Synthesis and Redox Properties of (3-Phenothiazinomesityl)- and (4-Phenothiazinoduryl)dimesitylphosphines and the Corresponding Arsines

Shigeru Sasaki,* Fumiki Murakami, and Masaaki Yoshifuji

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

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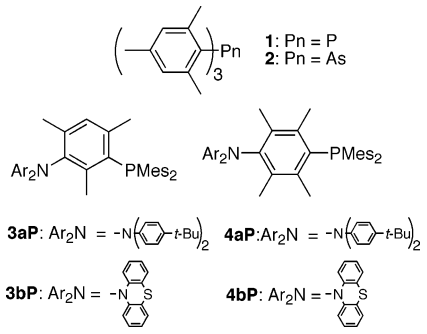
To construct the novel redox systems possessing the trimesitylphosphine- or trimesitylarsine-type substructure as a reversible redox site, dimesityl(3-phenothiazinomesityl)phosphine, dimesityl(4-phenothiazinoduryl)phosphine, and the corresponding arsines were synthesized (mesityl = 2,4,6-trimethylphenyl, duryl = 2,3,5,6-tetramethylphenyl). The key synthetic intermediates, (3-bromomesityl)-dimesitylphosphine, (4-bromoduryl)dimesitylphosphine, and the analogous arsines were prepared by successive addition of the corresponding Grignard reagents to phosphorus or arsenic trichloride. The (bromoaryl)phosphines and -arsines were converted to the corresponding (iodoaryl)phosphines and -arsines and coupled with phenothiazine in the presence of copper to afford the phenothiazinophosphino- and phenothiazinoarsinobenzenes. The cyclic voltammograms of the phenothiazinopnictogenobenzenes thus obtained exhibit two-step redox waves corresponding to oxidation on the pnictogen as well as phenothiazine redox centers. The phenothiazino group contributes to stability of the redox systems, and the phenothiazinophosphinobenzenes display two-step nearly reversible redox waves at −78 °C. On the other hand, the cyclic voltammograms of the phenothiazinoarsinobenzenes consist of the first reversible wave followed by the second irreversible wave, suggesting decomposition at the unstable arsenic redox center. The pnictogen redox centers of the phenothiazinopnictogenobenzenes are unstable as compared with those of the corresponding trimesityl derivatives. Chemical oxidation of the phenothiazinophosphinobenzenes and phenothiazinoarsinobenzenes by tris(4-bromophenyl)aminium perchlorate, which can oxidize trimesitylphosphine and trimesitylarsine to the corresponding cation radicals, was studied by EPR. However, only the nitrogen-centered cation radical was observed probably because of the instability of the phosphorus as well as arsenic radical centers.

Introduction

Triarylamines have been applied as components of functional molecules for a long time, since some of them are reversible redox systems and afford stable cation radicals.[1] Especially, synthesis of the conjugated oligo- or poly(triarylamines) and properties arising from the interaction between the nitrogen centers have been actively investigated to construct functional molecules such as multistep redox systems,[2] high-spin organic molecules,[3] and electro-optic devices.[4] Although most of the heavier group 15 element counterparts or triarylpnictogens (pnictogen: group 15 element),[5] which are generally irreversibly oxidized to undergo decomposition or further undesired reactions, are not suitable for such a purpose,[6] some of the crowded triarylpnictogens represented by trimesitylphosphine (**1**) and arsine (**2**) (mesityl = 2,4,6-trimethylphenyl) have the potential to substitute the triarylamine functional sites (Scheme 1). Trimesitylphosphine (**1**) has large C−P−C bond angles (average 109.7°)[7] and can be reversibly oxidized at a lower oxidation potential ($E_{1/2}$ = 0.784 V vs SCE)[8a] to give a stable cation radical,[8] as contrasted with triphenylphosphine, which has smaller C−P−C bond angles (average 103.0°)[9] and is irreversibly oxidized at a higher potential (E = 1.400 V vs SCE).[8a] Trimesitylarsine (**2**) also has C−As−C bond angles (average 107.6°)[10] wider than triphenylarsine (average 99.8°)[11] and can be reversibly oxidized to a stable cation radical.[12] Recently, we synthesized tris(2,4,6-triisopropylphenyl)pnictogens[13] and demonstrated that introduction of bulky aryl groups leads to thermodynamic as well as kinetic stabilization of the corresponding cation radicals and that they can be a promising way to construction of stable redox centers. To examine if the crowded triarylpnictogens can be applied as practical redox centers similarly to the triarylamines, we planned to construct intramolecularly interacting redox systems that have both the crowded triarylpnictogen and the generally used redox sites and investigate how they behave in the redox process. The crowded triarylphosphines or -arsines similar to the trimesityl derivatives

