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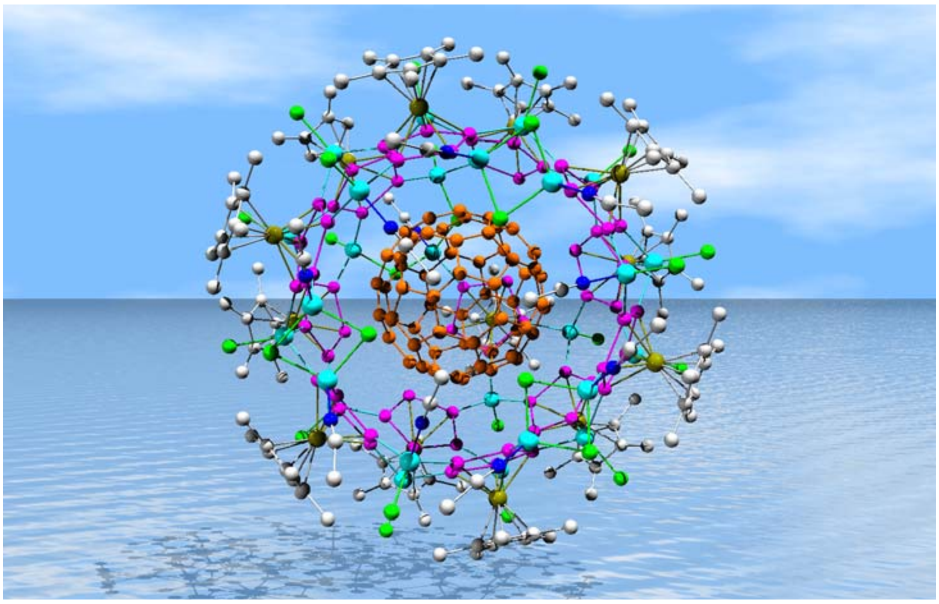

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Chemical functionality of poly(methylenephosphine): phosphine–borane adducts and methylphosphonium ionomers†‡

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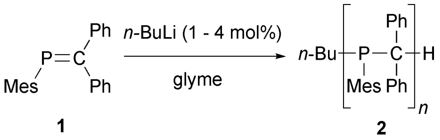
The chemical functionality of poly(methylenephosphine) *n*-Bu[MesP–CPh_2]$_n$H (**2**) is examined in reactions with two isoelectronic species, namely BH_3 and CH_3^+. The potential reactivity of polymer **2** is modelled by examining the reactivity of molecular phosphines bearing similar substituents as the polymer. In particular, the phosphine–borane adducts Mes(Me)P(BH_3)–CPh_2H (**4a**) and Mes(Me)-P(BH_3)–CPh_2SiMe_2H (**4b**) are prepared from the reaction of $BH_3{\cdot}SMe_2$ with Mes(Me)P–CPh_2H (**3a**) or Mes(Me)P–CPh_2SiMe_2H (**3b**), respectively. Treating **3a** with MeOTf affords the methylated model compound, [Mes(Me)$_2$P–CPh_2H]OTf (**5**). X-Ray crystal structures are reported for each model compound. The reaction of *n*-Bu[MesP–CPh_2]$_n$H ($M_n = 3.89 \times 10^4$, PDI = 1.34) with $BH_3{\cdot}SMe_2$ affords the phosphine–borane polymer *n*-Bu[MesP(BH_3)–CPh_2]$_n$H (**6**) ($M_n = 4.13 \times 10^4$, PDI = 1.26). In contrast, methylation of phosphine polymer **2** gives *n*-Bu[MesP–CPh_2]$_x$–/–[MesP(Me)–CPh_2]$_y$H·(OTf)$_y$ (**7**) where approximately 50% of the phosphine moieties are methylated (from ^{31}P NMR).

Introduction

Recent advances in the development of main-group-element-containing macromolecules have played a major role in the renaissance that is underway in main group chemistry.[1,2] The prospect of finding materials with unique properties imparted by *p*-block elements is the impetus for the current widespread interest in this area. A principle barrier to the development of inorganic macromolecules is the lack of general synthetic methods to link inorganic elements into long chains. Most work has focused on using ring-opening and condensation polymerization techniques. We are interested in expanding addition polymerization, the most commonly used method in organic polymer synthesis, to inorganic multiple bonds.

Given their close analogy to C=C bonds, we chose to begin our investigations with P=C bonds. Phosphaalkenes were first synthesized thirty years ago and their chemistry closely parallels that of alkenes.[3] We have discovered that P=C bonds can be polymerized to afford a new class of phosphorus containing polymer, poly(methylenephosphine).[4] When phosphaalkene **1**, originally reported by Bickelhaupt,[5] is distilled or heated in the presence of radical initiators a polymer with an alternating phosphorus-carbon backbone is obtained in low isolated yield. Recently, we improved upon the synthesis of poly(methylenephosphine) with the development of the room temperature living anionic polymerization of **1**.[6] Specifically, treating monomer **1** with *n*-BuLi (1–4%) in glyme at 25 °C affords polymer **2** (Scheme 1). This living polymerization route affords phosphine polymers in high yield and with controllable molecular weights under mild conditions.



