Synthesis and Characterization of Sulfur-Containing Nongeminal Cyclic and Polymeric Alkylarylphosphazenes

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ABSTRACT: The methyl groups in both cyclic and polymeric methylphenylphosphazenes, $[Me(Ph)PN]_3$ and $[Me(Ph)PN]_n$, were modified using deprotonation−substitution and subsequent oxidation reactions to incorporate both thioether and sulfone functional groups. The new cyclic phosphazenes, *cis*-$[Ph(RSCH_2)PN]_3$, **3** and **5**, and *cis*-$\{Ph[RS(O)_2CH_2]PN\}_3$, **6** and **7**, where R = Me or Ph, and the corresponding copolymers $[Me(Ph)PN]_x[Ph(RSCH_2)PN]_y$, **8** and **9**, and $[Me(Ph)PN]_x[\{Ph[RS(O)_2CH_2]PN\}_y$, **10** and **11**, with varying ratios of *x*:*y*, were characterized by NMR and IR spectroscopy and thermal analysis. Crystallographic analysis of the cyclics **3** and **6** show that these molecules retain the basket shape of the nongeminal cis isomers with all the new functional groups opposite from the phenyl groups about the planar P_3N_3 ring. A cyclic trimer, *cis*-$[Ph_3(MeSCH_2)_2MeP_3N_3]$, **4**, in which only two thioether groups had been incorporated was also isolated. The thioether-substituted polyphosphazenes, **8** and **9**, were used as phase-transfer reagents and stabilizing hosts for the synthesis of gold nanoparticles. Analysis by UV spectroscopy and transmission electron microscopy indicated that the average gold particle size in these polymer nanocomposites was 3.2(0.9) nm. In solution, some aggregation of the nanoparticles was observed after one week, but the nanocomposites remain unchanged in the absence of solvent.

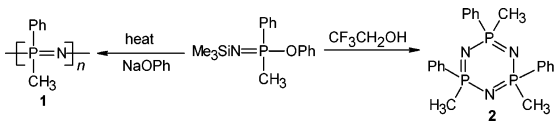
Introduction

Sulfur-containing compounds are well-studied ligands for transition metals and are often used to stabilize metal nanoparticle composites.[1] Polyphosphazenes that contain sulfur groups have been used in the first case for complexation and extraction of metal ions,[2] while a simple poly(alkyl/arylphosphazene) with no sulfur groups was used to stabilize gold nanoparticles, presumably through interaction of the metal with the basic nitrogen in the polymer backbone.[3] Quantum-confined semiconducting CdS nanoparticles have also been formed by matrix encapsulation in the water-soluble, well-studied polymer, poly(methoxyethoxyethoxyphosphazene), MEEP.[4] The diverse properties of the cyclic and polymeric phosphazene system, which are a consequence of the substituents at phosphorus, enhance the potential applications of this inorganic system for the design of transition metal extraction agents, novel ligands for transition metal catalysts, and hosts in a variety of nanocomposite materials.

The preparation of polyphosphazenes such as MEEP or numerous cyclic phosphazenes is generally accomplished by nucleophilic substitution of the chlorine atoms on $[Cl_2PN]_n$ or the corresponding cyclic trimer $[Cl_2PN]_3$, respectively.[5,6] This approach was used to prepare sulfur-containing cyclics $[(RS)_2PN]_3$[5] and, more recently, several sulfur containing polymers.[2,7,8] An alternate approach to new cyclic[9] and polymeric[10,11] phosphazenes is deprotonation−substitution of poly(alkyl/arylphosphazenes). These P−C bonded compounds are initially prepared from condensation reactions of *N*-silylphosphoranimines that contain simple P-alkyl and P-aryl groups, rather than by nucleophilic substitution at P−Cl bonds. Along with somewhat different properties, the condensation process readily affords phosphazenes with nongeminal substitution, i.e., two different substituents at each phosphorus atom.[11−13] This is particularly significant in the synthesis of cyclic phosphazenes since the nongeminal substitution affords both cis and trans isomers. The cis isomers of alkylaryl substituted cyclics, e.g., $[Me(Ph)PN]_3$, are basket-shaped molecules with the aromatic rings on the same side of the almost planar P_3N_3 ring. In this paper, we report the preparation of new sulfur-containing cyclic and polymeric phosphazenes via deprotonation−substitution reactions. The oxidation reactions of the new thioether derivatives and the ability of these new compounds to stabilize metal nanoparticles will also be presented.

Results and Discussion

Reactions on cyclic phosphazenes are often used as models for the polymer analogues.[5] Until recently, however, most poly(alkyl/arylphosphazenes) such as $[Me(Ph)PN]_n$, **1**, had no simple cyclic analogues for comparison. Nonetheless, reactions of poly(methylphenylphosphazene), **1**, (PMPP) at the methyl, phenyl, and backbone nitrogen have been demonstrated, and the deprotonation of the methyl groups and subsequent reaction with electrophiles have yielded a number of new phosphazene polymers and copolymers.[11] In 2002, we reported that the cyclic analogue, $[Me(Ph)PN]_3$, **2**, of PMPP could be prepared from the same *N*-silylphosphoranimine that undergoes thermal condensation polymerization to form PMPP (eq 1). Both the cis and the



(1)

trans isomers of **2** are formed, are readily separated by column chromatography, and have been structurally characterized.[13] The deprotonation−substitution reactions of the cyclic trimers are under active investigation in our labs, and new cyclic phosphazenes with ethyl, haloalkyl, and thioester groups have been reported

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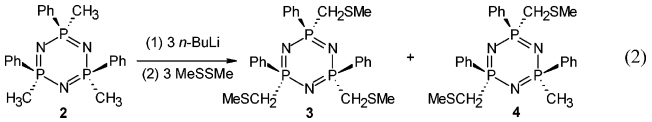
using this method.[9] Not unexpectedly, we have often found that the reactions are not perfectly analogous to the polymer chemistry in terms of reaction conditions, side reactions, etc.

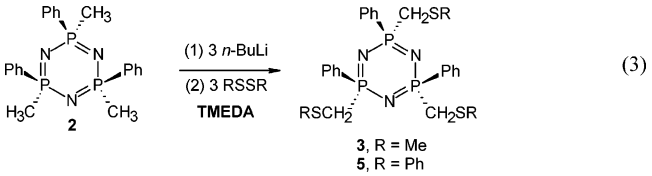
Cyclic Phosphazenes. In this study, we found that sequential treatment of the basket-shaped cis isomer of the cyclic trimer **2** with 3 equiv of *n*-BuLi and dimethyl disulfide (eq 2) produced a mixture of the tri-



(2)

and disubstituted thioether derivatives **3** and **4** in a 60:40 ratio. It is likely that the deprotonation step is not complete since the intermediate anion is insoluble and a slurry is formed upon addition of *n*-BuLi. These compounds were separated by column chromatography.

If, however, tetramethylethylenediammine, TMEDA, was added to enhance the deprotonation of the methyl groups, over 90% conversion to the trisubstituted thioether cyclophosphazene, **3**, was obtained using either diphenyl disulfide or dimethyl disulfide (eq 3). Com-

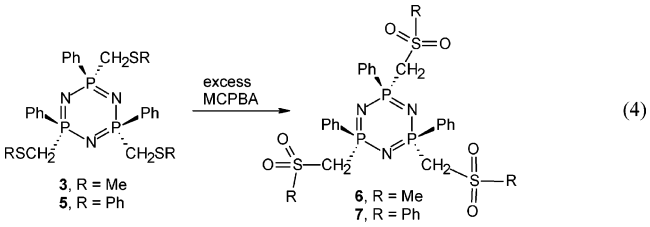


(3)

pound **3** was purified by dissolution into dichloromethane and washing with KOH, while compound **5** was purified using column chromatography. All three compounds, **3**−**5,** are soluble in organic solvents and stable in the air.