Scheme 1. Crowded Triarylpnictogens



* Corresponding author. E-mail: sasaki@mail.tains.tohoku.ac.jp.

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connected to the other redox sites through *meta* or *para* arylene linkage especially attracted our interest as the most basic systems, since the *meta* phenylene bridge often leads to ferromagnetic coupling between the radical centers,[14] and the donors and/or acceptors conjugated by the *para* phenylene bridge are the prototype of the multistep redox systems.[15] However, our first attempt to investigate aminophosphinobenzenes **3aP** and **4aP** (Scheme 1)[16] did not give decisive results, since their cyclic voltammograms are very complicated as well as irreversible, contrary to our expectation. In this article, we employ a phenothiazino group as the second redox site in order to improve stability of the whole redox system. Phenothiazino groups have been successfully used as radical centers to construct the stable high-spin di(cation radical)[3k] and are expected to survive even in a highly oxidized state. Synthetic sequences of the aminophosphinobenzenes turned out to be applicable to the arsenic counterparts, and now we can compare redox properties of the phosphorus and arsenic derivatives. Herein, we report the synthesis and redox properties of dimesityl(3-phenothiazinomesityl)phosphine **3bP** and dimesityl-(4-phenothiazinoduryl)phosphine **4bP** (duryl = 2,3,5,6-tetramethylphenyl) as well as the corresponding arsines. An EPR study of the oxidation of phenothiazinophosphinobenzene **3bP** and phenothiazinoarsinobenzenes **3bA** was performed to clarify the redox process.

Results and Discussion

Synthesis and Structure. We have synthesized aminophosphinobenzenes **3aP** and **4aP** by construction of the crowded triarylphosphine moiety followed by introduction of the diarylamino group by Ullmann coupling as outlined in Scheme 2.[16] Development of the key synthetic intermediates, (3-bromomesityl)dimesitylphosphine (**5aP**) and (4-bromoduryl)dimesitylphosphine (**6aP**), was essential, and they were synthesized by successive introduction of one bromoaryl group and two mesityl groups. Crucial points of this step are employment of the arylmagnesium bromide and method of addition. Addition of the arylmagnesium bromide to the phosphorus chlorides in tetrahydrofuran at −78 °C was found to be best for selective introduction of mesityl or similar bulky aryl groups on the phosphorus atom among the several known reactions of mesityllithium or mesitylmagnesium bromide with phosphorus chlorides for the synthesis of dichloromesitylphosphine,[17] chlorodimesitylphosphine,[18] or trimesitylphosphine.[19] Especially, introduction of the third aryl group proceeds quantitatively to give the triarylphosphine without formation of tetraaryldiphosphanes such as tetramesityldiphosphane,[19] which are otherwise formed. Contrary to our expectation, the corresponding arsenic compounds were not obtained analogously. Addition of 3 equiv of mesitylmagnesium bromide to phosphorus trichloride at −78 °C in THF affords **1** quantitatively,[16] but arsine **2** was obtained only in a low yield under similar conditions and an excess amount of mesitylmagnesium bromide had to be added to arsenic trichloride at −78 °C in THF to obtain **2** quantitatively. Thus, an excess amount of the Grignard reagent was added to the diarylchloroarsine in order to introduce the third aryl group, and arsines **5aA** and **6aA** were obtained in moderate yields. Use of chlorodioxarsolane[20] in place of arsenic trichloride did not improve the results. Phosphines **7** and **8** and arsine **9** were prepared analogously. (Bromoaryl)phosphines **5aP** and **6aP** and (bromoaryl)arsines **5aA** and **6aA** were converted to the corresponding iodides **5bP**, **6bP**, **5bA**, and **6bA** in good yields by lithiation followed by quenching with iodine.[21] The diarylamino group was introduced by Ullmann coupling, which is less sensitive to the steric environment than the palladium-catalyzed couplings. The diarylamines were coupled with (iodoaryl)-