Scheme 1

Although macromolecules possessing trivalent phosphorus atoms in the main chain are common,[7] polymer **2** is the only alternating phosphorus–carbon polymer. The phosphine moieties in **2** provide a unique opportunity for facile post-polymerization modifications to tailor the polymer properties. With the exception of oxidation and sulfurization, the chemical functionality of poly(methylenephosphine)s has remained virtually unexplored.[4] Although well-defined metal complexes have not yet been isolated, we have illustrated that random copolymers of **1** and styrene are effective supports for Pd-catalyzd Suzuki cross-coupling.[8] Simple main group complexes such as phosphine–borane adducts are of interest as potential protecting groups for the slightly air-sensitive phosphine environments in **2** and for their potential use as pre-ceramic materials.[9] In addition, alkylation of the phosphine moieties would provide a convenient route to novel phosphonium ionomers.[10] Ionomers, or polymers with ionic groups, are of interest in applications ranging from drug delivery to fuel cell membranes.[11] The successful methylation of **2** would provide access to polymers with a high ion density in the main chain due to the close proximity of phosphorus atoms.

Herein, we describe our work on the chemical functionalization of phosphine polymer **2** through boronation and methylation reactions. To simplify polymer characterization, the potential reactivity of the high polymer is first assessed by comparison to molecular model systems. Although borane functionalities may

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‡ CCDC reference numbers 668085–668087. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718140j

be incorporated at every atom along the main chain in **2**, only *ca.* 50% of the phosphine units were methylated by MeOTf.

Results and discussion

Synthesis of molecular model compounds

Phosphines **3a** and **3b** were prepared from **1** following the literature procedures.[12] These molecular compounds function as useful models to evaluate the chemical functionality of polymer **2**. In an attempt to form a phosphine–borane adduct, a pale yellow solution of **3a** in THF was treated with $BH_3{\cdot}SMe_2$ in Et_2O at −78 °C (Scheme 2). Analysis of the reaction mixture using ^{31}P NMR spectroscopy revealed that the signal for free phosphine **3a** ($\delta = -24.0$) was replaced by a new signal ($\delta = 18.3$). Likewise, treating silyl-terminated **3b** with $BH_3{\cdot}SMe_2$ affords a single product as judged by its ^{31}P NMR spectrum ($\delta = 24.8$ *cf.* **3b**: $\delta = -23.9$). Crystals of each product were obtained directly from the reaction solutions. Analysis of the crystals by X-ray crystallography confirmed that phosphine–boranes **4a** and **4b** had been formed successfully (see Fig. 1 and 2). Compounds **4a** and **4b** were further characterized using ^1H and ^{13}C NMR spectroscopy. Interestingly, the borane can conveniently be removed to regenerate **3** by treating either phosphine–borane with amines such as diethylamine.

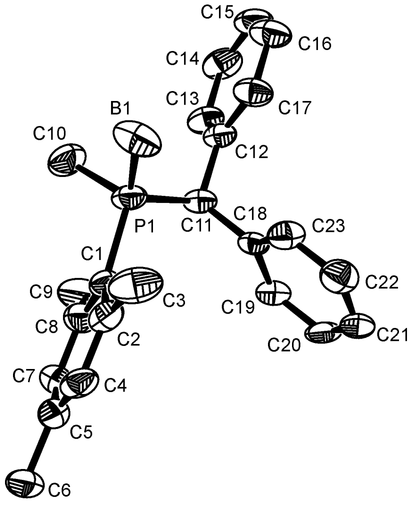
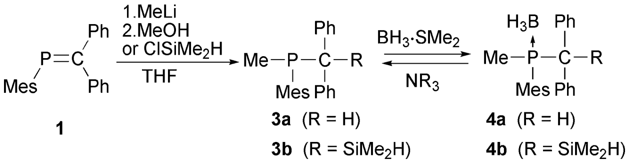


Fig. 1 Solid-state molecular structure of **4a**. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)–C(1) = 1.814(4), P(1)–C(10) = 1.795(5), P(1)–C(11) = 1.837(4), P(1)–B(1) = 1.831(6); C(1)–P(1)–C(11) = 105.0(2), C(2)–C(1)–P(1) = 120.4(4), C(8)–C(1)–P(1) = 121.0(3), C(12)–C(11)–P(1) = 111.6(3), C(18)–C(11)–P(1) = 112.0(3), C(10)–P(1)–B(1) = 102.6(3), B(1)–P(1)–C(11) = 115.1(3), C(1)–P(1)–B(1) = 121.1(3).



Scheme 2

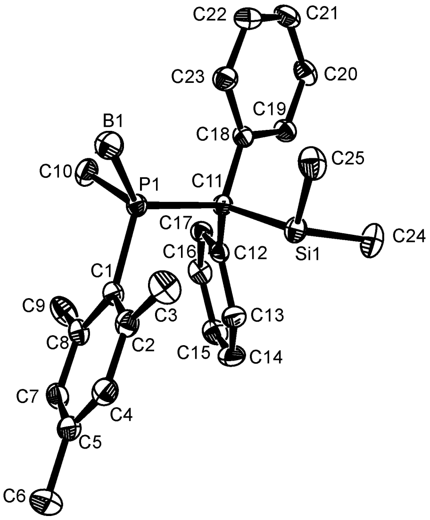
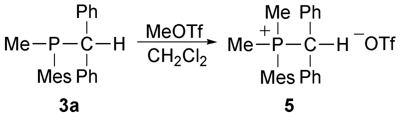


