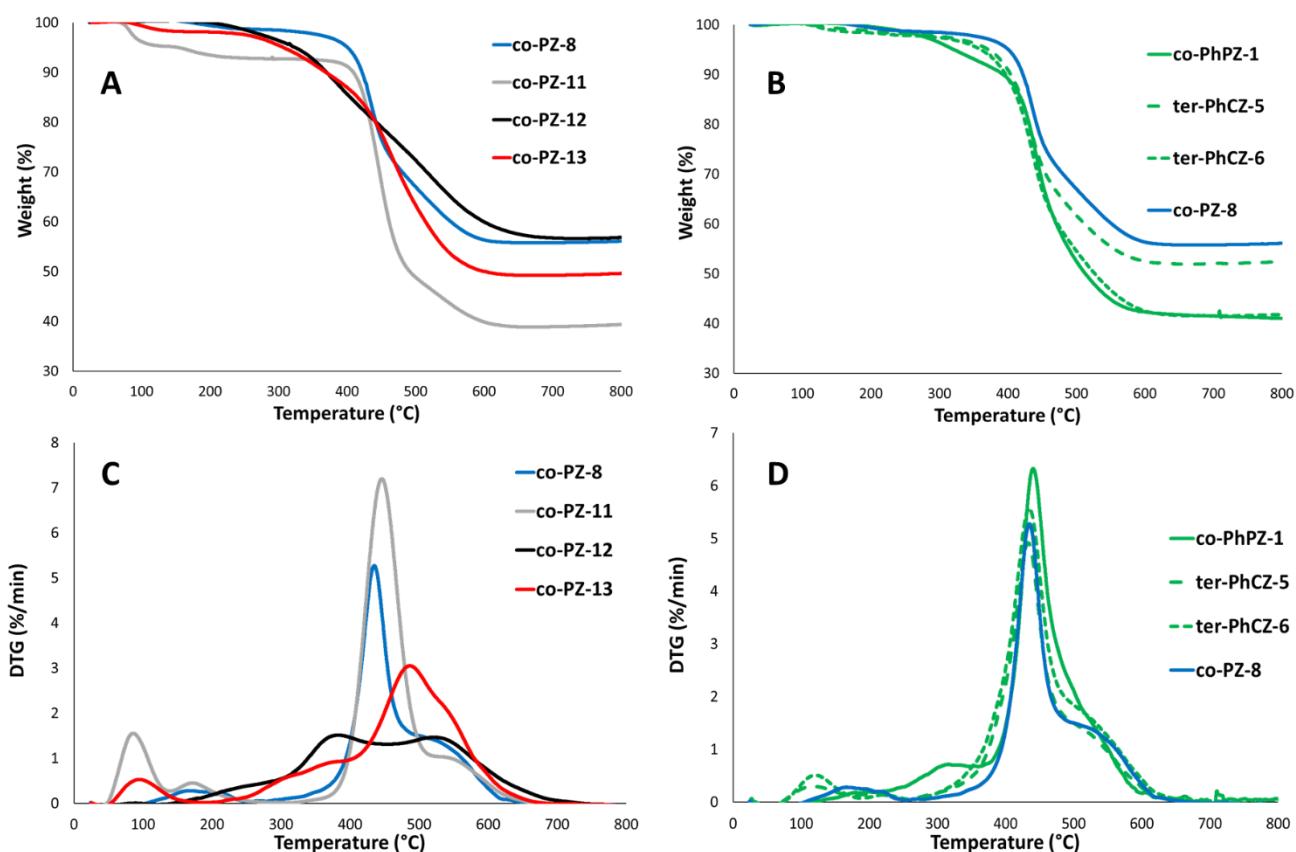


Figure 8. Thermogravimetric analysis (A and B) and corresponding differential thermogravimetric (C and D) curves for the tested polycarbosilazanes (heating rate $1\text{ }^{\circ}\text{C s}^{-1}$, nitrogen flow 100 mL min^{-1}).