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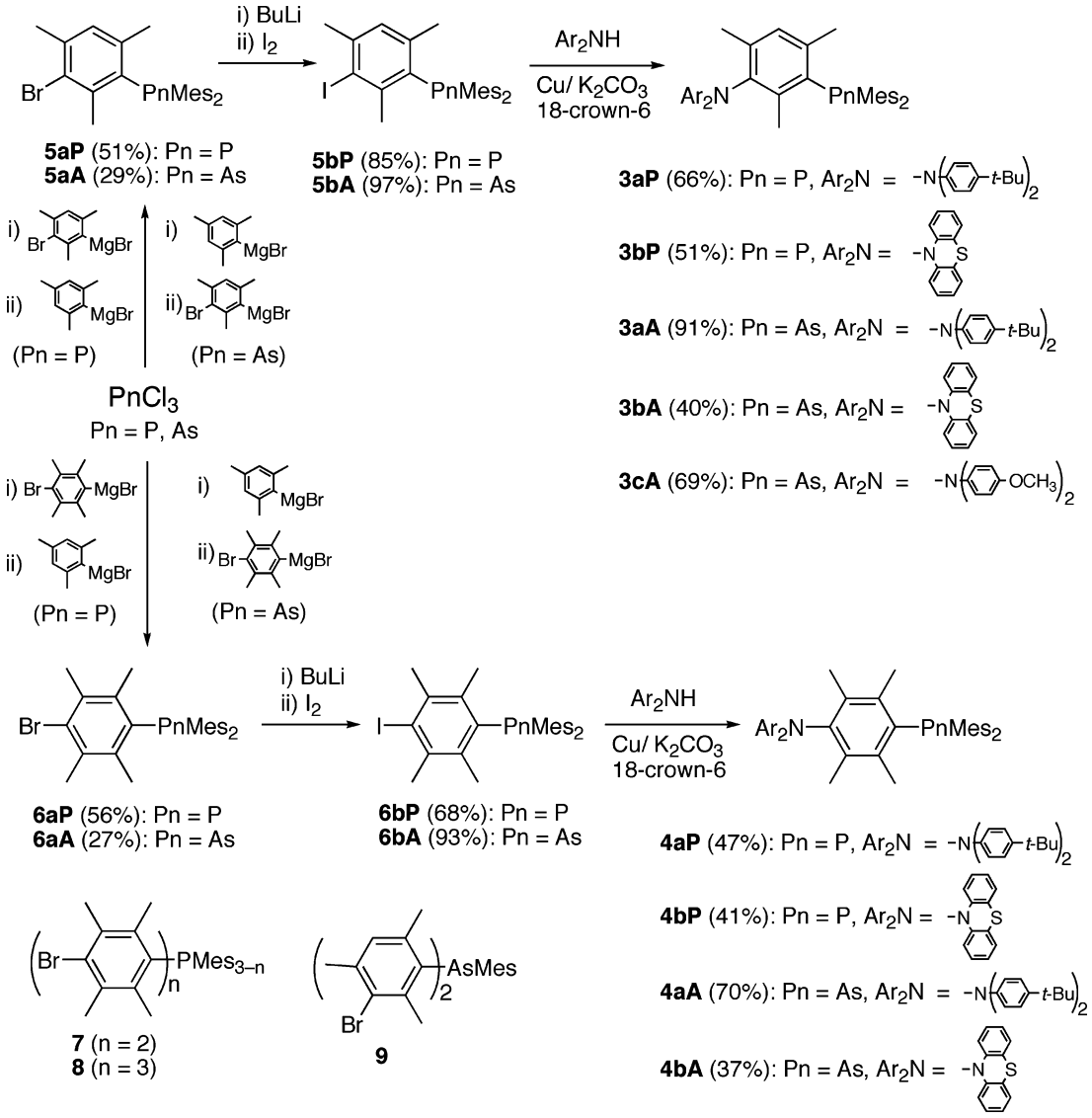
Scheme 2. Synthesis of the Dimesityl(phenothiazinoaryl)pnictogens and Related Compounds