While each of the new cyclic phsosphazenes exhibited the characteristic ring PN stretching absorption at 1195 cm^{-1}, NMR spectroscopy was much more informative and clearly distinguished between the di- and trisubstituted sulfide derivatives **3** and **4**. Since only the cis isomer was present, the spectra were relatively simple. For **3** and **5**, singlets at $\delta = 18.6$ and 17.6, respectively, were observed in the ^{31}P NMR spectra, indicating that all phosphorus nuclei were identical. The ^{31}P spectrum of **4**, on the other hand, consisted of two resonances, $\delta = 18.3$ and 20.7, with a relative intensity of 2:1. The signal at $\delta = 18.3$ was due to the two phosphorus atoms with CH_2SMe groups and is similar to the phosphorus resonance in **3** ($\delta = 18.6$). As reported for other disubstituted cyclic phosphazenes, no PNP coupling was observed.[9] The ^1H and ^{13}C NMR spectra also displayed the simplicity of the cis isomers. In the ^{13}C NMR spectra for **3** and **5**, doublets were observed at $\delta = 38.40$ ($J_{PC} = 98.5$ Hz) and $\delta = 38.74$ ($J_{PC} = 95.3$ Hz), respectively, for the methylene carbon atoms, along with typical aromatic signals for the phenyl groups. A doublet at $\delta = 17.85$ ($J_{CP} = 1.9$ Hz) for the SCH_3 groups was also observed for **3**. Similarly, the ^1H NMR spectra of **3** and **5** both contained doublets at $\delta = 3.02$ ($J_{PH} = 9.3$ Hz) and $\delta = 3.60$ ($J_{PH} = 10.3$ Hz) for the PCH_2 protons and the expected aromatic signals. A signal assigned to the SCH_3 group was found at $\delta = 2.18$ in the spectrum of **3**. In contrast, the ^1H and ^{13}C NMR spectra for **4** were somewhat more complicated. Here the ^1H NMR spectra contained two doublets at $\delta = 1.87$ ($J_{PH} = 14.3$ Hz) and $\delta = 2.98$ ($J_{PH} = 8.8$ Hz) with an intensity ratio of 3:4 for the PMe and PCH_2S groups, respectively, and a singlet at $\delta = 2.24$ (relative intensity = 6) arising from the SMe groups.

The sulfur (II) atoms in the newly attached thioether groups in the trisubstituted cyclics **3** and **5** were oxidized to sulfur (VI) or sulfone groups upon treatment with *m*-chloroperoxybenzoic acid (MCPBA) in chloroform (eq 4). After 30 min, simple extraction with CH_2-



(4)

Cl_2 and solvent removal gave spectroscopically pure sulfone derivatives **6** and **7**. Compound **6** readily recrystallized from dichloromethane, but **7** only formed powderlike solids on attempted recrystallization, even after purification by column chromatography. Strong absorptions in the IR spectra at 1194 cm^{-1} of **6** and 1206 cm^{-1} of **7** for the ring P═N stretching frequency indicate that the ring remained intact, while new absorptions at 1302 and 1310 cm^{-1} in **6** and **7** were assigned to the characteristic SO_2 symmetric and asymmetric stretching frequencies. A carbonyl signal was not observed, indicating that excess MCPBA had been removed. In the ^1H and ^{13}C NMR spectra, the significant polarity of the sulfone groups moved the chemical shifts of the PCH_2S in **6** and **7** to $\delta = 4.01$ and 4.01 in the ^1H NMR spectra and to $\delta = 58.9$ and 60.0 in the ^{13}C NMR spectra, respectively. In the ^{31}P NMR spectra, the singlets at $\delta = 9.2$ and 7.4 for **6** and **7** were slightly upfield from the phosphorus signals in the corresponding thioethers **3** and **5**.

Differential scanning calorimetry (DSC) showed strong exothermic transitions for the new compounds, **3**−**7**, which correspond to the melting points. Not surprisingly, incorporation of the large polar sulfone group drastically increased the melting points of sulfones **6** and **7** (259 and 272 °C) relative to the thioethers **3** and **5** (104 and 77 °C). The latter melting points are lower than that of the parent compound **2** (156 °C), presumably due to changes in intermolecular interactions and molecular packing. This effect was also reported for both the cis and trans isomers of the ethyl cyclics, $[Et(Ph)PN]_3$.[9] Other than the transitions corresponding to sublimation, which were confirmed by thermogravimetric analysis (TGA), there were no other exothermic transitions up to 600 °C, indicating that ring-opening polymerization of these compounds did not occur. TGA of **3**−**7** showed major onsets of weight loss from 305 to 362 °C. Compounds **6** and **7** had char yields of ca. 25% at 780 °C, as might be expected for PNS residues.

The crystal structures of **3** and **6** were determined and are shown in Figures 1 and 2. The crystal data are listed in Table 1, and selected bond lengths and angles are given in Table 2. As indicated by NMR spectroscopy, both molecules have a cis geometry with all the phenyl groups on one side of the P_3N_3 rings, which are planar to within ±0.025 Å for **3** and within ±0.016 and ±0.026 Å for **6**, where two different molecules and two molecules of $CHCl_3$ were found in an asymmetric unit. The two molecules of **6** are conformers in which the two sulfur atoms, S(2) and S(5), display different geometries

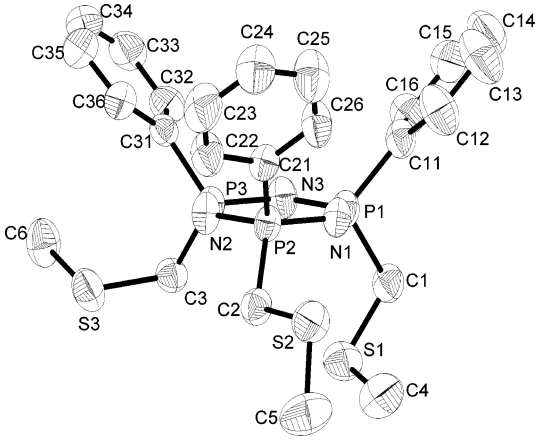


Figure 1. Thermal ellipsoid plot of **3**, *cis*-[Ph(MeSCH$_2$)PN]$_3$. (50% probability ellipsoids for nonhydrogen atoms are shown).

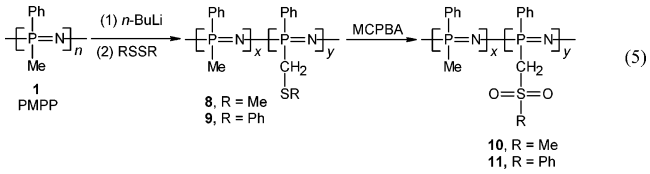
Table 1. Crystal Data[a] and Structure Refinement for 3 and 6

compound	**3**	**6**·CHCl$_3$
empirical formula	$C_{24}H_{30}N_3P_3S_3$	$C_{24}H_{30}N_3O_6P_3S_3{\cdot}CHCl_3$
formula weight	549.60	764.97
crystal diam (mm)	0.30 × 0.20 × 0.10	0.30 × 0.20 × 0.10
space group	P2(1)	P$\bar{1}$
a, Å	11.796(1)	11.698(2)
b, Å	8.755(1)	12.727(1)
c, Å	13.806(1)	24.367(2)
α, deg	90.00	91.544(6)
β, deg	103.653(6)	103.398(7)
γ, deg	90.00	105.138(8)
temp, °C	293	293
Z	2	4
V, *Å*^{3}	1385.5(2)	3391.8(7)
D_{calcd}, g/cm^3	1.317	1.498
m, mm^{-1}	0.459	0.639
R$_1$ [$I > 2\sigma(I)$][b]	0.036	0.059
wR$_2$[all data][b]	0.091	0.159

[a] Graphite monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [2F_c^2 + F_o^2]/3$.

