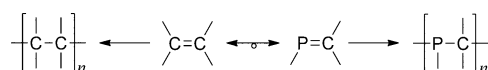


# Isomerization Polymerization of the Phosphaalkene MesP=CPh<sub>2</sub>: An Alternative Microstructure for Poly(methylenephosphine)s\*\*

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The synthesis and study of main-group-element analogues of alkenes and alkynes containing genuine (p-p)π bonds involving p-block elements is a central theme of inorganic chemistry.<sup>[1,2]</sup> The prospect to “copy” the predictable and sophisticated reaction chemistry of C=C and C≡C bonds utilizing functional inorganic systems is particularly enticing. However, in many instances, the investigation of multiple bonds of heavy elements leads to fascinating, albeit unexpected, outcomes that reinforce the fundamental differences between the first and subsequent periods.

Inspired by the intriguing analogy between P=C and C=C bonds in molecular chemistry,<sup>[3]</sup> we developed the addition polymerization of phosphaalkenes as a route to new functional phosphorus-containing polymers (Scheme 1).<sup>[4]</sup>



**Scheme 1.** The isolobal analogy between olefins and phosphaalkenes as applied to addition polymerization to afford polyolefins and poly(methylenephosphine).

Although the synthesis of phosphorus-containing macromolecules is of widespread interest because of their attractive properties and potential applications,<sup>[5]</sup> the study of the addition polymerization of P=C bonds remains in its infancy. Our studies showed that MesP=CPh<sub>2</sub> (**1**) and related monomers polymerize in the presence of radical or anionic initiators to afford poly(methylenephosphine) (Scheme 1).<sup>[6]</sup> The living anionic polymerization of **1** permits the formation of functional phosphine-containing block copolymers,<sup>[7,8]</sup> and the radical-initiated copolymerization of **1** with styrene affords random copolymers.<sup>[9]</sup>

In order to explore the mechanism of radical addition to P=C bonds during polymerization, we investigated the reactions of monomer **1** with TEMPO-derived radical sources. Herein, we report the discovery of a fascinating isomerization polymerization of phosphaalkene **1** in the presence of

radical alkoxyamine initiators. These striking results led to a revision of the proposed microstructure for poly(methylenephosphine) that was produced by a radical reaction.

In an effort to understand the initiation step in the radical polymerization of **1**, we investigated its reaction with TEMPO (1–2 equiv). <sup>31</sup>P NMR spectroscopic analysis of the reaction mixtures suggested the formation of multiple products, including radical species, which were detected by EPR spectroscopy. To date, none of these products have been successfully isolated or unambiguously identified. In contrast, employing the complex **1**·AuCl<sup>[10,11]</sup> instead of **1** affords a single product with TEMPO. Specifically, treatment of a solution of **1**·AuCl in toluene with TEMPO (1 equiv) resulted in 50% conversion of **1**·AuCl (δ = 167.1) to a new species, as determined by <sup>31</sup>P NMR spectroscopy. Addition of more TEMPO (1 equiv, that is, 2 equiv total) resulted in complete conversion of **1**·AuCl to two products in a ratio of approximately 1:3, which displayed <sup>31</sup>P signals at 135.6 ppm (d, J<sub>PH</sub> = 18 Hz) and 130.5 ppm (d, J<sub>PH</sub> = 18 Hz). The magnitudes of the <sup>31</sup>P–<sup>1</sup>H coupling constants are not consistent with the expected product Mes(TEMPO)P(AuCl)-C-(TEMPO)Ph<sub>2</sub>.