pnictogens **5bP**, **6bP**, **5bA**, and **6bA** in refluxing solvents such as 1,2-dichlorobenzene or 1,2,4-trichlorobenzene in the presence of copper powder and 18-crown-6[22] to give the corresponding aminopnictogenobenzenes in moderate yields. Use of 1,2,4-trichlorobenzene as a solvent reduced reaction time owing to the higher boiling point than that of 1,2-dichlorobenzene. Nitrobenzene significantly enhanced the rate of the reaction, but the yield was not improved due to difficult removal of the solvent. All new compounds possessing the trimesitylphosphine or arsine substructure described here suffered from oxidation to the corresponding phosphine or arsine oxides during the workup and purification process especially when handled in a small amount.

Phosphines **5aP**, **5bP**, **6aP**, **6bP**, **3aP**, **3bP**, **4aP**, **4bP**, **7**, and **8** exhibit ^{31}P NMR chemical shifts typical of the crowded triarylphosphines[8a] ranging from $\delta_P = -25$ to -36. Phosphines **6aP** ($\delta_P = -31.6$), **7** ($\delta_P = -27.9$), and **8** ($\delta_P = -24.4$) show an obvious trend of the chemical shift by replacement of the mesityl groups with the 4-bromoduryl groups. ^{1}H and ^{13}C NMR spectra of the phosphines and arsines are rather simple, and they do not show significant broadening at room temperature. The mesityl and the 4-substituted duryl groups are observed as C_2 symmetrical substituents, which suggests rapid rotation of the carbon−pnictogen bond on the time scale of 200 MHz NMR. Among newly synthesized compounds described here, tris(4-bromoduryl)phosphine (**8**) and (4-iododuryl)dimesitylarsine (**6bA**) afforded crystals suitable for X-ray crystallography (Figure 1). The phosphine **8** has P−C bond lengths (average 1.85 Å) and C−P−C bond angles (average110.4°) slightly larger than those of **1** (average 1.837 Å, 109.7°).[7] Considerable elongation of the P−C bond comparable to those of tris(2,4,6-triisopropylphenyl)phosphine[13] (average 1.845 Å, 111.5°) can be attributed to steric pressure arising from full substitution on the aromatic rings. Arsine **6bA** displays the molecular structure around the arsenic center (average 1.975 Å, 107.1°) similar to **2** (average 1.976 Å, 107.6°).[10]

Redox Properties. Cyclic voltammograms of aminophosphinobenzenes **3bP** and **4bP** and aminoarsinobenzenes **3bA** and **4bA** are shown in Figures 2−5. Redox potentials of the newly synthesized phosphines and arsines obtained by cyclic voltammetry are summarized in Table 1. (Bromoaryl)phosphines **5aP**, **6aP**, **7**, and **8**, (iodoaryl)phosphines **5bP** and **6bP**, (bromoaryl)-arsines **5aA**, **6aA**, and **9**, and (iodoaryl)arsines **5bA** and **6bA** are reversibly oxidized to the corresponding cation radicals similarly to **1** and **2**, although the measurement under air makes