in the solid state. The mean P−N [**3**, 1.596(8); **6**, 1.600(4) Å], P−aryl [**3**, 1.805(5); **6**, 1.801(5) Å], and P−alkyl [**3**, 1.811(5); **6**, 1.832(4) Å] distances are similar to cyclophosphazenes with P−C-bonded substituents, e.g., [Me(Ph)P=N]$_3$,[13] (Ph$_2$P=N)$_3$,[14] (Me$_2$P=N)$_3$,[15] [Et(Ph)P=N]$_3$,[9] and [XCH$_2$(Ph)P=N]$_3$.[9] The mean values of the P−N−P and N−P−N angles in **3** [122.2(7)° and 117.6(6)°] and **6** [122.2(5)° and 117.7(5)°] are also typical of cyclotriphosphazenes with P−C-bonded substituents.[9,13−16] Two of the C−P−C angles in **3** [103.7(9) and 105.3(33)] are typical of other simple cyclic alkylarylphosphazenes,[9,13] but like the halosubstituted PCH$_2$X, compounds,[9b] the C(1)−P(1)−C(11) angle of 102.7° is slightly smaller. This is the PCH$_2$SR group that wraps under the P$_3$N$_3$ ring, while the other two are oriented far from the ring. The effect is more pronounced for **6** where the C(1)−P(1)−C(11) and C(4)−P(4)−C(41) angles are 101.9(2)° and 100.5(2)° for the two independent molecules with the remaining C−P−C angles ranging from 100.5° to 108.9°.

Polymeric Phosphazenes. Six random copolymers with thioether groups were prepared by the same general reaction sequence used to prepare the cis thioether cyclophosphazene derivatives. Treatment of the poly(methylphenylphosphazene), **1,** (PMPP) in THF with 0.3−0.6 equiv of *n*-BuLi followed by quenching the reaction with the electrophiles, dimethyl disulfide and diphenyl disulfide (eq 5), gave copolymers with degrees



(5)

of substitution {[$y/(x + y)$]100%} ranging from 23% to 46% as shown in Table 3. With the smaller electrophile, MeSSMe, the degree of substitution was greater than the degree of substitution with larger PhSSPh, presumably because of the steric differences as observed in the high degrees of substitution when MeI is used as an electrophile.[17] The addition of TMEDA does not enhance the deprotonation−substitution reactions of the polymer **1**, which is undoubtedly due to the strong coordinating ability of this polyphosphazene backbone and its strong affinity for the lithium cation.[18]

Although the synthesis of **8a**−**c** and **9a**−**c** was straightforward, the purification was somewhat challenging relative to purifying other polyphosphazene polymers prepared by deprotonation−substitution methods.[19] Typically, precipitation into nonsolvents such as

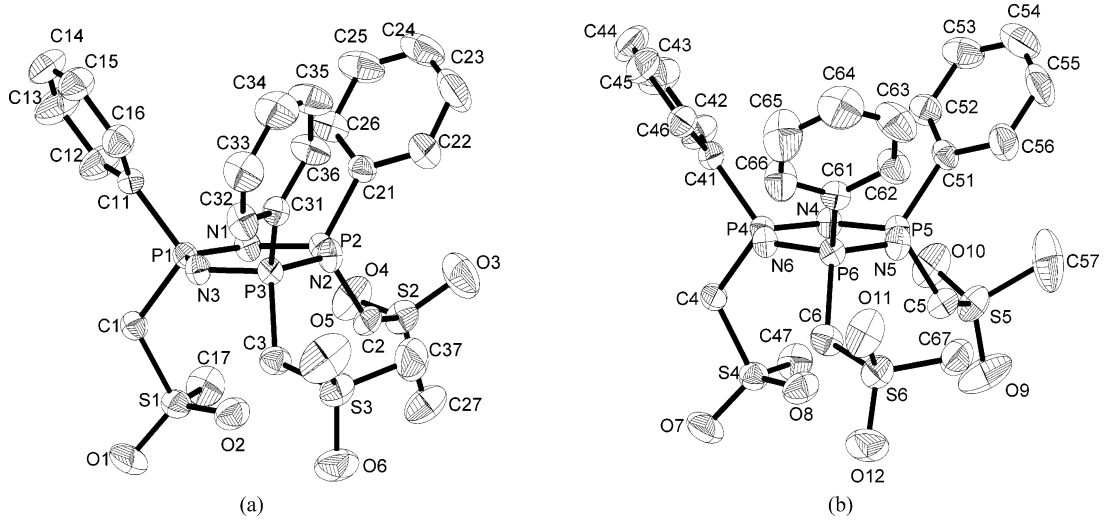


Figure 2. Thermal ellipsoid plot of **6**, *cis*-[Ph(MeS(O)$_2$CH$_2$)PN]$_3$; (a) molecule 1, (b) molecule 2. (50% probability ellipsoids for nonhydrogen atoms are shown).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[Ph(MeS(O)$_2$CH$_2$)PN]$_3$, 3, and cis-{Ph[Me(O)S(O)CH$_2$]PN}$_3$, 6

3					
P(1)−N(1)	1.589(4)	P(1)−C(1)	1.814(5)	C(1)−S(1)	1.794(5)
P(1)−N(3)	1.592(4)	P(1)−C(11)	1.809(5)	C(2)−S(2)	1.811(4)
P(2)−N(1)	1.599(3)	P(2)−C(2)	1.806(5)	C(3)−S(3)	1.818(4)
P(2)−N(2)	1.597(3)	P(2)−C(21)	1.807(4)	C(4)−S(1)	1.788(7)
P(3)−N(2)	1.589(3)	P(3)−C(3)	1.814(4)	C(5)−S(2)	1.797(8)
P(3)−N(3)	1.611(3)	P(3)−C(31)	1.800(5)	C(6)−S(3)	1.794(6)
N(1)−P(1)-N(3)	118.3(2)	P(3)−N(3)-P(1)	121.5(2)	P(2)−C(2)-S(2)	113.4(2)
N(2)−P(2)-N(1)	117.1(2)	C(1)−P(1)-C(11)	102.7(2)	P(3)−C(3)-S(3)	114.6(2)
N(3)−P(3)-N(2)	117.4(2)	C(2)−P(2)-C(21)	104.5(2)	C(1)−S(1)-C(4)	101.3(3)
P(1)−N(1)-P(2)	122.3(2)	C(3)−P(3)-C(31)	103.9(2)	C(2)−S(2)-C(5)	101.0(3)
P(2)−N(2)-P(3)	122.9(2)	P(1)−C(1)-S(1)	111.3(2)	C(3)−S(3)-C(6)	102.5(2)
6 (molecule 1)					
P(1)−N(1)	1.599(3)	P(2)−C(2)	1.832(4)	C(27)−S(2)	1.757(5)
P(1)−N(3)	1.595(3)	P(2)−C(21)	1.795(4)	C(37)−S(3)	1.750(6)
P(2)−N(1)	1.605(3)	P(3)−C(3)	1.828(4)	S(1)−O(1)	1.435(3)
P(2)−N(2)	1.598(3)	P(3)−C(31)	1.801(4)	S(1)−O(2)	1.439(3)
P(3)−N(2)	1.596(3)	C(1)−S(1)	1.782(4)	S(2)−O(3)	1.441(4)
P(3)−N(3)	1.607(3)	C(2)−S(2)	1.775(4)	S(2)−O(4)	1.433(3)
P(1)−C(1)	1.830(4)	C(3)−S(3)	1.779(4)	S(3)−O(5)	1.430(4)
P(1)−C(11)	1.808(4)	C(17)−S(1)	1.769(5)	S(3)−O(6)	1.441(3)
N(1)−P(1)-N(3)	118.1(2)	C(1)−P(1)-C(11)	101.9(2)	C(1)−S(1)-C(17)	103.5(2)
N(2)−P(2)-N(1)	117.6(2)	C(2)−P(2)-C(21)	106.8(2)	C(2)−S(2)-C(27)	102.9(2)
N(3)−P(3)-N(2)	116.8(2)	C(3)−P(3)-C(31)	108.9(2)	C(3)−S(3)-C(37)	105.7(2)
P(1)−N(1)-P(2)	121.7(2)	P(1)−C(1)-S(1)	115.9(2)	O(1)−S(1)-O(2)	117.8(2)
P(2)−N(2)-P(3)	123.0(2)	P(2)−C(2)-S(2)	120.5(2)	O(3)−S(2)-O(4)	118.3(2)
P(3)−N(3)-P(1)	122.5(2)	P(3)−C(3)-S(3)	123.8(2)	O(5)−S(3)-O(6)	117.2(3)
6 (molecule 2)					
P(4)−N(4)	1.599(3)	P(5)−C(5)	1.838(4)	C(57)−S(5)	1.753(6)
P(4)−N(6)	1.598(3)	P(5)−C(51)	1.796(4)	C(67)−S(6)	1.744(5)
P(5)−N(4)	1.603(3)	P(6)−C(6)	1.827(4)	S(4)−O(7)	1.433(3)
P(5)−N(5)	1.600(3)	P(6)−C(61)	1.801(4)	S(4)−O(8)	1.438(3)
P(6)−N(5)	1.598(3)	C(4)−S(4)	1.778(4)	S(5)−O(9)	1.423(4)
P(6)−N(6)	1.603(3)	C(5)−S(5)	1.778(4)	S(5)−O(10)	1.430(3)
P(4)−C(4)	1.835(4)	C(6)−S(6)	1.776(4)	S(6)−O(11)	1.437(4)
P(4)−C(41)	1.807(4)	C(47)−S(4)	1.764(5)	S(6)−O(12)	1.439(4)
N(4)−P(4)-N(6)	117.9(2)	C(4)−P(4)-C(41)	100.5(2)	C(4)−S(4)-C(47)	104.5(2)
N(5)−P(5)-N(4)	117.9(2)	C(5)−P(5)-C(51)	105.9(2)	C(5)−S(5)-C(57)	105.6(3)
N(6)−P(6)-N(5)	118.0(2)	C(6)−P(6)-C(61)	107.5(2)	C(6)−S(6)-C(67)	106.9(2)
P(4)−N(4)-P(5)	122.1(2)	P(4)−C(4)-S(4)	116.7(2)	O(7)−S(4)-O(8)	118.1(2)
P(5)−N(5)-P(6)	121.9(2)	P(5)−C(5)-S(5)	121.3(2)	O(9)−S(5)-O(10)	117.1(2)
P(6)−N(6)-P(4)	122.0(2)	P(6)−C(6)-S(6)	122.9(2)	O(11)−S(6)-O(12)	118.0(2)