Heat release rate (HRR) curves are often comparable to DTG curves because the heating process is similar (linear heating rate in nitrogen flow) even if the heating rate is higher in PCFC. Nevertheless, as the peaks correspond to heat release in PCFC and mass loss in TGA, their relative intensity changes from one analytical method to another. The tendencies already observed in TGA are confirmed in PCFC (Figure 9). **co-PZ-12** and **co-PZ-13** start releasing heat at low temperature (ca. 200 and $300\text{ }^{\circ}\text{C}$, respectively), and the heat release continues over a large temperature range with a main peak of HRR (pHRR) of weak intensity observed at high temperature ($> 500\text{ }^{\circ}\text{C}$). Moreover, the total heat release (THR) for **co-PZ-12** is lower (13.2 kJ g^{-1}) than for all other polycarbosilazanes (in the range $17\text{--}23\text{ kJ g}^{-1}$). By contrast, polycarbosilazanes that contain methyl groups on N-atoms start decomposing at higher temperature, but their pHRR is much higher and occurs at lower temperature ($420\text{--}450\text{ }^{\circ}\text{C}$). Overall, the HRR and DTG curves are in excellent agreement.

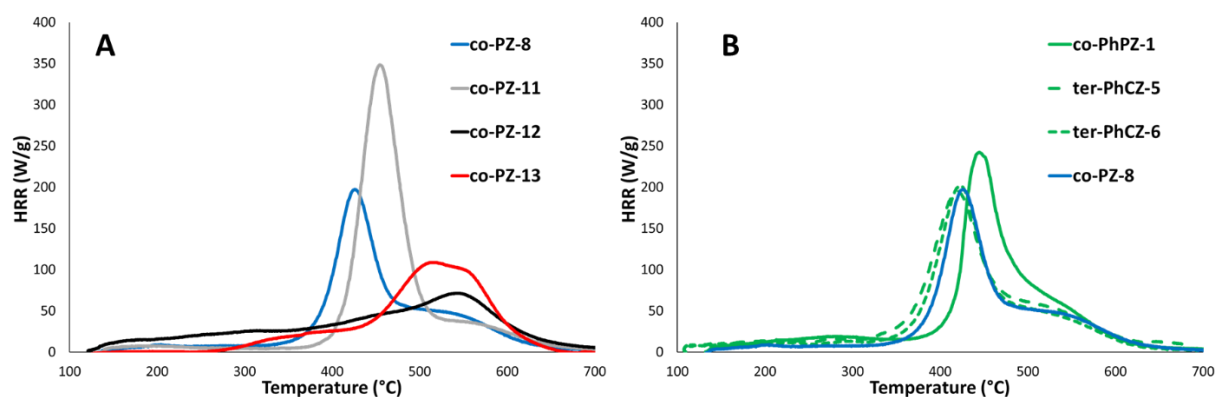


Figure 9. HRR curves for the tested polycarbosilazanes in pyrolysis-combustion flow calorimeter ($1\text{ }^{\circ}\text{C s}^{-1}$).

Figure 10 depicts the flammability properties measured in PCFC (anaerobic pyrolysis), namely, the main peak of heat release rate, the total heat release and the temperature at pHRR for a large variety of polymers (commercial or home-made, bio-based or synthetic thermoplastics, thermosets, elastomers but also some natural fibres) from our in-house database as well as Lyon and Walters' published set.^{55,56} It can be observed that pHRR and THR are roughly correlated while both parameters are dependent on the heat release. Considering that the heat release capacity (HRC) is related to pHRR according to $\text{HRC} = \text{pHRR}/\beta$, where β is the heating rate ($1\text{ }^{\circ}\text{C s}^{-1}$), the ratio between THR and HRC is approximately equal to 50 K, a value close to the peak width at mid-height of many HRR curves. Nevertheless, there are many exceptions, with some polymers releasing faster their heat and other ones releasing their heat over a larger range of temperature. This is particularly the case for **co-PZ-12** and **co-PZ-13**, with a very low pHRR (100 W g^{-1} or less) in comparison to their moderate THR values ($13.2\text{--}17.3\text{ kJ g}^{-1}$).

