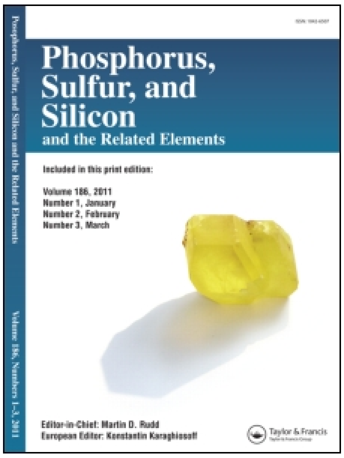

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PHOSPHORUS-NITROGEN COMPOUNDS INCORPORATING TRANSITION METALS

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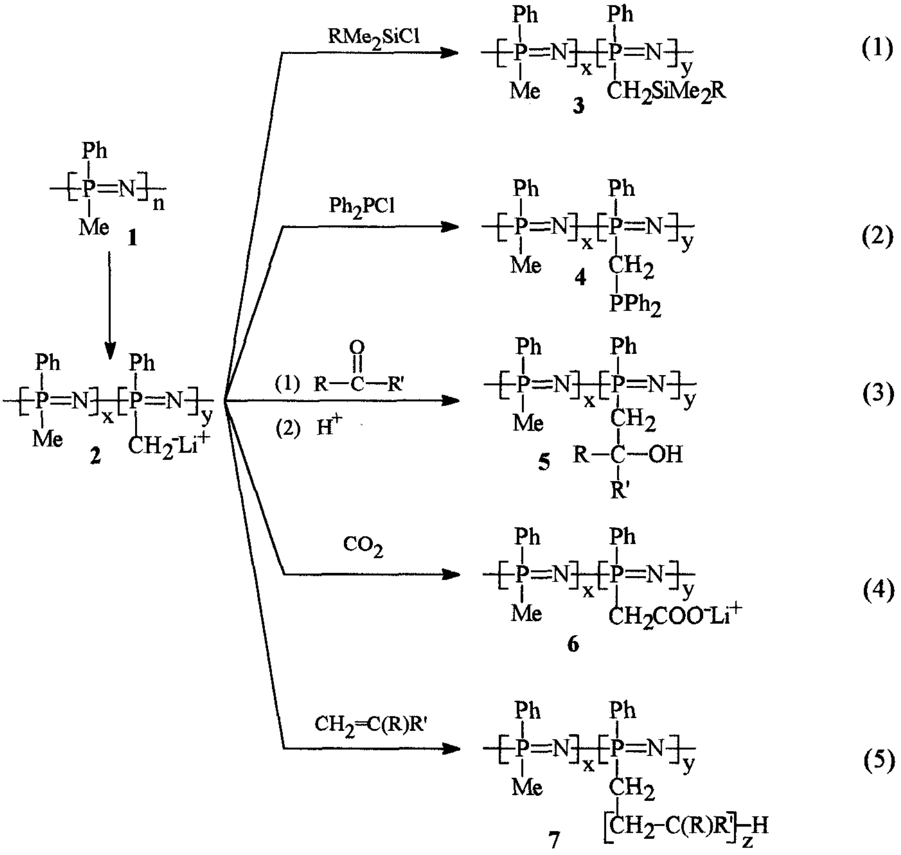
The use of deprotonation-substitution reactions on poly(alkyl/arylphosphazenes) for the preparation of new types of poly(phosphazenes) is summarized. Emphasis is placed on those with metal-containing side groups. The coordination of lithium and silver tetrafluoroborate to the backbone of $[Me(Ph)PN]_n$ and $[Me_2PN]_n$ is also discussed. In the second part of this paper, the synthesis and characterization of new types of the μ-phosphorus-bridged diiron compounds are reviewed. Many of these incorporate amino and silylamino substituents and are derived from the reactions of low-coordinate P-N compounds with the diiron ion, $[(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})Fe_2(CO)_6]^-$.