Fig. 2 Solid-state molecular structure of **4b**. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)–C(1) = 1.846(2), P(1)–C(10) = 1.819(2), P(1)–C(11) = 1.894(2), P(1)–B(1) = 1.977(2), C(11)–Si(1) = 1.941(2), C(24)–Si(1) = 1.857(2); C(1)–P(1)–C(11) = 107.8(1), C(2)–C(1)–P(1) = 117.6(1), C(8)–C(1)–P(1) = 124.1(1), C(12)–C(11)–P(1) = 106.6(1), C(18)–C(11)–P(1) = 112.0(1), C(10)–P(1)–B(1) = 100.7(1), C(11)–P(1)–B(1) = 122.9(1), C(1)–P(1)–B(1) = 110.6(1).

We are also interested in the functionalization of poly(methylenephosphine) with CH_3^+ which is isoelectronic to BH_3. From a polymer perspective, this would provide access to novel methylphosphonium polyelectrolytes. We chose MeOTf as the methylating agent rather than milder agents due to the anticipated difficulty fully alkylating the closely spaced phosphorus atoms in **2**. Thus, a solution of **3a** in CH_2Cl_2 was treated with excess MeOTf to give compound **5** (δ $^{31}P = 29.8$) (Scheme 3). Slow evaporation of the solvent afforded large crystals of the air-stable phosphonium salt **5** which were analyzed using X-ray diffraction (Fig. 3). The analytically pure crystals were further characterized by ^{31}P, ^1H, ^{13}C and ^{19}F NMR spectroscopy and by elemental analysis. The ^1H NMR spectrum for compound **5** (in DMSO-d_6) is consistent with the proposed product, although it is not possible to assign the overlapping signals for the methyl protons (*i.e.* P-CH_3, *o*-CH_3 and *p*-CH_3). In the ^{19}F NMR spectrum, a sharp signal is observed at −77.5 ppm which is characteristic of free triflate.



Scheme 3

X-Ray crystallography‡

Compounds **4a**, **4b** and **5** were characterized crystallographically and the molecular structures are shown in Fig. 1, 2 and 3, respectively. Important metrical parameters are found in the Figure captions and details of the structure solution and refinement are given in Table 1. Interestingly, the P(1)–B(1) bond [1.831(6) Å] in **4a** is shorter than the analogous bond in **4b** [1.977(2) Å].

Table 1 X-Ray crystallographic data of **4a**, **4b** and **5**

Crystal	**4a**	**4b**	**5**
Formula	$C_{23}H_{28}PB$	$C_{25}H_{34}PBSi$	$C_{25}H_{28}PSO_3F_3$
Formula weight	346.23	404.39	496.50
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P\,2_1/n$	$P\bar{1}$	$P2_1/n$
Color	Colourless	Colourless	Colourless
a/Å	8.342(2)	10.128(1)	10.118(1)
b/Å	13.896(3)	10.750(1)	17.583(1)
c/Å	16.931(3)	12.890(1)	13.314(1)
α/°	90	108.324(4)	90
β/°	99.909(11)	93.499(3)	98.166(1)
γ/°	90	117.089(4)	90
V/Å^3	1933.4(10)	1151.0(2)	2344.6(2)
Z	4	2	4
T/K	173(2)	173(2)	173(2)
μ(Mo Kα)/cm^{-1}	1.45	1.80	2.56
Crystal size/mm	0.90 × 0.60 × 0.20	0.40 × 0.20 × 0.10	0.45 × 0.40 × 0.20
D_{calcd}/g cm^{-3}	1.189	1.167	1.407
2θ (max)/°	47.3	56.0	55.8
No. of reflections	26 106	23 770	40 481
No. of unique data	2889	5485	5623
R_{int}	0.077	0.029	0.055
Reflections/parameters ratio	12.45	14.10	18.56
R_1, $wR_2[I > 2\sigma(I)]^a$	0.073; 0.190	0.036; 0.091	0.044; 0.094
R_1, wR_2 (all data)^a	0.110; 0.222	0.045; 0.097	0.075; 0.108
GOF	1.10	1.04	1.00

[a] $R_1 = \sum \|F_o| - |F_c\|/\sum |F_o|$. $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$.

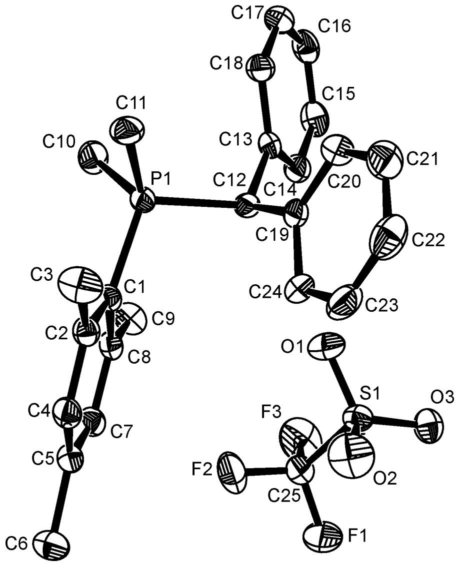


Fig. 3 Solid-state molecular structure of **5**. Thermal ellipsoids at 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°). P(1)–C(1) = 1.809(2), P(1)–C(10) = 1.797(2), P(1)–C(11) = 1.790(2), P(1)–C(12) = 1.854(2); C(1)–P(1)–C(12) = 107.2(1), C(2)–C(1)–P(1) = 124.1(2), C(8)–C(1)–P(1) = 116.5(2), C(12)–P(1)–C(11) = 109.0(1), C(12)–P(1)–C(10) = 110.6(1).