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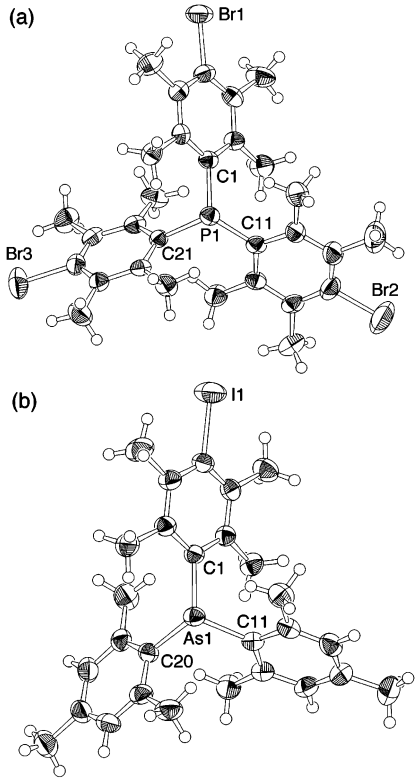

Figure 1. ORTEP drawing of (a) **8** and (b) **6bA** with 50% thermal ellipsoids. Selected bond lengths (Å) and angles (deg). **8**: P1−C1 1.858(4); P1−C11 1.847(5); P1−C21 1.847(5); C1−P1−C11 112.6(2); C1−P1−C21 105.2(2); C11−P1−C21 113.3(2). **6bA**: As1−C1 1.989(5); As1−C11 1.978(5); As1−C20 1.973(5); C1−As1−C11 105.0(2); C1−As1−C20 110.6(2); C11−As1−C20 106.4(2).

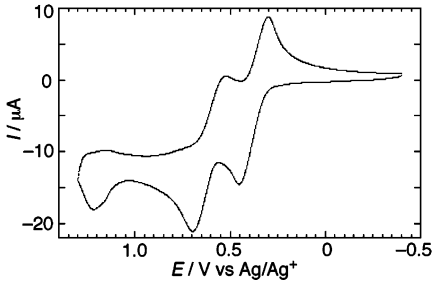

Figure 2. Cyclic voltammogram of **3bP** at −78 °C.

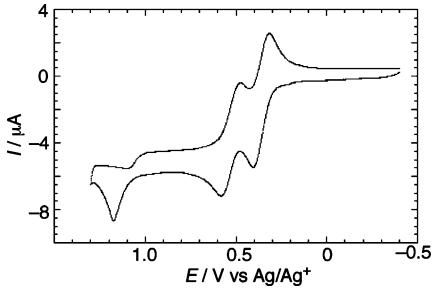

Figure 3. Cyclic voltammogram of **4bP** at −78 °C.

the cathodic peak weaker. The oxidation potentials of the phosphines and arsines, ranging from $E_{1/2}$ = 0.38 to 0.46 and 0.73 to 0.85 V vs Ag/Ag$^+$, respectively, are close to those of the trimesityl derivatives. A small but clear substituent effect of the 4-bromoduryl group is observed for phosphines **6aP** ($E_{1/2}$ = 0.41 V vs Ag/Ag$^+$), **7** (0.44 V), and **8** (0.49 V), where the oxidation potentials become higher as the number of 4-bromoduryl groups increases. Phenothiazino-substituted phosphines **3bP** and **4bP** display nearly reversible two-step redox waves followed by an irreversible oxidation peak at −78 °C (Figures 2, 3). The first and second redox waves are attributed to the oxidation to the cation radicals and di(cation radicals). However, the assignment of the first and second redox waves is not decisive from the voltammogram, since trimesitylphosphine (**1**) ($E_{1/2}$ = 0.38 V vs Ag/Ag$^+$) and *N*-mesitylphenothiazine (0.36 V) have similar oxidation potentials. The third irreversible oxidation around 1.2 V is attributed to the second oxidation of the phenothiazino moiety,[23] which is observed at 1.10 V for *N*-mesitylphenothiazine. Introduction of a phenothiazino moiety

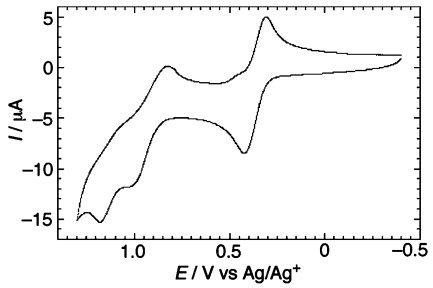

Figure 4. Cyclic voltammogram of **3bA** at −78 °C.