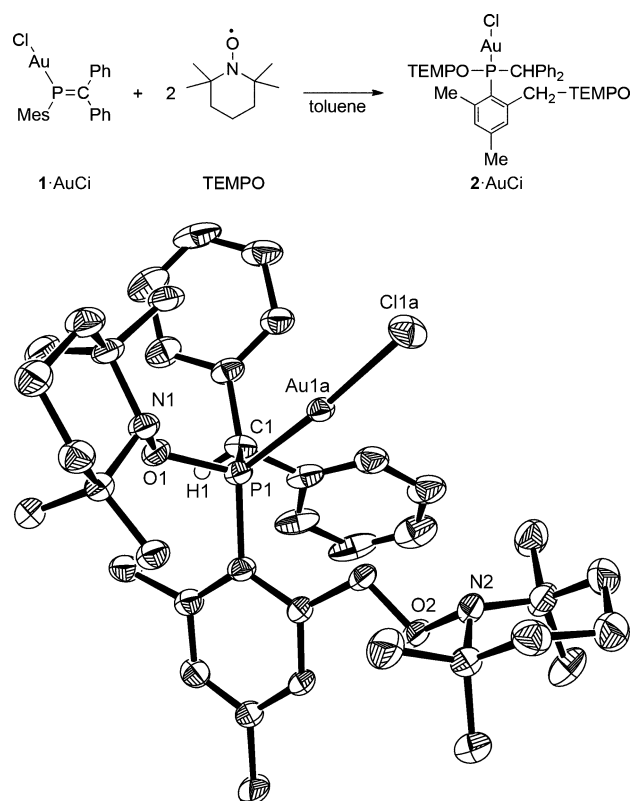
Colorless crystals were obtained by slow diffusion of hexanes into the reaction mixture at –30 °C. Analysis of the crystals by X-ray crystallography showed that the product was the intriguing di-TEMPO species **2**·AuCl (Figure 1).<sup>[11]</sup> As anticipated, one of the TEMPO moieties was bound to phosphorus. Surprisingly, the second TEMPO moiety was not bound to the methylene carbon atom of the former P=C bond. Instead, this moiety was transformed to a CHPh<sub>2</sub> group and the former *ortho*-bound CH<sub>3</sub> moiety of the mesityl group was now a CH<sub>2</sub>(TEMPO) group. Presumably, TEMPO adds to **1**·AuCl to afford a carbon-centered radical intermediate (i.e., {Mes(TEMPO)P(AuCl)}Ph<sub>2</sub>C·) to which H· from the *ortho*-bound CH<sub>3</sub> of the Mes group migrates. Although the chemical or electrochemical one-electron oxidation and reduction of phosphaalkenes has been studied extensively,<sup>[12]</sup> to our knowledge, the nature of the addition of neutral radicals to P=C bonds is not well understood.<sup>[13]</sup> The <sup>31</sup>P and <sup>1</sup>H NMR spectra and elemental analysis were consistent with the formulation of the product **2**·AuCl. Interestingly, there are two isomers of **2**·AuCl, which we speculate are diastereomers resulting from the stereogenic phosphorus center and atropisomerism of the substituents.

In light of the observed formation of **2**·AuCl from **1**·AuCl, we hypothesized that a similar C–H activation might occur in the polymerization of **1** using radical initiators. Thermolysis of phosphaalkene **1** in the presence of substoichiometric quantities of TEMPO did not affect polymerization. In contrast, heating the neat monomer **1** in the presence of the alkoxy-

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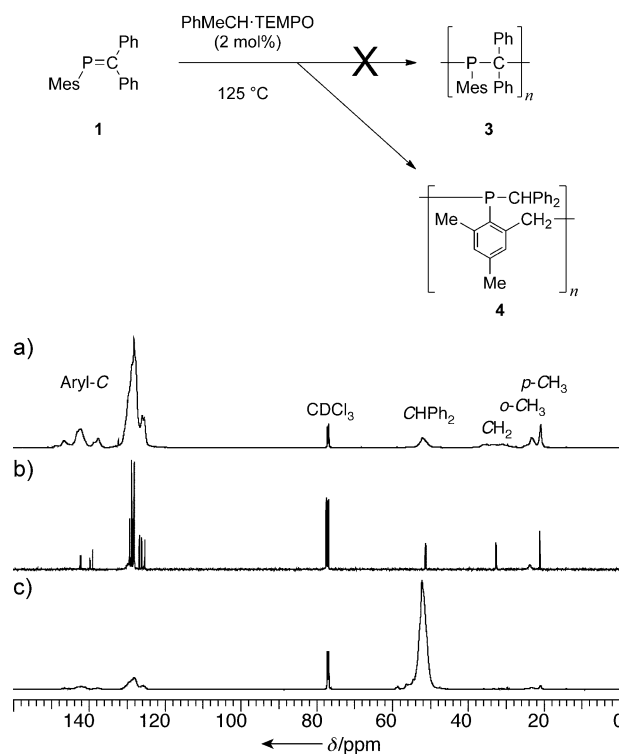
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201301881>.