Temperature at pHRR is in the range $350\text{--}500\text{ }^{\circ}\text{C}$ for most polymers. Low temperatures at pHRR are found for some aliphatic polyesters.⁵⁷ On the contrary, high temperatures at pHRR are found for high-performance polymers that contain aromatic rings in their backbone (as PEEK) or fluorinated polymers.⁵⁸ Silicones are also known to have a high thermal stability (but they are not represented here; besides, the decomposition of silicones generates silica which clogs filters and leads to incorrect measurements in PCFC). Most polysilazanes exhibit a moderate stability with a temperature at pHRR in the range $400\text{--}450\text{ }^{\circ}\text{C}$. Once again, **co-PZ-12** and **co-PZ-13** have a specific behaviour, with a higher thermal stability and temperature at pHRR higher than $500\text{ }^{\circ}\text{C}$. These two polymers release an amount of heat similar or only slightly lower than the other polycarbosilazanes, but over a much higher temperature range whereas their low pHRR is observed at higher temperature. A reason for such behaviour may be related to the absence of methyl groups on nitrogen atoms. Hence, the presence of -NH secondary amine groups in **co-PZ-12** and **co-PZ-13** may result in hydrogen bonding between macromolecules. On the other hand, methyl groups obviously preclude such interactions in the other polycarbosilazanes, which hence display lower thermal stability and a fast heat release when decomposition starts.

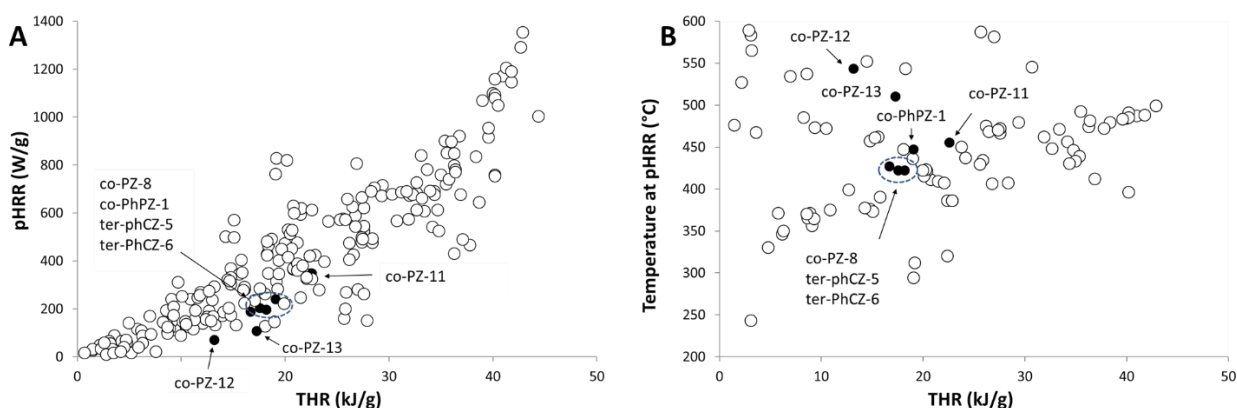


Figure 10. Flammability properties of pure polymers measured in pyrolysis combustion flow calorimetry (black dots are the new materials, white ones correspond to in-house database and ref. 55)