Table 3. Analytical, Size-Exclusion Chromatography (SEC), and Thermal (DSC) Data for Polymers 8 and 9

								GPC			DSC	TGA	
					elemental analyses[c]								
polymer	*n*-BuLi (equiv)	x^a	y^a	yield[b] (%)	%C	%H	%N	M_w (x 10^3)	M_n (x 10^3)	M_w/M_n	T_g[d] (°C)	onset[e] (°C)	50 wt% loss (°C)
2								83	36	2.3	37	391	446
8a	0.3	0.77	0.23	65	58.38 (58.79)	5.83 (5.77)	9.15 (9.48)	99	51	1.9	40	361	386
8b	0.4	0.63	0.37	58	56.83 (57.42)	5.95 (5.71)	9.06 (9.08)	104	58	1.8	41	364	381
8c	0.5	0.54	0.46	41	56.42 (56.60)	5.93 (5.68)	8.94 (8.85)	106	64	1.7	43	357	455
9a	0.4	0.84	0.16	63	62.19 (61.91)	5.60 (5.64)	8.45 (9.07)	107	56	1.9	44	367	393
9b	0.5	0.70	0.30	54	62.19 (62.33)	5.48 (5.47)	8.31 (8.26)	115	69	1.7	53	354	395
9c	0.6	0.62	0.38	35	62.60 (62.54)	5.14 (5.38)	7.86 (7.86)	122	71	1.7	57	349	389

[a] Values based on ^{1}H NMR analysis and the best fit of elemental analysis data with different degrees of substitution. [b] Based on theoretical yield calculated from the degree of substitution. [c] Calculated values are in parentheses. [d] Value after at least three heating cycles. [e] Obtained under an atmosphere of nitrogen. Values are typically 30−50° lower in air.

water and hexane facilitate polymer purification, but in this case, removal of the relatively water-insoluble byproducts RSH, formed from LiSR, was further complicated by possible interactions between the acidic RSH and the basic nitrogen of the polymer backbone. Hence, numerous reprecipitations from THF or CH_2Cl_2 into water, methanol, and hexane were done with some adverse effect on the reaction yields which ranged from 35 to 65%.

Polymers **8a**−**c** and **9a**−**c** were characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy, elemental analysis, DSC, TGA, and gel permeation chromatography (GPC). Integration of the ^{1}H NMR spectra was used to establish the ratio of methyl to methylene protons, and these data

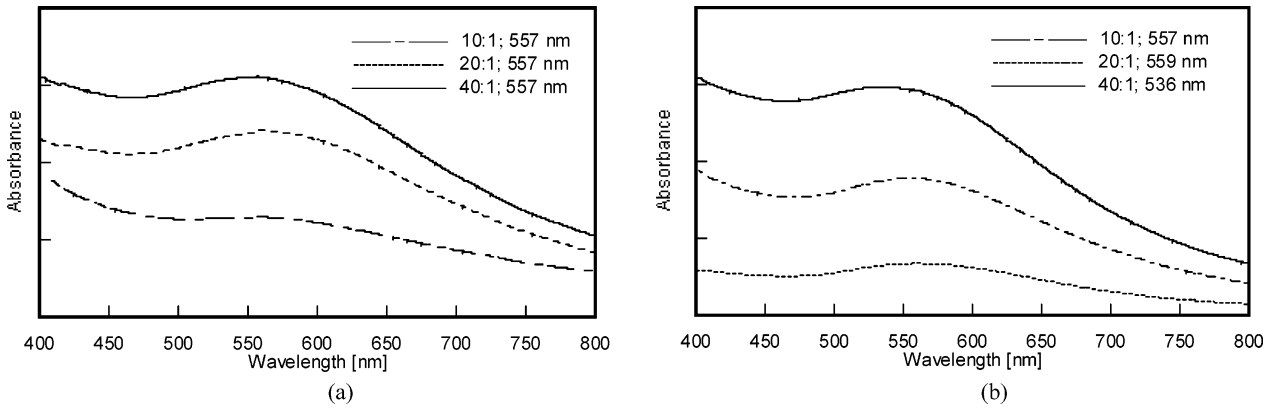
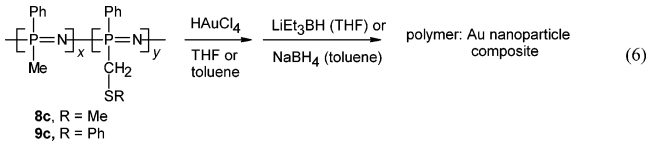


Figure 3. UV absorption spectra of Au/polyphosphazene composites from **8c** after 6 days (a) in toluene; (b) in THF.

formed the basis of the calculated elemental analysis (Table 3). Elemental analyses were consistent with these degrees of substitution and further established the purity of the isolated polymers. Like the ^{1}H NMR spectra, the ^{13}C NMR spectra showed broad signals for the new PCH_2S groups and the unsubstituted PMe groups, as well as the resonances for the phenyl groups. The ^{31}P NMR spectra showed two broad signals at ca. $\delta = 1$ and -0.3 for the PMe and PCH_2S, respectively. The molecular weights (Table 3) of the new polymers were generally larger than that of the parent polymers, thus indicating that no chain degradation occurred during the deprotonation−substitution process. The variations in the molecular weight data may be attributed to factors such as new side group−solvent interactions and polymer conformations that affect the actual shape and size of the new polymers in solution.[19] The glass transition temperature (T_g) of polymers **8a**−**c** with small SMe groups showed almost no change from that of the parent polymer **2** (37 °C), but the incorporation of the bulkier SPh groups, especially where the degree of substitution was over 30%, raised the T_g by 20 °C. The onsets of decomposition temperatures (T_{onset}) of the new sulfur-containing polymers were somewhat lower than that of the parent polymer PMPP, as has been observed for almost all derivatives of PMPP, with higher degrees of substitution giving the lowest onset temperatures.[19,20]