**Figure 1.** Molecular structure of **2-AuCl** (50% probability ellipsoids). With the exception of H1, all hydrogen atoms are omitted for clarity.

amine  $\text{PhMeCH}\cdot\text{TEMPO}^{[14]}$  under conditions typical for nitroxide-mediated polymerization (NMP; neat,  $[\text{M}]:[\text{I}] = 50$ ,  $T = 125^\circ\text{C}$ ,  $t = 3\text{ h}$ ;  $\text{M} = \text{monomer}$ ,  $\text{I} = \text{initiator}$ ),<sup>[15]</sup> afforded poly(methylenephosphine). Subsequent analysis of the solution of the crude reaction mixture in THF by  $^{31}\text{P}$  NMR spectroscopy showed signals that can be assigned to monomer ( $\delta = 233$ ) and polymer ( $\delta = -10$ ) in ratios that suggested approximately 41% conversion<sup>[16]</sup> to poly(methylenephosphine). After precipitation from the THF solution with hexanes ( $\times 3$ ), polymer free of monomer **1** was isolated in 10% yield [gel-permeation chromatography (GPC) with light scattering:  $M_n = 10\,000\text{ g mol}^{-1}$ , polydispersity index (PDI) = 1.3]. We speculate that the low yield of isolated polymer likely results from fractionation of the low-molecular-weight polymer during precipitation. Importantly, heating of monomer **1** under identical conditions in the absence of initiator did not afford polymer. Therefore, the alkoxyamine is necessary to affect the polymerization of **1**. However, the present data does not confirm whether or not an NMP mechanism is followed and further studies are underway to investigate this interesting possibility.

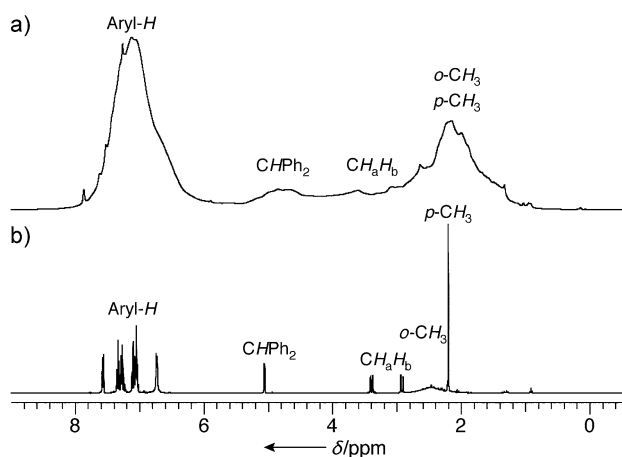
The microstructure of the polymer obtained under NMP conditions was elucidated using NMR spectroscopy. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (151 MHz; Figure 2a) was recorded using a high sensitivity cryoprobe. At first glance, the spectrum looks similar to that previously described for VAZO-polymerized **1** (VAZO = 1,1'-azobis(cyclohexanecarbonitrile) and assigned to microstructure **3**.<sup>[6]</sup> Closer examination shows a very broad signal at 33.0 ppm, which is much



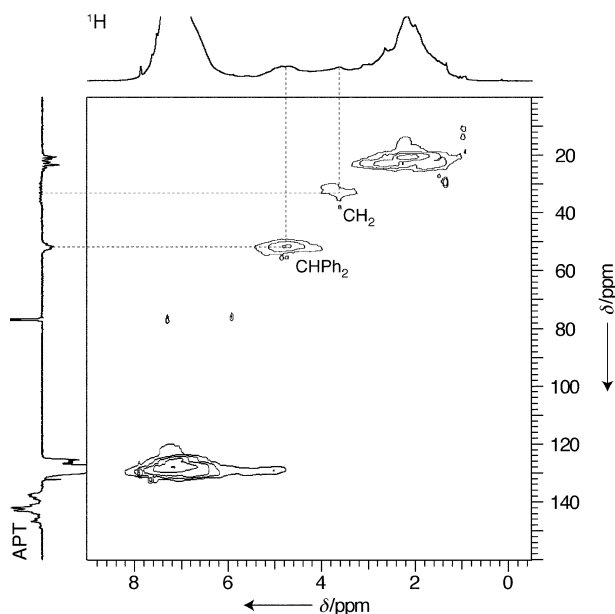
**Figure 2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (151 MHz,  $\text{CDCl}_3$ , 298 K) of: a) poly(methylenephosphine) (**4**) prepared from **1** and  $\text{PhMeCH}\cdot\text{TEMPO}$  (2 mol %); b)  $\text{PhCH}_2\text{-P}(\text{Mes})\text{-CHPh}_2$ ; c) poly(methylenephosphine) ( $^{13}\text{C}$ -**4**;  $M_n = 10\,000\text{ g mol}^{-1}$ , PDI = 1.3) prepared from  $\text{MesP} = ^{13}\text{CPh}_2$  and  $\text{PhMeCH}\cdot\text{TEMPO}$  (5 mol %).