The group contribution method is largely used to calculate various properties of polymers.⁵⁶ The chief advantage of this method is its simplicity. Another point is that interactions are deliberately not considered. This is of course a strong limitation of the method, but nonetheless, when the calculated property does not fit well with the experimental value, it may be seen as an indication that interactions exist between some groups. One drawback of this method is that the number of groups allowing to predict the properties of a set of polymers is often quite high. For example, we have shown that the contributions of 31 functional groups were needed to predict the flammability of a set of 107 polymers.⁵⁹ Lyon and Walters were the first to use this method from the properties measured in PCFC.^{55,60} Pursuing these efforts, we have calculated the contributions of groups present in many (mainly thermoplastic) polymers,⁵⁹ and also in thermosets.⁶¹ More recently, we have also calculated and discussed the contributions of two phosphorus-based functional groups, namely DOPO (aka 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and phosphonates.⁶² The predicted properties included HRC, THR and char residue. In the present study, two new groups can be considered. First, the SiCN backbone of the polycarbosilazanes. This structure could be decomposed in several smaller units, but we have chosen to consider only one large structure because it is the found in all samples (except for the side groups on nitrogen and silicon atoms). Second, the phosphorus-based PPh₂ dangling group which is not known to be used as flame retardant group. Other groups considered are methyl and phenyl groups. The contributions of these groups have been already calculated (even if they are bound here to silicon or nitrogen atoms and not to carbon atoms as it is most usual).⁵⁹ Table 2 collects the calculated contributions for the two new groups, and those for methyl and phenyl groups previously determined. The calculated and experimental values for the polycarbosilazanes are compared in Figure 11. For char content, data from TGA (residue yield at 700 °C) were used.

Contributions to THR and HRC were hence calculated using the group contribution method. Contributions to char were calculated using two methods: the group contribution method (as for THR

and HRC) but also using Equation 1 based on energy balance.⁶¹ As shown in Table 2, the calculated values for the two methods are in good agreement.

$$\mu = \frac{\Delta h - THR}{\Delta h_{char}} \quad (1)$$

where Δh is the maximum heat which can be released by the polymer according to the well-known Huggett's relation⁶³ (13.1 MJ of heat is released when 1 kg of oxygen is consumed) and Δh_{char} is the heat stored by char, considered as a constant equal to 37.2 kJ g⁻¹.

Table 2. Calculated contributions to HRC, THR, Δh and char

Group	Molar mass (g mol ⁻¹)	Contributions to				
		HRC (J/g.K)	THR (kJ/g)	Δh (kJ/g)	Char (g/g) ^a	Char (g/g) ^b
CH ₃	15	1400	45	49		0.1
C ₆ H ₅	77	900	35	39		0.1
SiCN	164	-320	2.9	31	0.76	0.75
PPh ₂	261	500	27	37	0.25	0.26

^a From group contribution method, see reference 59. ^b From Equation (1).

The contribution of the SiCN backbone to Δh is high due to the presence of many carbon atoms. This fragment has also a high contribution to char (0.75) and therefore, the contribution to THR is much lower (2.9 kJ g⁻¹) than the contribution to Δh . This is unsurprising, since the SiCN part contains aromatic rings and silazane groups in the backbone. Its contribution to HRC is even negative. Of course, such contribution is not suitable for the “pure” SiCN structure, but it fits well for most polycarbosilazanes, even those that include also phenyl and methyl units as other Si- and N-bound groups. This suggests that this type of structure reduces the heat release rate of the whole polymer, which should be much higher due to the presence of high-contributing methyl and phenyl groups. Nevertheless, it must be noted that the contribution to HRC is not really satisfactory, especially because the calculated HRC for **co-PZ-13** does not match the experimental value. This agrees with the HRR curve of this polymer (and, incidentally, that of **co-PZ-12** as well, but its HRC is much lower, and the absolute difference between the experimental and calculated HRC is not so high): the decomposition and the heat release continuously occur over a very large range of temperatures. We have surmised above that extensive hydrogen bonding may account for this behaviour. If this assumption is true, their impact cannot be considered in the group contribution method without adding interaction terms. The phosphine-based functional group PPh₂ is present in **co-PhPZ-1** and in the two terpolymers **ter-PhCZ-5** and **ter-PhCZ-6**. It exhibits much higher contributions to HRC, THR and Δh , but also a moderate though not negligible contribution to char. From these contributions, it is clear that the PPh₂ group is less flammable than methyl and phenyl groups. Nevertheless, due to its high molar weight, its impact on the flammability of