For comparison, the typical range for P–B bonds is 1.90 to 1.95 Å[13] and the bond length in Ph_3P–BH_3 [1.917 Å].[14] We speculate that the apparent shortening of the P–B bond in **4a** results from difficulty modelling the disorder in the crystal rather than providing chemical insight into the bonding in **4a** (see Experimental for details).

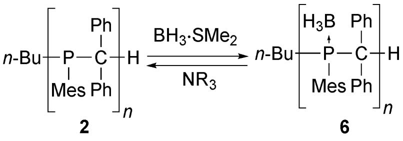
The P–C bonds in **4a** [avg. 1.815(8) Å] and **4b** [avg. 1.853(3) Å] are in the range typical for P–C bonds (1.85–1.90 Å).[13] For comparison, the analogous bonds in **3a** [avg. 1.858(2)] and **3b** [avg. 1.853(3) Å] are similar in length to those in **4a** and **4b**. Interestingly, the longest P–C bond is the P–CPh_2R bond [**4a**: P(1)–C(11) = 1.837(4) Å, **4b**: P(1)–C(11) = 1.894(1) Å]. These P–CPh_2R bonds in **4a** and **4b** are shorter than in the free phosphines [**3a**: 1.882(1) Å, **3b**: 1.902(1) Å].[12] The shortening is less significant between **3b** and **4b** than between **3a** and **4a**. Presumably, this reflects the increased steric congestion in the former [–$CPh_2(SiMe_2H)$ *vs.* –$CPh_2(H)$]. Similarly, in methylphosphonium **5** the P–Me (avg. 1.794(3) Å] and P–Mes [P(1)–C(1) = 1.809(2) Å] bonds are significantly shorter than the P–CPh_2H bond [P(1)–C(12) = 1.854(2) Å]. The P–C bonds in **5** are all shortened considerably with respect to the analogous bonds in **3a** [P–Me: Δ(P–C) = 0.046(3); P–Mes: Δ(P–C) = 0.043(2); P–CPh_2H: Δ(P–C) = 0.030(2) Å].

For the most part, the bond angles in compounds **4a**, **4b** and **5** are unremarkable with the exception of the Mes–P–CPh_2R angles. In particular, this angle is found to expand significantly upon coordination. For example, Mes–P–CPh_2R angle is between 105 and 108° in **4a**, **4b** and **5** whereas the analogous angle in **3a** is just 100°. This is likely a consequence of increased *s*-character in the phosphorus bonds upon quaternization of the phosphorus lone pair.

Chemical functionalization of poly(methylenephosphine)

Following the synthesis and characterization of the model compounds, the preparation of phosphine–borane and methyl phosphonium polymers was attempted. The anionic polymerization of **1** in glyme using ^{n}BuLi as the initiator afforded poly(methylenephosphine) **2** (M_n of 3.89 × 10^4 g mol^{-1}; PDI = 1.34).[6] The polymerization was not conducted using the rigorous standards required for a living polymerization and, consequently, the molecular weight distribution (PDI) is greater than 1.1.

In an attempt to prepare poly(methylenephosphine borane) **6**, the phosphine polymer **2** was treated with $BH_3{\cdot}SMe_2$ (1.4 equiv) (Scheme 4). Polymer **6** was isolated as a colorless solid after the volatiles were removed *in vacuo*. The ^{31}P NMR spectrum of **6** is shown in Fig. 4(b) and the chemical shift for the borane polymer is similar to models **4a** and **4b** (δ = 18.3 and 24.8, respectively). The spectrum shows no evidence for the presence of uncoordinated phosphine moieties [*cf.* Fig 4(a)]. Interestingly, the signals observed for **6** are much sharper and are better resolved than those observed for **2**. For example, the ^{31}P NMR spectrum of phosphine–borane polymer **6** exhibits two signals at 32.4 ppm (minor) and 26.8 ppm (major). In addition, a small shoulder is observed on the high field end of the signal at 26.8 ppm. In contrast, uncomplexed poly(methylenephosphine) **2** shows broad unresolved signals that likely encompass the different environments which are resolved in **6**. We speculate that the observation of multiple signals in the ^{31}P NMR spectrum of macromolecule **6** may be an indication of the tacticity in poly(methylenephosphine)s. Alternatively, the minor signal at 32.4 ppm may be attributed to polymer end-groups, however, the integrated ratios are not consistent with the degree of polymerization ($DP_n \approx 125$) determined using GPC.