Several attempts were made to isolate the sulfone derivatives which were prepared by the oxidation of the thioether derivatives **8c** and **9c** with a slight excess (1.1 equiv) of the oxidizing agent *m*-chloroperoxybenzoic acid (MCPBA) (eq 5). This is similar to the oxidation of thioether-functionalized polystyrene,[21] some alkoxythioether phosphazenes,[8] and the cyclic phosphazene sulfide derivatives discussed above. The sulfone polyphosphazene derivatives **10** and **11** were even more difficult to purify than the thioether derivatives due to the high degree of protonation of the backbone nitrogen under these strong acidic conditions. Thus, the workup procedure included neutralization with an aqueous solution of sodium bicarbonate. Infrared spectroscopy supported the presence of sulfone functional groups (SO_2 *asym*, 1305 cm^{-1}, and SO_2 *sym* 1152 cm^{-1}),[22] but the ^{31}P NMR spectroscopic analysis revealed that the polymers **10** and **11** were not pure. The chemical shift of phosphorus was downfield ($\delta = 20$) from the parent thioether polymer (ca. $\delta = 1.0$ and -0.3), which correlated to the chemical shift of the protonated polymer backbone.[18,23] It is interesting to note, however, that TGA indicated that the sulfone polymers **10** and **11** were significantly more thermally stable with onsets of decomposition temperatures of 497 and 520 °C, respectively. This is particularly significant because the protonated poly(alkylarylphosphazene) derivatives tend to undergo thermal degradation at elevated temperatures.[18,24]

Gold Nanoparticle Composites. Since several thioether ligands[25] and poly(alkylarylphosphazenes)[3] have been used for the passivation of gold colloids, the new thioether polymers **8a**−**c** were used to prepare gold nanoparticle composites. This was accomplished in either solutions of THF or toluene by room-temperature reduction of $HAuCl_4$ using an adaptation of the Brust−Schiffrin method[26] (eq 6). Because these polymers were



(6)

sufficiently amphiphilic to move the $AuCl_4^-$ from the aqueous phase into the organic phase of either THF or toluene, it was not necessary to use an alkylammonium salt as a phase-transfer reagent. For this study, polymers with the highest incorporation of thioether groups, **8c** and **9c**, were used. Three composites were made for each polymer using polymer-to-gold ratios of 40:1, 20:1, and 10:1.

The UV/vis absorption spectra of the 10:1, 20:1, and 40:1 composites of both polymers showed strong absorption bands with $\lambda_{max} = 526$, 523, and 534 nm for the composites from **8c** and 537, 543, and 541 nm for the composites from **9c**. These bands, which are distinctly different from the absorption at 245 nm for simple PMPP in solution,[27] are characteristic of the surface plasmon oscillation modes of the conducting electrons in the gold nanoparticles.[1] In some cases, the λ_{max} values are somewhat smaller than those observed for simple PMPP/Au nanocomposites ($\lambda_{max} = 540$ nm).[3] Although some aggregation of the nanoparticles begins to occur after 6 days in either toluene or THF solutions, the nanocomposites with a larger ratio of polymer appear to be somewhat more stable, as shown in Figure 3.By transmission electron microscopy (TEM) analysis, it appears that the polymer/Au ratio had little real effect on the size of the nanoparticles. For example, the average particle size was 3.2(0.9) nm in a 20:1 composite (Figure 4) and 3.2(0.7) nm in a 40:1 composite (Figure 5) of the SMe-substituted polymer **8c**, but some aggregation was observed for the 40:1 composite (Figure 5). Slightly larger particles of 4.9(1.1) nm were observed

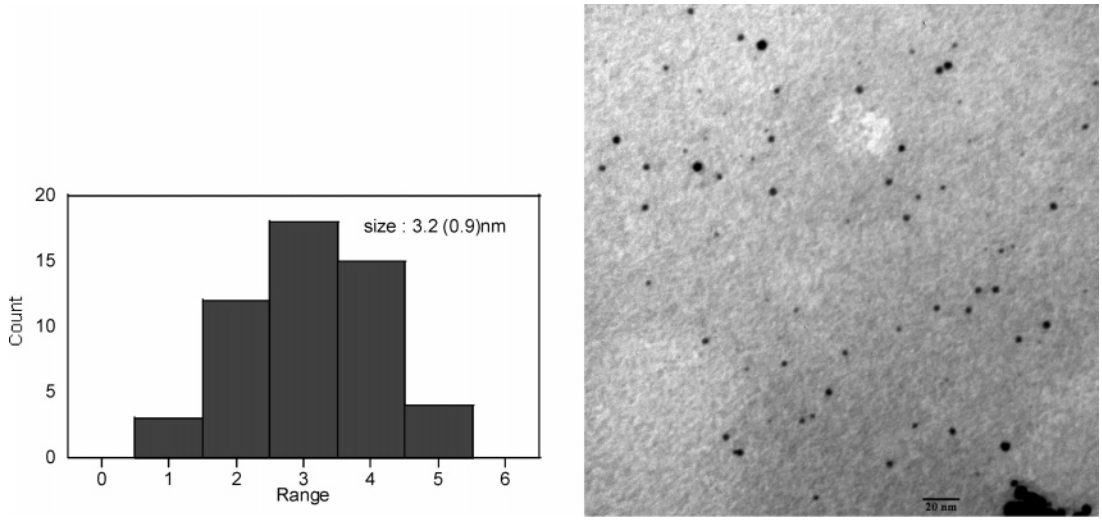


Figure 4. Nanocomposite from **8c**, polymer/Au = 20:1; scale bar 20 nm.

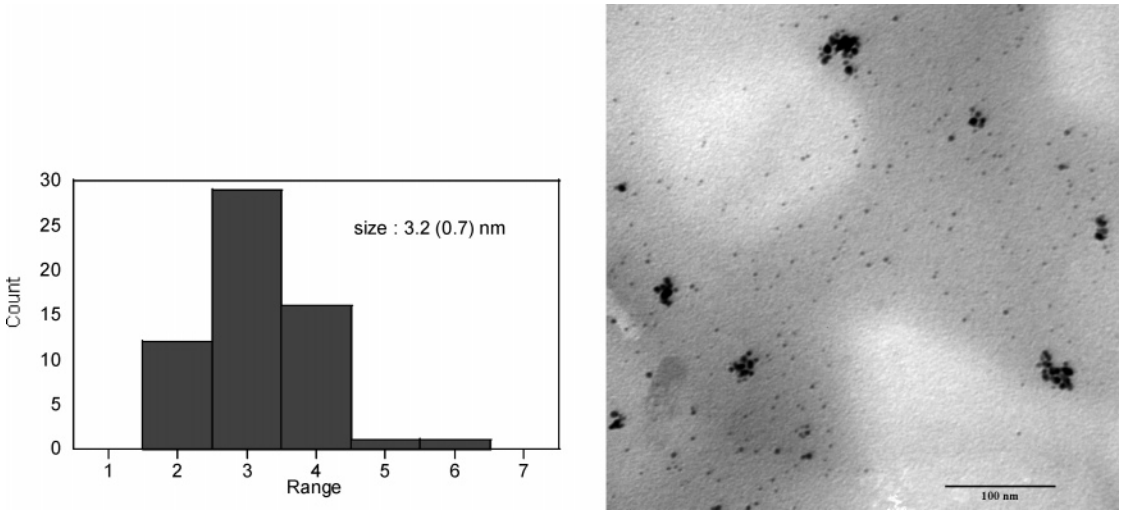


Figure 5. Nanocomposite from **8c**, polymer/Au = 40:1; scale bar 100 nm.

for the SPh polymer **9c** composites. In general, these particle sizes are smaller than those of simple PMPP/Au nanocomposites (5−7 nm), suggesting that the thioether groups may assist in stabilizing the nanoparticles.