polysilazanes is higher. For this reason, **co-PhPZ-1** has intermediate properties between **co-PZ-8** and **co-PZ-11**. It must be noted that the contributions of PPh_2 are questionable. Indeed, we have shown above that the SiCN backbone probably interacts with its neighbouring groups to reduce the heat release rate. In all polymers studied herein, PPh_2 is always associated to SiCN. Measuring flammability properties of other polymers containing PPh_2 groups but not SiCN units would be needed to test these calculations. Yet, with the exception of the heat release capacity for **co-PZ-13**, the predicted properties fit overall well with the experimental ones for all the polysilazanes.

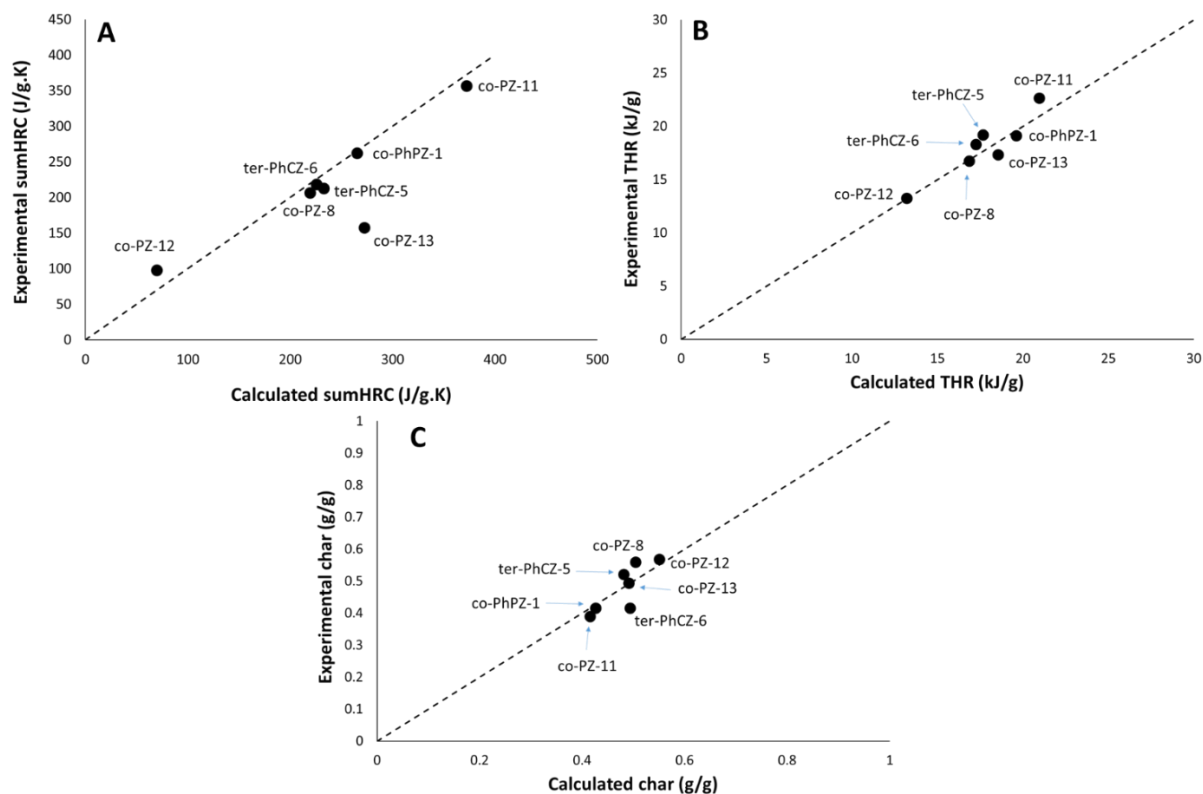


Figure 11. Experimental versus predicted flammability properties for the polycarbosilazanes tested herein.