Scheme 4

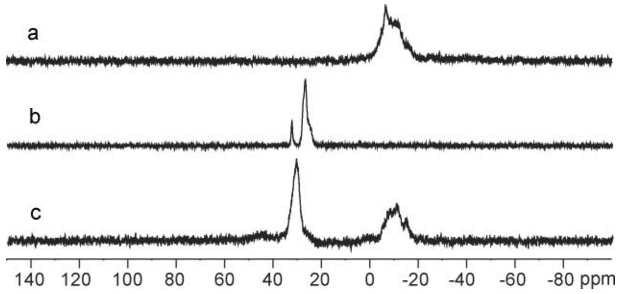
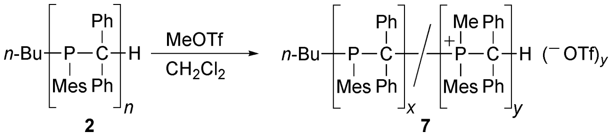


Fig. 4 Stack plot showing the ^{31}P NMR spectra (121.5 MHz) of: (a) poly(methylenephosphine) **2** in THF, (b) poly(methylenephosphine borane) **6** in $CDCl_3$, and (c) poly(methylene phosphonium triflate) **7** in DMSO-d^6.

The absolute number average molecular weight (M_n) of **6** was determined using triple detection GPC (M_n = 4.13 × 10^4 g mol^{-1}; PDI = 1.26) which showed a slight increase over that for **2** (M_n = 3.89 × 10^4 g mol^{-1}; PDI = 1.34). The similarity in the molecular weights of **2** and **6** confirms that no backbone degradation occurs during the BH_3 protection. Notably, the molecular weight distribution is much narrower for **6** than for **2**. We postulate that the larger PDI for **2** is due to some interaction of the phosphine moieties in the main chain with the GPC columns which has been observed previously for phosphine polymers.[15] The reaction of polymer **6** with excess amine such as NEt_3 results in the clean deprotection of the BH_3 group to form poly(methylenephosphine) **2**. The reformation of **2** was confirmed by ^{31}P NMR spectroscopy and GPC analysis (M_n = 3.71 × 10^4 g mol^{-1}; PDI = 1.36). Thus, borane may prove to be a useful protecting group for the mildly air-sensitive polymer.

The synthesis of poly(methylenephosphonium triflate) proved to be more difficult than the borane polymer. A solution of **2** in CH_2Cl_2 was treated with MeOTf (excess) and was heated to 50 °C. The reaction mixture was monitored by ^{31}P NMR spectroscopy and signals for free phosphine were still observed even after several days. The ^{31}P NMR spectrum of the product after precipitation is shown in Fig. 4(c). Importantly, a signal is observed at 31 ppm which is consistent with methylphosphonium moieties by comparison to the chemical shift of **5** (δ = 29.8). Integrating the signals for the methylated (δ = 31) and unmethylated ($\delta = -10$) phosphorus atoms in **7** suggests that approximately 50% of the phosphorus atoms are methylated (Scheme 5). This experiment was repeated several times and, even after several days of heating **2** with excess MeOTf, the degree of methylation never exceeded 50%. Complete methylation would require a formal positive charge at every second atom in the polymer backbone. We speculate that phosphorus atoms are methylated in a roughly alternating fashion rather than in a completely random fashion as shown in Fig. 5. For both steric and electronic (*i.e.* repulsive) reasons the alternating addition would be favourable and would lead to *ca.* 50% methylation.



Scheme 5

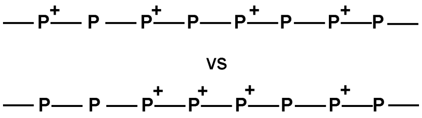


Fig. 5 Depictions of possible methylation patterns for methylated poly(methylenephosphine) **7**: (top) alternating positive charge, (bottom) random distribution of positive charge.

Polymer **7** was characterized by ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of poly(methylenephosphonium triflate) **7** in DMSO-d^6 is shown in Fig. 6 (bottom) and, although the signals are broadened significantly, the spectrum shows signals in the same regions with that for model compound **5** [Fig. 6 (top)]. Of note, are the signals assigned to P-CH_3 (δ = 13.2) and O_3SCF_3 (δ = 120.7, q, $^{1}J_{CF}$ = 322 Hz). Macromolecule **7** is not soluble in THF and, consequently GPC analysis in THF could not be obtained. Static light scattering experiments were attempted with this ionic polymer but reliable molecular weight data could not be attained.

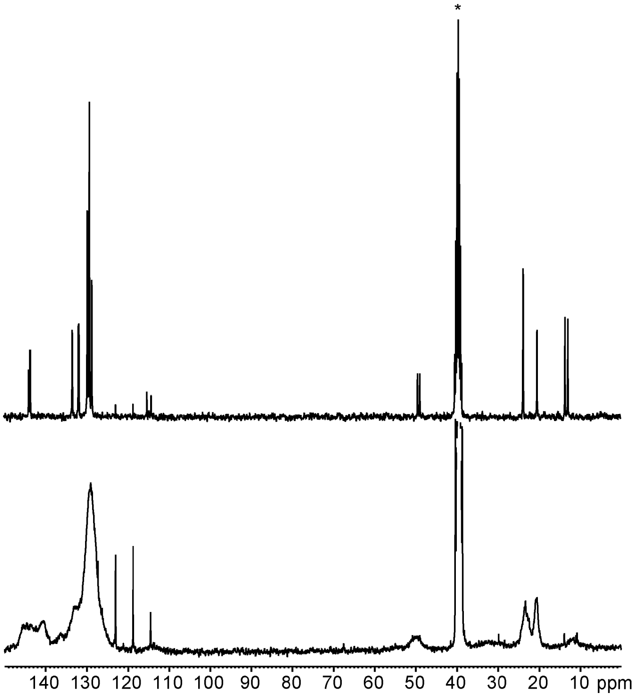


Fig. 6 ^{13}C NMR spectra (75.5 MHz, DMSO-*d*^{6}) of compound **5** (top) and macromolecule **7** (bottom). * DMSO–*d*^{6}.