Key Words: poly(phosphazene), polymer-bound transition metals, phosphido-bridged diiron complexes, low-coordinate phosphorus compounds

INTRODUCTION

One aspect of our work involves the modification of poly(alkyl/arylphosphazenes). These inorganic polymers consist of a chain of alternating single and double bonds between phosphorus and nitrogen with two substituents at phosphorus that are attached by direct phosphorus-carbon bonds. Poly(phosphazenes) with simple alkyl and aryl groups, e.g., $[Me(Ph)P{=}N]_n$, are prepared by the condensation polymerization of appropriate N-silylphosphoranimines such as $Me_3SiN{=}P(OR)(Me)Ph$.[2] Because this approach is limited to the preparation of polymers with a narrow range of P-C bonded functional side-groups, we have developed several synthetic strategies for modification of preformed polymers such as poly(methylphenylphosphazene), $[Me(Ph)PN]_n$. These methods can be grouped into three general categories: (a) electrophilic aromatic substitution at the phenyl groups,[3] (b) deprotonation-substitution reactions of the methyl substituents,[4 - 10] and (c) Lewis base coordination at the backbone nitrogen.[11] The deprotonation-substitution reactions have provided access to the most new poly(phosphazenes) (eq 1 - 5). For example, a variety of functional groups are readily attached through C-Si spacer groups (eq 1) where R = CH_3, H, $CH{=}CH_2$, $(CH_2)_3CN$,[4] $(CH_2)_nCH_3$ (n = 2, 3, 7, 9, 17), $CH_2CH_2(CF_2)_nCF_3$ (n = 0, 5, 7),[5a] and

$(CH_2CH_2O)_nCH_3$ (n = 1, 2).[5b] Other reactive halogen-element compounds, such as $ClPPh_2$ (eq 2), Br_2, and $BrCH_2CH{=}CH_2$, also react straightforwardly with the intermediate anion, **2**, formed by deprotonation of $[Me(Ph)PN]_n$. A third type of new polymers is the alcohols formed in the reaction of **2** with aldehydes and ketones (eq 3).[6] This facilitates the incorporation of a variety of groups, including such novel moieties as ferrocene (see below)[7] and thiophene groups.[6] Water soluble poly(phosphazenes) containing carboxylic acid and salt side-groups are accessible from the reaction of **2** with carbon dioxide (eq 4).[8] Finally, a variety of new grafted poly(phosphazenes) that combine both the inorganic poly(phosphazene) backbone and either organic (eq 5)[9] or inorganic silicone[10] backbones can also be prepared using the anion sites in **2** for anionic polymerization reactions. Such modifications greatly extend the range of properties of this class of polymers.



An active area of interest in polymer chemistry is the incorporation of transition metals into polymers. Such materials may possess a variety electro- and/or catalytically active properties. However, reactions of poly(alkyl/arylphosphazenes) that involve transition metal moieties are not always straightforward because of the basicity of the backbone nitrogen in these polymers. These aspects of derivatization of poly(alkyl/arylphosphazenes) are discussed in the first section below.

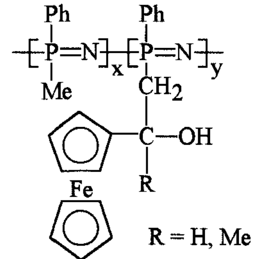
A second area of work in our lab involves the preparation of new μ-phosphido-bridged diiron compounds either related to or derived from low-coordinate phosphorus compounds. This is based on the reactivity of the diiron anion $[(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})Fe_2(CO)_6]^-$, which is conveniently prepared by the warming of a THF solution of $Fe_3(CO)_{12}$, *n*-BuLi, and *t*-BuSH from -78 °C to room temperature,[12] with electrophiles such as $ClC(=O)R$[13] and CS_2.[14] Reactions of this ion with some low-coordinate phosphorus compounds are discussed in the second part of this paper.

RESULTS AND DISCUSSION

Poly(alkyl/arylphosphazenes) with Transition Metal Substituents

The incorporation of several transition metal moieties into poly(phosphazenes) prepared through ring-opening polymerization has been reported. These include osmium and cobalt carbonyl clusters bound through pendant phosphine ligands on P-aryloxygroups,[15, 16] chromium tricarbonyl groups attached via π coordination of phenoxy groups,[17] ferrocene and ruthenocene groups attached via the cyclopentadienyl ring,[15, 18] and $Fe(Cp)(CO)_2$ groups attached directly to the backbone phosphorus[15] or to phenoxy substituents.[19]