The contributions obtained for the two SiCN and PPh_2 groups are compared to the contributions already calculated from our previous works^{59,61,62} in Figure 12. It shows that there is a rough correlation between the contributions to THR and HRC for most groups, including PPh_2 and SiCN. It agrees with the correlation between THR and HRC already found for polymers in Figure 10A. From Figures 12B and 12C, it can be seen that SiCN is a group exhibiting a high discrepancy between the contributions to THR and Δh , due to its huge ability to char. This is not obvious for PPh_2 , owing to its moderate capability to char. With the exception of its ability to char, the contributions of PPh_2 are close to those of DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthren-10-oxide), while the phosphonate group exhibits different behaviour (low HRC and THR, higher char ability).⁶² This may be related to the oxidation state of the phosphorus in these functional groups (formally +III in DOPO and the PPh_2 group, and +V in

phosphonates and the even more oxidised phosphates), as the flame retardant properties of phosphorus groups are indeed known to depend on the degree of oxidation of the phosphorus.^{64,65} Phosphate and phosphonate groups are also known to act as char promoter. On the contrary, phosphine oxide or phosphinate groups are poor char promoters, and act preferentially as flame inhibitors, i.e. they disturb combustion and, in turn, combustion efficiency is reduced. Nevertheless, combustion in PCFC is forced to be complete. Therefore, groups such as DOPO, and probably also PPh₂, are not effective in PCFC and their flame-retardant effect (measured through the calculation of their respective contributions) is underestimated. Several groups (heteroatomic rings and phosphorus-based groups) known to improve the flammability are highlighted in Figure 12D. SiCN exhibits one of the lowest contributions to HRC and one of the highest contributions to char, confirming that this group as polymer backbone should be a suitable basis for flame retardant polymers.