more pronounced than that in our previously reported spectra (measured at 75 MHz). In our earlier studies, the broadening of the signals assigned to the *ortho*-bound  $\text{CH}_3$  groups in **3** was rationalized as arising from restricted rotation of the Mes group. Similar broadening had been noted in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the phosphines  $\text{MesRP-CPh}_2\text{R}'$  ( $\text{R} = \text{Bu}$ ,  $\text{R}' = \text{H}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$ ,  $\text{P}(\text{NET}_2)_2$ ,  $\text{SiHMe}_2$ ,  $\text{SiMe}_3$ ), the structures of which were confirmed by X-ray crystallography.<sup>[17]</sup> In light of the C–H activated **2-AuCl**, a  $^{13}\text{C}$  APT (attached-proton test) NMR experiment was conducted on the polymer. Remarkably, this experiment suggested that the signal at 33.0 ppm could not result from a  $\text{CH}_3$  moiety and must result from either a quaternary carbon atom or a  $\text{CH}_2$  group. Therefore, we speculated that this signal might be indicative of an  $\text{Ar-CH}_2\text{-P}$  moiety within a polymer with microstructure **4**. For comparison, we prepared and fully characterized benzylphosphine  $\text{PhCH}_2\text{-P}(\text{Mes})\text{-CHPh}_2$ , which displayed a similar  $^{13}\text{C}$  NMR chemical shift for the  $\text{Ph-CH}_2\text{-P}$  moiety ( $\delta = 32.5$ , d,  $^1J_{\text{CP}} = 20\text{ Hz}$ ; Figure 2b).

The broad resonance at 52.4 ppm (Figure 2a), formerly assigned to the backbone carbon atom (e.g.  $\text{P-CPh}_2\text{-P}$ ), provided additional evidence for microstructure **4**. The  $^{13}\text{C}$  APT NMR experiment suggested that this resonance could not be from a quaternary  $\text{P-CPh}_2\text{-P}$  moiety and must be either from a  $\text{CHR}_2$  or a  $\text{CH}_3$  moiety. To obtain further support for the presence of a  $\text{CHPh}_2$  moiety, the  $^1\text{H}$  NMR spectrum (600 MHz) was recorded (Figure 3a). Alone, the  $^1\text{H}$  NMR spectrum is fairly uninformative, showing very



**Figure 3.**  $^1\text{H}$  NMR spectra (600 MHz,  $\text{CDCl}_3$ , 298 K) of: a) poly(methylenephosphine) **4** prepared from **1** and PhMeCH-TEMPO (2 mol %); b) PhCH<sub>2</sub>-P(Mes)-CHPh<sub>2</sub>.

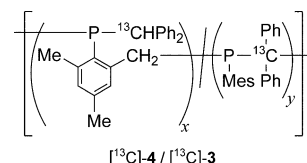


**Figure 4.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum (600 MHz for  $^1\text{H}$ ,  $\text{CDCl}_3$ , 298 K) of poly(methylenephosphine) **4**. The ordinate shows the  $^{13}\text{C}$  APT NMR spectrum and the abscissa shows the  $^1\text{H}$  NMR spectrum.