There are far fewer examples of transition metal groups attached to the poly(alkyl/arylphosphazenes) that are obtained from condensation polymerization. Our early efforts in this area included the preparation of ferrocene substituted compounds, **5**, from the corresponding aldehydes and ketones (eq 3)[7] and the $Fe(CO)_4$ containing polymer, **8**, derived from a phosphine substituted polymer derivative.[20] The electrochemistry of the ferrocene substituted polymers was investigated in solution and as thin films at the electrode surface. Charge transport in both cases increased with increasing degree of ferrocene substitution and appears to be caused by both physical diffusion and electron hopping.[21]



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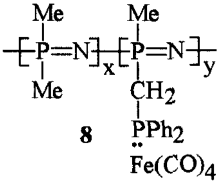

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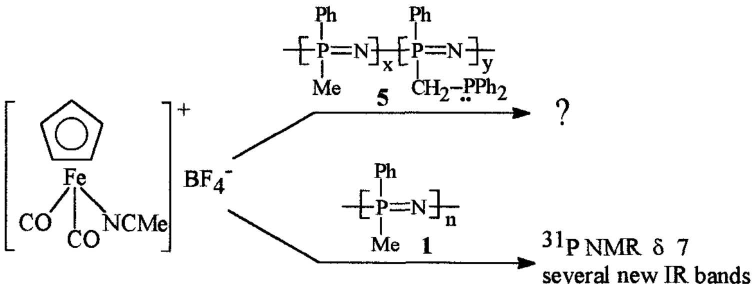
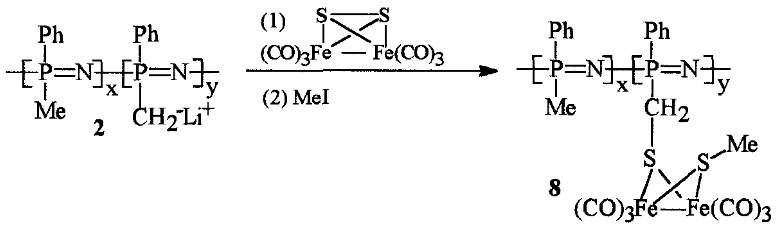
Attempts to prepare other types of poly(alkyl/arylphosphazenes) with transition metal substituents have often been less straightforward. For example, treatment of the polymer anion **2** with $CpFe(CO)_2I$ gave complex mixtures that were not readily characterized. Similarly the reaction of the $[CpFe(CO)_2NCCH_3]^+$ cation with a phosphine substituted poly(phosphazene) was also complicated (eq 6). The ^{31}P NMR spectrum of the reaction mixture contained several new signals. In fact the simple parent polymer **1** (eq 7) also interacts with this cation, presumably through coordination of the backbone nitrogen as suggested by the downfield signal at δ 7 observed in the ^{31}P NMR spectrum of the reaction mixture.[11]



(6)

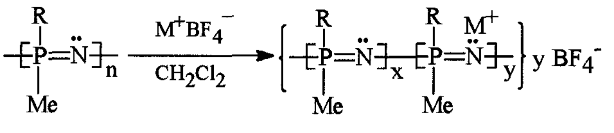
(7)

The reaction of polymer anion **2** with the disulfur diiron complex, μ-dithiobis(tricarbonyliron),[22] followed by quenching with MeI (eq 8) provided a better way to incorporate transition metals as side groups. This reaction is based on similar reactions of organolithium reagents with the disulfur diiron complex.[22] In addition to ^1H and ^{31}P NMR spectroscopic evidence for derivative **8**, the IR spectrum clearly showed carbonyl stretches at slightly lower frequencies than the starting μ-dithiobis(tricarbonyliron), as reported for the small molecule analogs.



(8)

In many of the derivatization reactions of the poly(alkyl/arylphosphazenes) we have encountered the strong coordinating ability of the backbone nitrogen atoms. This is particularly important for this class of poly(phosphazene) because of the presence of electron releasing alkyl and aryl groups at phosphorus. To better understand this phenomenon, both poly(dimethylphosphazene) and poly(methylphenylphosphazene) were treated with simple silver and lithium cations (eq 9).[11] Among the interesting features of these complexes are (a) these complexes remain soluble with up to 30 % of the backbone units coordinated, i.e. $x = 0.7$, $y = 0.3$; (b) the glass transition temperatures are higher than the parent polymers, but still remain as low as -20 C for **9a**; and (c) the ^{31}P NMR spectra of each complex contained only one broad signal significantly downfield from resonances for the parent polymers. These shifts increased with higher degrees of coordination. A low temperature ^{31}P NMR spectroscopic study showed increased broadening of the resonance with resolution into two distinct signals at ca. -90 C for **9a**. One of these resonances corresponds to that of uncoordinated polymer and the other is significantly lower. This suggests that the cations move freely among the backbone nitrogen atoms at ambient temperatures.[11]