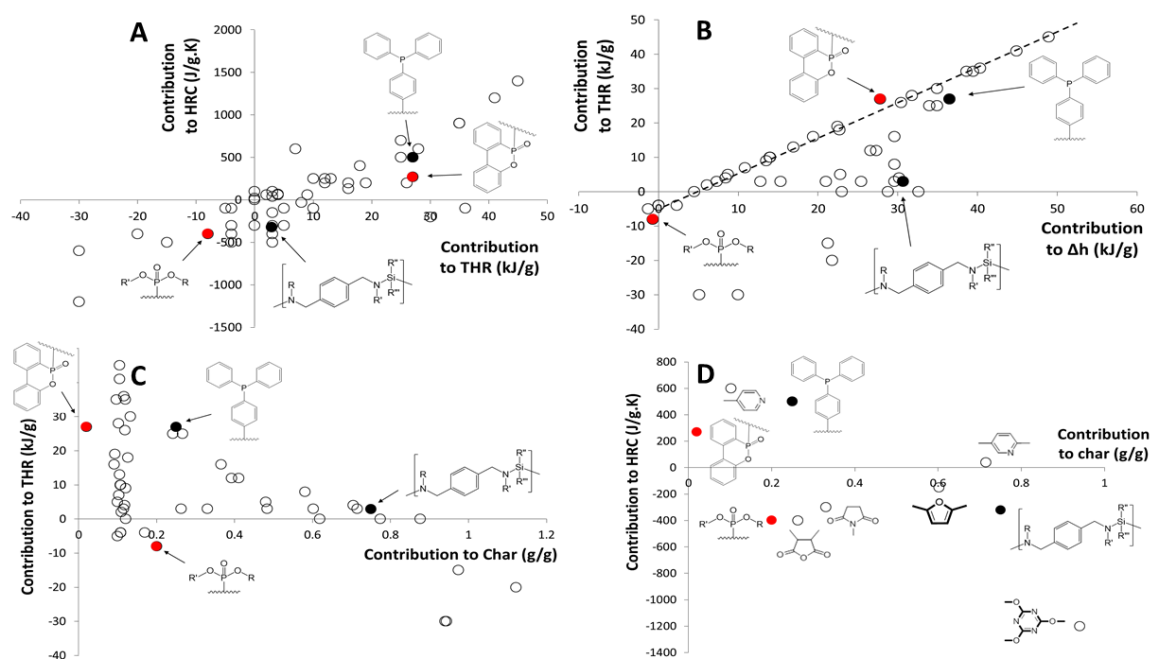


Figure 12. Contributions to flammability properties for various functional groups^{59,61,62} and for the two groups studied herein: PPh₂ and SiCN.

Conclusion

Building on our earlier preparation of polycarbosilazanes, barium-mediated molecular catalysis has now allowed for the synthesis of polycarbosilazanes functionalised by pendent PPh₂ phosphines, of general formulation $-\text{[Si(4-C}_6\text{H}_4\text{PPh}_2\text{)H-N(Me)CH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{N(Me)]}_n-$, upon dehydropolymerisation of the comonomers 4-Ph₂P-C₆H₄SiH₃ (**A**) and 1,4-{CH₂NHMe}₂-C₆H₄ (**C**) specifically made for this purpose. Despite difficulties in controlling accurately the initial feed ratio of the two comonomers, we have been able to produce linear, amine-capped polymers with molecular weights that reached around 8000 g mol⁻¹, as established by end-group and DOSY NMR analyses. These materials, along model molecules and starting materials, have been comprehensively characterised by 1- and 2-D NMR spectroscopy, and, whenever relevant and possible, by mass spectrometry and elemental analysis. In link with these results, we have also obtained terpolymers with various contents of PPh₂ groups upon dehydropolymerisation of **A**, **C**, and PhSiH₂R (R = H or Ph). Although we have not been able so far to ascertain the distribution of the two silicon-containing comonomers in backbone of the final materials, their contents in the polymers reflected faithfully their relative proportions in the initial feed ratio.

Preliminary flammability and flame retardancy carried out on these materials indicated that polycarbosilazanes exhibit a rather low flammability, with a high residue fraction and a low heat release rate. This is mainly ascribed to the silazane group-bearing backbone. Methyl groups on nitrogen atoms delay the beginning of the decomposition but the peak of heat release rate is significantly enhanced. The contributions to flammability of PPh₂ were calculated using a group contribution method, and compared to those of other phosphorus-based groups, as phosphonate and DOPO. It appears that, like DOPO, PPh₂ is a poor char promoter, while phosphonate groups which contain a highly oxidised phosphorus are much more efficient. Nevertheless, analyses at microscale are unable to assess the potential flame inhibitor effect of PPh₂ in the gas phase, and hence further tests will be conducted to conclude about the potential of PPh₂ as flame retardant group. The use of materials functionalised by phosphine oxide, instead of the phosphine, would be an obvious way to try and improve on the flame-retardant properties of these materials. However, this is not amenable to the general chemistry described herein: phosphine-oxide containing substrates would very likely not be compatible with the barium precatalyst, and it would also evidently be prone to reduction by the hydrosilane. Besides, the sensitivity of the materials described here renders them unsuitable for post-polymerisation oxidation protocols.

Author contributions

P. M. Chapple and A. Soran performed synthetic experimental work and data analysis, and assisted in the writing of the draft. participated to the design of experiments and analysis of experimental data. C. Longuet and R. Sonnier conducted the analysis of polymer properties, and participated to the preparation of the manuscript. J.-F. Carpentier and Y. Sarazin secured the funding, participated to the design of experiments, analysis of experimental data and writing of the draft.

Acknowledgements

The authors are thankful to the *Agence National de la Recherche* for the provision of a research grant (ANR-17-CE07-0017-01).

Conflict of Interest

The authors declare no conflict of interest.

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