broad resonances in the aromatic and the aliphatic regions. However, the  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum (Figure 4) showed two important cross correlations. Namely, signals were detected and assigned to the CHPh<sub>2</sub> moiety ( $\delta(^{13}\text{C}) = 52.4$ ,  $\delta(^1\text{H}) = 4.8$ ) and the CH<sub>2</sub> moiety ( $\delta(^{13}\text{C}) = 33.0$ ,  $\delta(^1\text{H}) = 3.6$ ) in **4**. For comparison, these  $^1\text{H}$  NMR chemical shifts are similar to those assigned to the methine and diastereotopic methylene protons in the model PhCH<sub>2</sub>-P(Mes)-CHPh<sub>2</sub> (Figure 3b;  $\delta = 5.06$  (d, CHPh<sub>2</sub>,  $^2J_{\text{PH}} = 4$  Hz), 3.40 (dd, CH<sub>a</sub>H<sub>b</sub>,  $^2J_{\text{HH}} = 13$  Hz,  $^2J_{\text{PH}} = 3$  Hz), 2.93 (dd, CH<sub>a</sub>H<sub>b</sub>,  $^2J_{\text{HH}} = 13$  Hz,  $^2J_{\text{PH}} = 3$  Hz)). Together with the aforementioned structure of **2**·AuCl, which results from treating **1**·AuCl with TEMPO

(2 equiv), these data are consistent with microstructure **4** for poly(methylenephosphine).

Although the NMR spectroscopic data discussed thus far are consistent with the proposed microstructure **4** for the polymer produced by radical reaction, the aforementioned experiments could not rule out the presence of small amounts of microstructure **3**. In order to investigate this possibility, the  $^{13}\text{C}$ -labeled polymer ( $M_n = 10000$  g mol<sup>-1</sup>, PDI = 1.3) was prepared from MesP= $^{13}\text{C}$ Ph<sub>2</sub> ( $[^{13}\text{C}]$ -**1**)<sup>[18]</sup> and PhMeCH-TEMPO (5 mol %) as a sensitive probe for the presence of traces of P- $^{13}\text{C}$ Ph<sub>2</sub>-P enchainment (i.e., microstructure  $[^{13}\text{C}]$ -**4**/ $[^{13}\text{C}]$ -**3** where  $x > y$ ). The corresponding  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum is shown in Figure 2c. Importantly, the dominant signal is assigned to  $^{13}\text{C}$ CHPh<sub>2</sub> ( $\delta = 52.4$ ). To confirm  $^{31}\text{P}$ - $^{13}\text{C}$  coupling, we measured the  $^{31}\text{P}$ - $^{13}\text{C}$  HMQC NMR spectrum of the labeled polymer, which showed the expected cross correlation. It must be noted that the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum exhibits smaller signals slightly downfield from the main broad signal ( $\delta = 55$ –60). The  $^{13}\text{C}$  APT NMR spectrum indicates that these moieties are not quaternary carbon atoms and, therefore, cannot be attributed to P- $^{13}\text{C}$ Ph<sub>2</sub>-P enchainment  $[^{13}\text{C}]$ -**3**. It is plausible that these small signals may be attributable to tacticity, end groups, or trace impurities. In conclusion, the head-to-tail microstructure  $[^{13}\text{C}]$ -**3** does not appear to be present in the polymer prepared by radical initiation, but rather the polymer consists entirely of structure  $[^{13}\text{C}]$ -**4**.



To place these striking observations for the radical-initiated polymerization of **1** into context, the reader is reminded that rearrangements and isomerizations may occur in the addition polymerization of many olefins. The simplest example is perhaps the highly irregular branched structure that results from H migrations in the radical polymerization of ethylene. In contrast, the intramolecular H migration that occurs in the present work appears to be highly selective and affords regioregular **4**. Moreover, the radical polymerization mechanism for **1** appears to be unique for systems with double bonds. Activation of the C–H bond of an *ortho*-bound CH<sub>3</sub> group has been observed in the molecular chemistry of compounds with P-Mes moieties, however it typically involves atom insertion into the C–H bond rather than H migration, as observed herein.<sup>[19]</sup> It is worth noting that an early report on the anionic polymerization of trimethylstyrene (MesCH=CH<sub>2</sub>) considered the possibility of C–H rearrangements, involving the *ortho*- or *para*-bound CH<sub>3</sub> moieties during propagation, but these possibilities were not considered further in subsequent publications.<sup>[20]</sup>

In conclusion, we have discovered that the radical-initiated addition polymerization of phosphalkene **1** affords poly(methylenephosphine) **4** with an unexpected, but highly regioregular, microstructure. The unusual isomerization poly-

merization described herein has not been reported for olefin monomers and may be applicable to other Mes-containing monomers. We are currently investigating, whether analogous isomerization processes may be occurring in the anionic polymerization for **1** and the radical-initiated copolymerization of **1** and olefins.

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