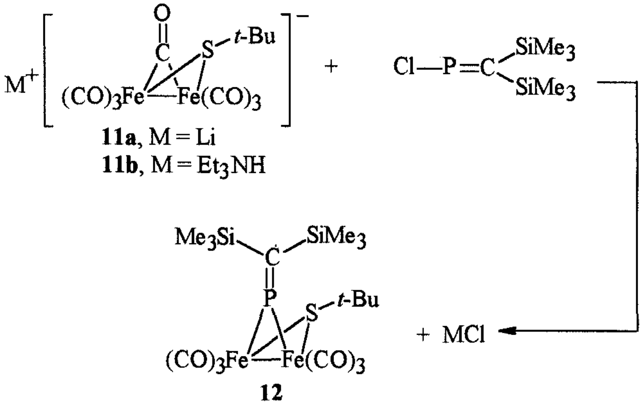
(9)

9a, R = Me, M = Li
9b, R = Me, M = Ag
10a, R = Ph, M = Li
10b, R = Ph, M = Ag

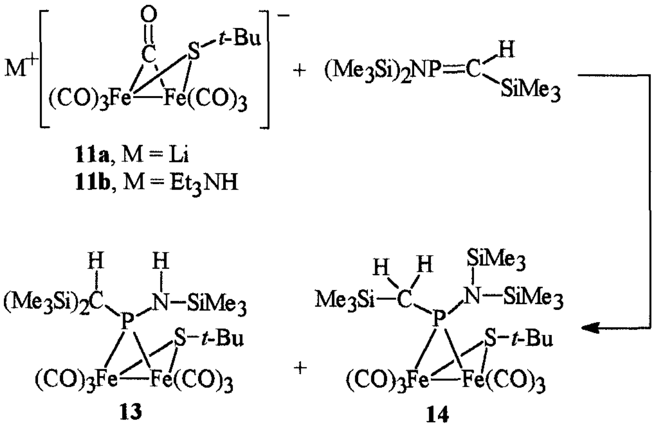
Both $[Me_2PN]_n$ and $[Me(Ph)PN]_n$ formed isolable complexes with H^+ upon treatment with anhydrous HCl. The parent polymers were recovered by washing with K_2CO_3. Similarly, silver cations were readily removed from the polymers by washing with NaCl.[11]

μ-Phosphorus-bridged Diiron Complexes

The reaction of low-coordinate phosphorus compounds with the diiron anion, [(μ-CO)(μ-S-*t*-Bu)$Fe_2(CO)_6]^-$, was shown to give novel and sometimes unexpected results.[23] For example, Cl-P=C$(SiMe_3)_2$ produced the low-coordinate phosphido bridged species, **12**, (eq 10). The reaction with the methylene phosphine, $(Me_3Si)_2NP{=}C(H)SiMe_3$, on the other hand, yielded two products (eq 11). The proportion of these products was, however, greatly influenced by the counterion to the diiron anion. Thus, when M^+ was Li^+ the predominant product was complex **13** and only trace amounts of the other isomer **14** were observed. The opposite ratios of products were obtained when the counterion was Et_3NH^+.[23]

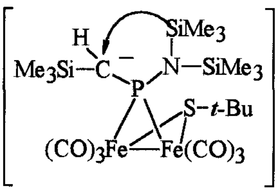


(10)



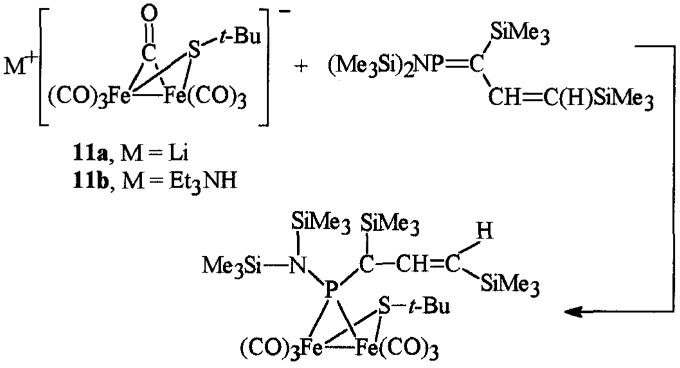
(11)