Conclusion

New thioether derivatives of cyclic and polymeric methylphenylphosphazenes were prepared by deprotonation−substitution reactions with dialkyl disulfides serving as the electrophiles. The thioether groups were oxidized to the corresponding sulfones. Both the melting points of the sulfone derivatives of the cyclic phosphazenes and the glass transition temperatures of the corresponding polymers were significantly higher than the corresponding thioether derivatives. The structures of the cyclics were basket shaped with the all sulfur atoms on the same side of the almost planar phosphorus−nitrogen ring. This controlled shape could make these new phosphazenes useful ligands for transition metal complexes. The thioether-substituted polyphosphazenes serve as both a phase-transfer agent and a stabilizing medium for the synthesis of gold nanoparticles. The particle sizes are somewhat smaller than those formed in the presence of simple PMPP, where no sulfur atoms are present. The polymer/gold nanocomposites are stable for periods of at least months but show some aggregation in solution over one week.

Experimental Section

Benzene, hexanes, and dichloromethane were distilled from CaH_2; THF and diethyl ether were distilled from Na/benzophenone and stored over molecular sieves under nitrogen until they were needed. Most reagents, including *n*-BuLi (2.5 M in hexanes), dimethyl disulfide, diphenyl disulfide, tetramethylethylene diammine (TMEDA) (Sure/Seal bottle), ammonium chloride, methanol, lithium triethylborohydride, sodium borohydride, and hydrogen tetrachloroaurate(III) hydrate, were reagent grade, were obtained from commercial sources, and were used without further purification. MCPBA was washed with benzene prior to use. The cyclic trimer, *cis*-$[Me(Ph)PN]_3$, **2**,[13] and the polymer, $[Me(Ph)PN]_n$, **1**,[12] were prepared by published procedures via the condensation reactions of $Me_3SiNP(OPh)(Ph)(Me)$. All reactions were performed in flame-dried or oven-dried glassware by using standard Schlenk techniques, but workup and handling of the final products was done in the atmosphere.

NMR spectra were recorded on a SGI/Bruker DRX-400 sb spectrometer. Positive ^1H (400 MHz) and ^{13}C (101 MHz) NMR chemical shifts and ^{31}P NMR (162 MHz) shifts are downfield from the external references Me_4Si and H_3PO_4, respectively. Elemental analyses and IR spectra were obtained on a Carlo Erba Flash Elemental Analyzer 1112 and a Nicolet 560 IR spectrometer, respectively. Thermal data were collected on TA

instruments SDT 2960 and DSC 2010 using heating rates of 10 °C/min in an atmosphere of nitrogen. Molecular weights and molecular weight distributions, M_w/M_n, of polymer samples were obtained on a Waters Associates gel permeation chromatograph (GPC) using 500, 10^4, 10^5, and 10^6 Å μ-Styragel columns equipped with UV model 410 and refractive index detectors. The system was calibrated with a series of narrow-molecular-weight polystyrene standards in the molecular weight range of ca. 10^3-10^6 g/mol using Polymer Standard Service WINGPC 6 software for data processing. The samples were eluted with HPLC-grade THF containing 0.1 wt% of tetra-*n*-butylammonium bromide (*n*-Bu_4NBr) with a flow rate of 1.0 mL/min and column temperature of 30 °C. The injection volume of samples was 0.05 mL of a 0.1% solution. UV/vis absorption spectra of samples were obtained as solutions in distilled THF or toluene using a Beckman DU Series 600 spectrophotometer operating in the range of 200−800 nm with a scan speed of 1200 nm/min. The spectra were corrected for the background absorbance of the solvent (THF or toluene). TEM images were made using a JEOL 1200 EX microscope operating at an accelerating voltage of 120 kV. Samples were prepared by drop-casting a THF solution of the gold colloid onto transparent carbon-coated copper grids (200 mesh) and allowing to dry for 10 min. Digital TEM images were analyzed to determine particle sizes using Image J software.

X-Ray Crystallography. Crystals for analyses of **3**, *cis*-$[Ph(MeSCH_2)PN]_3$ and **6**, *cis*-$[Ph(MeSO2CH_2)P{=}N]_3{\cdot}CHCl_3$, were flat and colorless and grown from saturated ethyl acetate and chloroform, respectively. The crystals were manipulated under air during the mounting procedure. The X-ray data for **3** and **6** were collected on a Bruker P4 diffractometer using the *w* scan technique at room temperature. The important crystallographic data are summarized in Table 1. During the data reduction, Lorentz and polarization corrections, as well as a semiempirical absorption studies were applied. In the structure of **6**, there are two independent cyclic phosphazene and two chloroform molecules. Among the solvent molecules, one, C(72) through Cl(6), is disordered. Selected bond distances and angles are listed in Table 2. Structures were refined anisotropically on F^2 (SHELXL97).[28] Hydrogen atoms were constrained with a riding model. Further details regarding the crystal data and refinement, as well as full tables of bond lengths and angles for each structure reported in this paper, are presented in CIF format in the Supporting Information.

Preparation of *cis*-$[Ph(MeSCH_2)PN]_3$, 3. In a typical procedure, 1.0 g (2.4 mmol) of *cis*-$[Me(Ph)PN]_3$ was placed in a two-neck, 50 mL round-bottom flask with a magnetic stir bar, a nitrogen inlet adapter, and a rubber septum. Freshly distilled THF (10 mL) and excess TMEDA (1.0 mL, 6.6 mmol) were then added to the flask, and the mixture was cooled to −78 °C. Then, *n*-BuLi (3.0 equiv) was added to the solution. The white slurry was stirred for 4 h at that temperature, and then 3.0 equiv of MeSSMe (0.76 mL) was added to the solution at −78 °C. The mixture was stirred for 12 h before the volatiles were removed under vacuum. The residue was dissolved in 20 mL of benzene and then filtered through a glass frit and a layer of Celite. The volatiles were again removed under vacuum, giving a pale yellow solid. This was dissolved with dichloromethane and washed with KOH solution (1.5 M) to remove MeSH. After removal of solvent with a rotary evaporator, the residue was further dried at room temperature in a vacuum overnight. Yield: 1.3 g, 97%.

When the reaction was carried out *without* TMEDA, a 40:60 mixture of di- (**4**) and trisubstituted (**3**) thioether derivatives was obtained, as determined by ^1H and ^{31}P NMR spectroscopy. The two compounds were purified and separated by column chromatography [silica gel 60 Å columns (25 mm × 250 mm) and elution with 1:1 ethyl acetate/hexane]. Yield: **3**, 28%, $R_f = 0.56$; **4**, 16%, $R_f = 0.71$.

***cis*-$[Ph(MeSCH_2)PN]_3$, 3.** ^1H NMR ($CDCl_3$): δ 2.18 (s, 9H, PCH_2SMe), 3.02 (d, 6 H, PCH_2SMe, $J_{PH} = 9.3$ Hz), 7.27−7.32 (m, 9 H, Ph), 7.80−7.83 (m, 6 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.9 (d, PCH_2SMe, $J_{PC} = 1.9$ Hz,), 38.4 (d, PCH_2SMe, $J_{PC} = 98.5$ Hz), 127.5 (d, Ph, $J_{PC} = 13.5$ Hz), 130.2 (d, Ph, $J_{PC} = 11$ Hz), 130.4 (s, Ph), 136.1 (d, Ph, $J_{PC} = 128.5$ Hz). $^{31}P\{^1H\}$ ($CDCl_3$): δ 18.6. IR (KBr, neat, cm^{-1}): 3072 m, 3050 m, 2983 m, 2917 s, 2898 m, 2855 m, 1480 w, 1436 s, 1384 w, 1317 w, 1201 vs, 1157 vs, 1124 s, 1046 w, 1025 m, 997 m, 967 m, 859 m, 804 m, 791 m, 767 m, 742 m, 718 s, 696 s, 522 s, 473 m, 451 s, 423 s. Anal. Calcd for $C_{24}H_{30}P_3N_3S_3$: C, 52.45; N, 7.65; H, 5.50. Found: C, 52.62; N, 7.68; H, 5.67. mp: 104 °C.