Summary

In closing, we have investigated the chemical functionality of poly(methylenephosphine) **2** through phosphine coordination to main group Lewis acids. The chemical functionality of **2** was examined by reacting Mes(Me)P–CPh$_2$R [R = H (**3a**) or SiMe$_2$H (**3b**)], molecular model compounds for the high polymer, with BH$_3$·SMe$_2$ or MeOTf. Three new functionalized model systems were prepared and characterized crystallographically; namely, Mes(Me)P(BH$_3$)–CPh$_2$H (**4a**), Mes(Me)P(BH$_3$)–CPh$_2$H (**4b**) and Mes(Me)$_2$P–CPh$_2$H (**5**). The analogous reactions were successful when polymer **2** was used. Specifically, we report a new phosphine–borane polymer *n*-Bu[MesP(BH$_3$)–CPh$_2$]$_n$H (**6**) and a methylphosphonium polymer *n*-Bu[MesP–CPh$_2$]$_x$–/–[MesP(Me)–CPh$_2$]$_y$H·(OTf)$_y$ (**7**: x:y = *ca.* 1:1). These new polymers were fully characterized spectroscopically and absolute molecular weights were determined for **6**.

Future work will focus on studying the properties of the phosphine–borane and methylphosphonium polymers reported herein. The prospect of preparing water soluble phosphorus homo- or co-polymers by post-polymerization modification of **2** is an exciting synthetic target.

Experimental

Materials and general procedures

All manipulations of air- and/or water-sensitive compounds were performed under pre-purified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology Inc. glovebox. Hexanes, and dichloromethane were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. THF was freshly distilled from sodium/benzophenone ketyl. CDCl$_3$ was distilled from P$_2$O$_5$ and degassed. CD$_2$Cl$_2$ and DMSO–d^6 were purchased from Cambridge Isotope Laboratories and were used as received. Methanol was degassed prior to use. NEt$_3$, HNEt$_2$, DBU, MeLi (1.6 M in Et$_2$O) *n*-BuLi (1.6 M in hexanes), BH$_3$·SMe$_2$ (2 M in Et$_2$O) and MeOTf were purchased from Aldrich and used as received. Alkyllithium reagents were titrated prior to use. MesP=CPh$_2$ (**1**),[16,17] Me(Mes)P–CPh$_2$(H) (**3a**) and Me(Mes)P–CPh$_2$(SiMe$_2$H) (**3b**) were prepared using literature methods.[12] Polymer **2** was prepared according to literature procedure.[6]

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported relative to residual CHCl$_3$ (δ = 7.26 for ^{1}H and and 77.23 for ^{13}C), CHDCl$_2$ (δ = 5.32 for ^{1}H and and 54.00 for ^{13}C) and DMSO-d^5 (δ = 2.50 for ^{1}H and 39.52 for ^{13}C). CFCl$_3$ was used as an external standard δ = 0.0 for ^{19}F. 85% H$_3$PO$_4$ was used as an external standard δ = 0.0 for ^{31}P. Molecular weights were determined by triple detection gel permeation chromatography (GPC–LLS) using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm; HR5E, HR4 and HR2), Waters 2410 differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector-690 nm) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL min^{-1} was used and samples were dissolved in THF (*ca.* 2 mg mL^{-1}).

Preparation of Mes(Me)P(BH$_3$)–CHPh$_2$ (4a)

An ethereal solution of BH$_3$·SMe$_2$ (1.4 ml, 2 M, 2.8 mmol) was added dropwise by syringe to a cooled solution (−78 °C) of compound **3a** (0.94 g, 2.8 mmol) in THF (40 ml). The reaction mixture was allowed to warm slowly to room temperature and an aliquot was removed for analysis by ^{31}P NMR spectroscopy (δ = 18.3, br). After removal of the volatiles *in vacuo*, an oil was obtained which crystallized slowly over a period of 10 h. Yield: 0.72 g, 74%. δ_P(121.5 MHz; CDCl$_3$; H$_3$PO$_4$) 18.3 (br s). δ_H(300.1 MHz, CDCl$_3$; SiMe$_4$) 7.69–7.17 (10 H, m, aryl H), 6.86 (2 H, s, *m*–H of Mes), 4.86 (1 H, d, $^2J_{PH}$ = 17 Hz, CHPh$_2$), 2.40 (6 H, s, *o*–CH$_3$), 2.27 (3 H, s, *p*–CH$_3$), 2.0–0.5 (3H, br q, BH$_3$), 1.69 (3 H, d, $^2J_{PH}$ = 9 Hz, PCH$_3$). δ_C(75.5 MHz; CDCl$_3$;SiMe$_4$) unassigned) 143.9 (d, J_{PC} = 9 Hz), 140.9 (d, J_{PC} = 2 Hz), 137.2 (d, J_{PC} = 3 Hz), 131.1 (d, J_{PC} = 9 Hz), 129.9 (d, J_{PC} = 5 Hz), 129.4 (d, J_{PC} = 5 Hz), 128.6 (s), 128.1 (d, J_{PC} = 2 Hz), 127.4 (d, J_{PC} = 2 Hz), 127.1 (d, J_{PC} = 3 Hz), 123.4 (d, J_{PC} = 46 Hz), 51.8 (d, J_{PC} = 26 Hz), 24.4 (d, J_{PC} = 4 Hz), 20.8 (s), 15.7 (d, J_{PC} = 39 Hz).