These results were explained by the formation of the intermediate



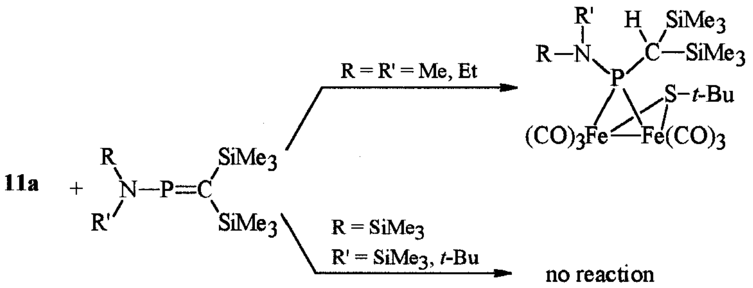
which can be formed by attack of $[(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})Fe_2(CO)_6]^-$ at the phosphorus in the methylene phosphine, a shift of electrons to the carbon, and loss of the bridging CO. In the presence of a proton source such as Et_3NH^+, the intermediate is simply quenched to give **14**. However, when the counterion is Li^+, there is sufficient time for migration of silicon from nitrogen to carbon to occur. Subsequent quenching gives complex **13**.

In view of these results, the diiron anion, $[(\mu\text{-CO})(\mu\text{-S-}t\text{-Bu})Fe_2(CO)_6]^-$, was treated with the phosphadiene, $(Me_3Si)_2NP{=}C(SiMe_3)CH{=}C(H)SiMe_3$,[24] a related low-coordinate compound (eq 12). Although a variety of products were conceivable, only complex **15** was obtained with no evidence for other isomers. This was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, elemental analysis, and X-ray crystallography.[25]



(12)

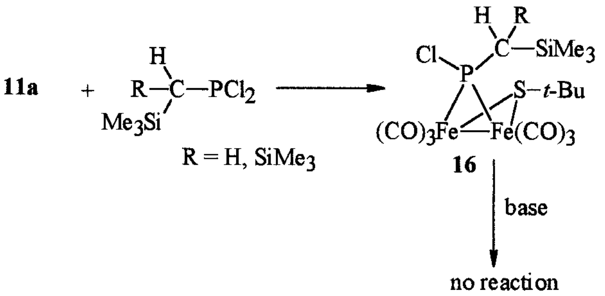
As shown in equation 11, the methylene phosphine, $(Me_3Si)_2N\text{-}P{=}C(H)SiMe_3$, reacted readily with the diiron anion, **11**. To ascertain the role of steric inhibition of substituents at carbon and nitrogen, the anion was treated with a series of related methylene phosphines with two trimethylsilyl groups at carbon (eq 13 and 14). Where R and R' were small groups (eq 13), the reaction proceeded as expected. However, with bulky groups at nitrogen and carbon (eq 14) no reaction occurred.[25]



(13)

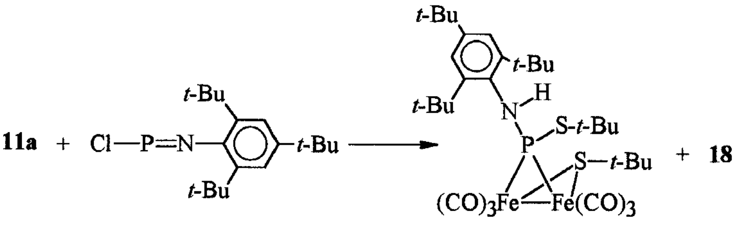
(14)

In view of the reactivity of P-Cl bonds toward the diiron anion as demonstrated in equation 10, several approaches to other low-coordinate phosphido-bridged diiron complexes were investigated. The μ-(chloro)phosphido-bridged complexes **16** were prepared (eq 15), but failed to undergo dehydrogenation upon treatment with several bases.[26]



(15)

More interestingly, the low-coordinate P-chlorophosphinimine, Cl-P=N(2,4,6-t-$Bu_3C_6H_2$),[27] reacted in an unexpected manner yielding primarily **17** with trace quantities of an unidentified compound. Potential pathways to compound **17** and its characterization by X-ray crystallography will be published elsewhere.[26]



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(16)

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