***cis*-$[Ph_3(MeSCH_2)_2MeP_3N_3]$, 4.** ^1H NMR ($CDCl_3$): δ 1.87 (d, 3H, PCH_3, $J_{Ph} = 14.3$ Hz), 2.24 (s, 6H, PCH_2SMe), 2.99 (d, 4 H, PCH_2SMe, $J_{PH} = 8.8$ Hz), 7.19−7.24 (m, 3H, Ph), 7.25−7.36 (m, 6 H, Ph), 7.63−7.69 (m, 2H, Ph), 7.76−7.82 (m, 4 H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 17.9 (d, PCH_2SMe, $J_{PC} = 1.9$ Hz,), 23.1 (d, PCH_3, $J_{PC} = 101.1$), 38.4 (d, PCH_2SCH_3, $J_{PC} = 99.1$ Hz), 127.6 (d, Ph, $J_{PC} = 13.6$ Hz), 127.7 (d, Ph, $J_{PC} = 10.7$), 129.94 (s, Ph), 129.96 (d, Ph, $J_{PC} = 11.7$ Hz), 130.0 (d, Ph, $J_{PC} = 10.7$ Hz), 130.4 (s, Ph), 136.4 (d, Ph, $J_{PC} = 128.3$ Hz), 138.5 (d, Ph, $J_{PC} = 124.4$ Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 18.3, 20.7. IR (KBr, neat, cm^{-1}): 3075 m, 3049 s, 3023 m, 3008 m, 2984 m, 2963 m, 2935 m, 2924 m, 2908 s, 2885 s, 1974 w, 1891 w, 1590 m, 1480 m, 1435 s, 1408 m, 1385 m, 1372 m, 1292 m, 1196 vs, 1158 vs, 1123 s, 1026 m, 999 m, 969 m, 914 m, 891 m, 861 s, 820 m, 795 m, 776 m, 748 m, 728 m, 716 s, 696 s, 668 m, 569 m, 522 s, 500 m, 470 m, 451 m, 435 m. Anal. Calcd for $C_{23}H_{28}P_3N_3S_2$: C, 54.86, N, 8.34, H, 5.60. Found: C, 55.02, N, 8.32, H, 5.77. mp: 116−117 °C.

Preparation of *cis*-$[Ph(PhSCH_2)PN]_3$, 5. This compound was prepared by a procedure analogous to that used for the preparation of **3** using TMEDA to assist in the deprotonation. The compound **5** was purified and isolated by column chromatography [silica gel 60 Å columns (25 mm × 250 mm); elution with 1:1 ethyl acetate/hexane] as a pale yellow colored solid. Yield **5**: 43%, $R_f = 0.37$. ^1H NMR ($CDCl_3$): δ 3.60 (d, 6 H, PCH_2SPh, $J_{PH} = 10.2$ Hz), 7.15 (t, 3H, Ph, $J_{HH} = 7.8$ Hz), 7.25 (t, 6H, Ph, $J_{HH} = 7.6$ Hz), 7.35−7.41 (m, 15 H, Ph), 7.96−8.02 (m, 6 H, Ph). ^{13}C NMR$\{^1H\}$ ($CDCl_3$): δ 38.7 (d, PCH_2SPh, $J_{PC} = 95.2$ Hz), 125.7 (s, Ph), 127.8 (d, Ph, $J_{PC} = 12.9$ Hz), 128.58 (s, Ph), 128.62 (s, Ph), 130.3 (d, Ph, $J_{PC} = 10.7$ Hz), 130.8 (s, Ph), 135.8 (d, Ph, $J_{PC} = 132.2$ Hz), 137.1 (d, Ph, $J_{PC} = 5.8$ Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 17.6. IR (KBr, neat, cm^{-1}): 3073 s, 3055 s, 3018 m, 2989 w, 2904 m, 1960 m, 1891 m, 1581 s, 1479 s, 1437 s, 1383 m, 1197 vs, 1156 vs, 1124 s, 1087 m, 1025 m, 998 m, 908 m, 870 m, 788 m, 736 m, 690 s, 569 s. Anal. Calcd for $C_{39}H_{36}P_3N_3S_3$: C, 63.66, N, 5.71, H, 4.93. Found: C, 63.65, N, 5.40, H, 4.86. mp: 77 °C.

Preparation of *cis*-$\{Ph[MeS(O)_2CH_2]PN\}_3$, 6. Compound **3** (0.59 g, 1.1 mmol) and 20 mL of chloroform were placed in a 50 mL two-neck round-bottom reaction flask, and the solution was cooled to 0 °C. Then, excess MCPBA was added. The mixture was stirred at room temperature for 30 min, and then distilled water (30 mL) was added to reaction mixture. The organic layer was separated, washed with distilled water (30 mL) twice, and dried over sodium sulfate. The volatiles were removed under reduced pressure to give a white powder (0.50 g, 69% yield) as a spectroscopically pure product. Recrystallization of **5** from dichloromethane afforded colorless crystals. ^1H NMR ($CDCl_3$): δ 3.069 (s, 9H, $PCH_2S(O)_2Me$), 4.51 (d, 6 H, $PCH_2S(O)_2Me$, $J_{HP} = 12.1$ Hz), 7.34−7.44 (m, 9 H, Ph), 7.82−7.87 (m, 6 H, Ph). ^{13}C NMR$\{^1H\}$ ($CDCl_3$): δ 43.6 (s, $PCH_2S(O)_2Me$), 58.9 (d, $PCH_2S(O)_2CH_3$, $J_{PC} = 84.6$ Hz), 128.1 (d, Ph, $J_{PC} = 14.6$ Hz), 130.0 (d, Ph, $J_{PC} = 11.7$ Hz), 131.7 (s, Ph), 134.4 (d, Ph, $J_{PC} = 142.9$ Hz). ^{31}P NMR$\{^1H\}$ ($CDCl_3$): δ 9.2. IR (KBr, pellet, cm^{-1}): 3059 m, 3011 m, 2960 s, 2912 s, 1984 w, 1904 w, 1774 s, 1708 s, 1590 m, 1574 m, 1481 m, 1437 s, 1360 w, 1303 vs, 1207 vs, 1176 s, 1145 vs, 1124 s, 1093 s, 1027 m, 997 m, 961 s, 890 m, 876 m, 837 m, 809 s, 767 s, 748 s, 693 s, 547 m, 512 m, 501 s, 446 s. Anal. Calcd for $C_{24}H_{30}N_3O_6P_3S_3$: C, 44.65, N, 6.51, H, 4.68. Found: C, 44.81, N, 6.50, H, 4.74. mp: 259 °C.