Reaction of 4a with Et$_2$NH

A solution of compound **4a** (0.72 g, 2.1 mmol) in THF (5 mL) was combined with Et$_2$NH (7 ml). The reaction mixture was stirred for 4 h and an aliquot was removed for analysis by ^{31}P NMR spectroscopy. Complete conversion to **3a** (−24 ppm) was observed and the solvent was removed *in vacuo.* The resultant oil was dissolved in CH$_2$Cl$_2$ and washed with water. The aqueous phase was then extracted with CH$_2$Cl$_2$ (3 × 20 mL). The colleted extracts were combined and dried over MgSO$_4$. Filtration of the CH$_2$Cl$_2$ solution and removal of the solvents *in vacuo* afforded **3a** as an oil. Yield: 0.22 g, 31%.

Preparation of Mes(Me)P(BH$_3$)–CPh$_2$SiMe$_2$H (4b)

An ethereal solution of BH$_3$·SMe$_2$ (0.6 ml, 2 M, 1.2 mmol) was added dropwise to a cooled solution (−78 °C) of phosphine **3b** (0.47 g, 1.2 mmol) in THF (20 mL). The reaction mixture was slowly warmed to room temperature. After evaporation of the solvent *in vacuo* a white solid was obtained. The solid was recrystallized by slow evaporation in an inert atmosphere from a concentrated THF solution. Yield: 0.11 g, 22%. δ_P(121.5 MHz; CDCl$_3$; H$_3$PO$_4$) 24.8 (br s). δ_H(300.1 MHz, CDCl$_3$; SiMe$_4$) 7.6–7.2 (10 H, m, aryl H), 6.69 (2 H, br s, *m*-Mes), 4.77 (1 H, m, Si–H), 2.5–0.5 (3H, br q, BH$_3$), 2.37 (6 H, br, *o*-CH$_3$), 2.22 (3 H, s, *p*-CH$_3$), 1.88 (3 H, d, $^2J_{PH} = 8$ Hz, PCH$_3$), 0.12 (3 H, d, $J = 3$ Hz, SiCH$_3$), 0.0 (3 H, d, $J = 3$ Hz, SiCH$_3$). δ_C(75.5 MHz, CD$_2$Cl$_2$: SiMe$_4$) 145.2 (s), 140.4 (d, $J_{PC} = 2$ Hz), 139.0 (d, $J_{PC} = 4$ Hz), 138.4 (d, $J_{PC} = 4$ Hz), 131.9 (s), 131.8 (s), 131.1 (d, $J_{PC} = 9$ Hz), 127.8 (s), 127.5 (s), 126.7 (s), 125.7 (d, $J_{PC} = 47$ Hz), 48.4 (s), 25.4 (br s), 20.8 (s), 16.8 (d, $J_{PC} = 39$ Hz), −3.5 (s), −3.6 (s).

Preparation of [Mes(Me)$_2$P–CPh$_2$H]OTf (5)

To a solution of compound **1** (2.00 g, 6.3 mmol) in THF (20 ml) was added MeLi (5.4 mL, 1.4 M, 7.6 mmol). The reaction mixture was stirred for 1 h and then solvent was removed *in vacuo.* Extraction of the reaction mixture with hexanes (3 × 10 mL) provided compound **3a** as an oil. This yellow oil was dissolved in CH$_2$Cl$_2$ and added to MeOTF (2 eq.) in the glovebox. The reaction mixture was placed in a vial and the salt crystallized overnight. The crystals were dried for 72 h. Yield: 0.60 g, 19%. δ_P(121.5 MHz; DMSO-d^6; H$_3$PO$_4$) 29.8 (s). δ_H(300.1 MHz, DMSO-d^6; SiMe$_4$) 7.57–7.39 (10 H, m, aryl H), 7.06 (2 H, s, *m*–H of Mes), 5.68 (1 H, d, $^2J_{PH} = 18$ Hz, CHPh$_2$) 2.33–2.27 (15 H, m, *o*–CH$_3$, *p*–CH$_3$, P–CH$_3$). δ_C(75.5 MHz; DMSO-d^6;SiMe$_4$) (unassigned) 144.0 (d, $J_{PC} = 3$ Hz), 143.6 (d, $J_{PC} = 10$ Hz), 133.4 (d, $J_{PC} = 4$ Hz), 131.8 (d, $J_{PC} = 12$ Hz), 129.7 (d, $J_{PC} = 6$ Hz), 129.2 (d, $J_{PC} = 2$ Hz), 128.6 (d, $J_{PC} = 2$ Hz), 120.7 (q, $^1J_{FC} = 322$ Hz), 114.7 (d, $J_{PC} = 77$ Hz), 49.1 (d, $J_{PC} = 43$ Hz), 23.7(d, $J_{PC} = 4$ Hz), 20.4 (s), 13.2 (d, $J_{PC} = 52$ Hz): δ_F(282.4 MHz; DMSO-d^6;CFCl$_3$) −77.5 (s, CF$_3$). Anal. calcd for C$_{25}$H$_{28}$PSO$_3$F$_3$: C, 60.47; H, 5.68. Found: C, 60.41; H, 5.66.