Preparation of *cis*-$(Ph(PhS(O)_2CH_2)P{=}N)_3$, 7. This compound was prepared from 0.60 g of **5** by a procedure analogous to that used for the preparation of **6**. Compound **7** was isolated in 64% as a pale yellow colored white powder by solvent removal and further purified by column chromatography [silica gel 60 Å columns (25 mm × 250 mm); elution with 5:5:2 ethyl acetate/hexane/methanol]. **7**, $R_f = 0.53$. ^1H NMR ($CDCl_3$): δ 4.01 (d, 6 H, $PCH_2S(O)_2Ph$, $J_{PH} = 12.5$ Hz), 7.3−7.9 (m, 9 H,

Ph), 7.43−7.46 (m, 9 H, Ph), 7.78−7.84 (m, 6 H, Ph), 7.93−7.95 (m, 6 H, Ph). ^{13}C NMR{^{1}H} ($CDCl_3$): δ 60.0 (d, P*C*H$_2$S(O)$_2$-Ph, J_{PC} = 81.6 Hz), 127.96 (s, Ph), 128.02 (d, Ph, J_{PC} = 15.6 Hz), 128.9 (s, Ph), 130.3 (d, Ph, J_{PC} = 12.6 Hz), 131.5 (s, Ph), 133.3 (s, Ph), 135.3 (dt, Ph, J_{PC} = 144.8 Hz, J_{PC} = 2.9 Hz), 141.9 (s, Ph). ^{31}P NMR{^{1}H} ($CDCl_3$): δ 7.4. IR (KBr, neat, cm^{-1}): 3155 m, 3063 m, 2981 m, 2923 m, 1480 m, 1448 m, 1439 m, 1383 m, 1309 vs, 1206 vs, 1176 vs, 1154 vs, 1127 m, 1085 s, 908 s, 799 s, 735 s, 651 s. Anal. Calcd for $C_{39}H_{36}P_3N_3O_6S_3$: C, 56.31, N, 5.05, H, 4.36. Found: C, 56.68, N, 4.56, H, 4.34. mp: 272 °C (broad).

Preparation of [Me(Ph)PN]$_x$[Ph(MeSCH$_2$)PN]$_y$, 8a−c. A 25 mL two-neck round-bottomed flask, equipped with a stir bar, a rubber septum, and a nitrogen inlet, was flame-dried under vacuum and charged with 1.0 g (7.3 mmol) of [Me(Ph)-PN]$_n$ that had been dried in a vacuum oven at T > 50 °C. Under a nitrogen atmosphere, the polymer was dissolved in 10 mL of THF. The solution was cooled to −78 °C, and 0.3 equiv of 2.5 M BuLi was added dropwise to the polymer solution. After being stirred for 1 h at −78 °C, the mixture was allowed to warm to room temperature and was allowed to stir for 2 h. Methyl disulfide (0.20 mL, 2.2 mmol, 0.30 equiv) was added via syringe to the polymer anion solution at 0 °C. After 5 min, the ice−water bath was removed and the reaction mixture was stirred overnight at room temperature. The reaction was quenched with sat. NH_4Cl (aq) (1−2 mL). After the solvent was removed by rotary evaporation, the copolymer was redissolved in THF and precipitated into water several times then reprecipitated into methanol and hexane. Polymer **8a** was dried for 24 h at room temperature then at 50 °C in a vacuum oven. Polymers **8b** and **8c** were made by a similar procedure using 0.4 and 0.5 equiv of *n*-BuLi and MeSSMe, respectively. Physical and analytical data are given in Table 3. ^{1}H NMR ($CDCl_3$): δ 1.5−2.0 (br, P*Me*, S*Me*), 2.9 (br, PC*H*$_2$S), 7.1−7.8 (br, Ph). ^{13}C NMR{^{1}H} ($CDCl_3$): δ 21.0−24.6 (P*Me*, S*Me*), 37.0−39.5 (P*C*H$_2$S, 127−138 (Ph) ^{31}P NMR{^{1}H} ($CDCl_3$): δ 1.3, −0.4.

Preparation of [Me(Ph)PN]$_x$[Ph(PhSCH$_2$)PN]$_y$, 9a−c. These polymers were synthesized by a method similar to that for the synthesis of polymers **8**. The stoichiometry was 0.40, 0.50, and 0.60 equiv of *n*-BuLi and PhSSPh relative to [Me-(Ph)PN]$_n$ for **9a**, **b**, and **c**, respectively. Physical and analytical data are given in Table 3. ^{1}H NMR ($CDCl_3$): δ 1.4−1.7 (br, P*Me*), 3.4 (br, PC*H*$_2$S), 7.1−7.8 (br, Ph). ^{13}C NMR{^{1}H} ($CDCl_3$): δ 22.3−24.6 (P*Me*), 38.0−39.5 (P*C*H$_2$S), 127−132 (Ph) ^{31}P NMR{^{1}H} ($CDCl_3$): δ 1.3, −2.5.

Preparation of [Me(Ph)PN]$_x$[{Ph[RS(O)$_2$CH$_2$]PN}$_y$, 10 and 11. A 25 mL two-neck round-bottom flask was equipped with a nitrogen inlet, a rubber septum, and a stir bar. Purified polymer **8c** (0.53 g, 3.1 mmol) was placed into the flask under nitrogen and dissolved in THF (15 mL). The solution was cooled to 0 °C, and MCPBA (0.76 g, 3.4 mmol) was added to the flask with constant stirring. After 15 min, the mixture was warmed to room temperature and stirred for 24 h. Then, the solvent was removed on a rotary evaporator, the resulting solid was dissolved in dichloromethane (20 mL), and the solution was washed with a 10% w/v aqueous solution of sodium metabisulfite (20−50 mL). The layers were separated, and the organic layer was made slightly basic with a saturated solution of sodium bicarbonate. After filtration, solvent was removed from the filtrate by rotary evaporation and the solid residue was purified by multiple precipitations from THF into water and hexane. The polymer was dried under vacuum at 50 °C. The product was characterized by ^{1}H and ^{31}P NMR spectroscopy, elemental and thermogravimetric analysis, and IR spectroscopy. Polymer **11** was prepared according to the same procedure by using the pure polymer **9c** (0.5) g, 2.81 mmol) dissolved in THF (15 mL). The reagents and quantities used were MPCBA (0.53 g, 3.1 mmol), sodium metabisulfite (10% w/v, 20−50 mL), and sodium bicarbonate (saturated solution). The IR spectra of both polymers **10** and **11** contained signals for SO_2 vibrations. Although the^{1}H NMR spectra revealed the presence of PCH_2SO_2 groups at 4.1 ppm, the ^{31}P chemical shift (δ = 20) was far downfield, which indicated that the polymer backbone was protonated.[23, 24]

Synthesis of Gold Nanoparticle Composites in THF. In six separate vials, 40, 80, and 160 mg of polymers **8c** and **9c** were dissolved in THF (0.050 M). An aqueous solution of $HAuCl_4$ (0.20 M) was added to each vial (0.12 mL, 0.025 mmol). Upon the adding of the aqueous Au^{3+} solution, the yellow-colored colloidal mixtures were stirred vigorously for 2 h. Each vial was placed in an ice bath, and the reducing agent $LiEt_3$-BH (0.30 mL, 1.0 M in THF) was added dropwise with vigorous stirring. The gold colloids formed instantaneously, as seen by the color change to dark purple. After 1 h of stirring, the solvent was removed on a rotary evaporator and the residue was dissolved in CH_2Cl_2 (2 mL) and washed with distilled water (2 mL). The dark purple precipitate was collected by centrifugation and dried in a vacuum oven overnight at room temperature.

Synthesis of Gold Nanoparticle Composites in Toluene. As described above, six separate vials of polymers **8c** and **9c** in toluene (0.050 M) were mixed with aq. $HAuCl_4$ and the mixtures were stirred vigorously for 2 h. The reducing reagent $NaBH_4$ was prepared by grinding a pellet into a powder and dissolving in 25 mL of water (0.40 M). This solution (3.0 mL) was added to each vial at room temperature with vigorous stirring. The color of the solutions changed to dark purple instantly. After vigorous stirring for an hour, the solvent was removed on a rotary evaporator. The residue was dissolved in CH_2Cl_2 (2 mL) and washed with distilled water (2 mL). The dark purple-black precipitate was collected by centrifugation and dried in the vacuum oven overnight at room temperature.

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Supporting Information Available: Initial UV absorption spectra of gold nanoparticle composites from **8c** and **9c** in toluene and X-ray crystallographic files in CIF format for **3** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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