Preparation of *n*-Bu[MesP(BH$_3$)–CPh$_2$]$_n$H (6)

Poly(methylenephosphine) **2** (0.35 g, 1.1 mmol) ($M_n = 3.89 \times 10^4$ g/mol, PDI = 1.34) was dissolved in THF (20 ml) and BH$_3$·SMe$_2$ (0.75 ml, 2 M, 1.5 mmol) was added dropwise *via* syringe at −78 °C. The reaction mixture was allowed to slowly warm up to room temperature. After evaporation of the volatiles *in vacuo* a solid was obtained. Yield: 0.25 g, 68%. GPC (THF): $M_n = 4.13 \times 10^4$ g/mol, PDI = 1.26. δ_P(121.5 MHz; CDCl$_3$; H$_3$PO$_4$) 32.4 (br s, ca. 10%), 26.8 (br s, ca. 90%). δ_C(75.5 MHz; CDCl$_3$;SiMe$_4$) (unassigned) 143–137 (br m), 132–122 (br m), 53 (br s), 26 (br s), 21 (br s).

Reaction of 6 with amines

A solution of the poly(methylenephosphine–borane) **6** (0.25 g) in THF was treated with excess amine (DBU, NEt$_3$, NEt$_2$H). The reaction was stirred for 12 h and an aliquot of the reaction was removed and analyzed using ^{31}P NMR spectroscopy ($\delta = -10$, br). Upon removal of the solvent *in vacuo*, the polymer was dissolved in CH$_2$Cl$_2$ (15 ml) and washed with degassed water (2 × 5 ml). The organic layer was dried over MgSO$_4$ and solvent was removed *in vacuo* affording **2**. Yield: 0.22 g, 91%. $M_n = 3.71 \times 10^4$ g/mol, PDI = 1.36.

Preparation of *n*-Bu[MesP–CPh$_2$]$_x$–/–[MesP(Me)–CPh$_2$]$_y$H (7)

To a solution of polymer **2** (0.40 g, 1.3 mmol) in CH$_2$Cl$_2$ (10 ml) was added excess methyl triflate (10 eq.). The reaction mixture was stirred overnight. Analysis of the mixture by ^{31}P NMR spectroscopy exhibited two broad singlets with one signal at 31 ppm and the other at −7 ppm. Integration of the two signals revealed an approximate 1:1 ratio of the two signals. The polymer was isolated by concentrating the reaction mixture (*ca.* 1 mL) and precipitating with hexanes (20 mL). The yellow solid was dried *in vacuo* at 80 °C overnight. Yield: 0.23 g, 46%. δ_P(121.5 MHz; DMSO-d^6; H$_3$PO$_4$) 31 (br s, ca. 50%), −10 (br s, ca. 50%). δ_H(300.1 MHz, DMSO-d^6; SiMe$_4$) 7.2 (12 H, br, *m*-Mes-*H*, Ph-*H*), 2.2 (15H, *o,p*-CH$_3$, P-CH$_3$); δ_C(75.5 MHz; DMSO-d^6;SiMe$_4$) (unassigned), 145 (s), 140 (s), 133 (s), 129 (s), 120.7 (q, $^1J_{CF} = 320$ Hz), 114 (s), 49 (s), 23 (s), 20 (s), 12 (s); δ_F(282.4 MHz; DMSO-d^6;CFCl$_3$) −78.7 (s, C*F*$_3$).

X-Ray crystallography

Crystal data and refinement parameters are listed in Table 1. Additional information can be obtained in the supplementary data.‡ All single crystal were immersed in oil and mounted on a glass fiber. Data were collected at 173.0 ± 0.1K on a Bruker X8 APEX 2 diffractometer with graphite-monochromated Mo Kα radiation. Data was collected and integrated using the Bruker SAINT[18] software package. All structures were solved by direct methods[19] and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms using the SHELXTL[20] crystallographic software package from Bruker-AXS. All data sets were corrected for Lorentz and polarization effects. Cif files are available as supplementary data.‡

All single crystals were immersed in Paratone-N oil and were mounted on a glass fiber. Compounds **4b** and **5** did not exhibit any crystallographic complexity. Data collection for compound **4a** was attempted to $2\theta = 56°$, however no significant reflections were observed beyond $2\theta \approx 46°$, which may be a consequence of disorder in the crystal lattice. In particular, we speculate that the apparent shortening of the P(1)–B(1) bond is due to disorder in these atom positions, however, we have been unable to model this satisfactorily. For the final refinement, only data below 47.2° was included.

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