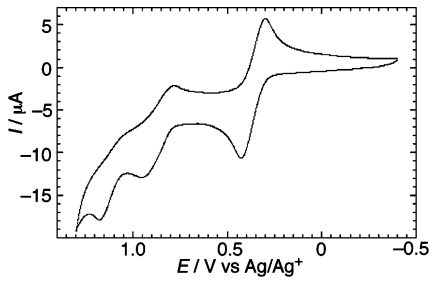

Figure 5. Cyclic voltammogram of **4bA** at −78 °C.

Table 1. Redox Potentials of the Crowded Triarylphosphines, Triarylarsines, Aminophosphinobenzenes, and Aminoarsinobenzenes

compound	$^1E_{1/2}$/V[a]	$^2E_{1/2}$/V[a]	ΔE/V[b]
1	0.38		
5aP	0.46		
5bP	0.44		
6aP	0.41		
6bP	0.42		
7	0.43		
8	0.46		
3aP[c]	0.39[d]	0.66[d]/0.78[d]	
3bP[c]	0.37	0.61[d]	0.24
4aP[c]	0.35[d]	0.61[d]/0.79[d]	
4bP[c]	0.37	0.54[d]	0.18
2	0.71		
5aA	0.78		
5bA	0.75		
6aA	0.73		
6bA	0.73		
9	0.85		
3aA[c]	0.50	0.93[d]	0.37
3bA[c]	0.37	1.02[d]/1.18	0.60
3cA[c]	0.29	1.072[d]	0.73
4aA[c]	0.57	0.64[d]/0.88[d]	
4bA[c]	0.36	0.95[d]/1.18	0.53

[a] V vs Ag/Ag$^+$ in dichloromethane with 0.10 mol L^{-1} *n*-Bu$_4$NClO$_4$ (ferrocene/ferrocenium = 0.18 V). Working electrode: glassy carbon. Counter electrode: Pt wire. Scan rate: 50 mV s^{-1}. Temperature: 20 °C. [b] $\Delta E = {}^2E_{ox} - {}^1E_{ox}$. [c] Temperature: −78 °C. [d] Irreversible. Peak potential.

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resulted in improvement of the redox properties as compared with **3aP** and **4aP**,[16] which gave very complex redox waves. However, stability of the redox system is still limited and the first two-step waves become less reversible and unresolved at room temperature. The difference of the first and the second oxidation peaks (ΔE = 0.25 (**3bP**), 0.20 (**4bP**) V) reflects the distance between the nitrogen and phosphorus atoms. The methyl groups on the central aromatic ring prevent the effective π-conjugation and delocalization of π-electrons through the central aromatic ring so that the Coulombic repulsion between two positive charges approximately depends on the distance between the cation centers. They are also responsible for the small substituent effect of the phenothiazino or dimesitylphosphino group on the oxidation potentials, which do not lower the oxidation potential of **3bP** and **4bP** markedly as compared with **1** or *N*-mesitylphenothiazine. The cyclic voltammograms of the aminoarsinobenzenes **3aA**, **3bA**, **3cA**, **4aA**, and **4bA** consist of the first reversible wave followed by two irreversible waves (Figures 4 (**3bA**) and 5 (**4bA**)). The first and second waves are assigned as the oxidation on the nitrogen and arsenic redox centers, respectively, by taking the oxidation potentials of arsine **2** and *N*-mesitylphenothiazine into consideration. Oxidation of the aminoarsinobenzenes suffers from instability of the arsenic-centered cation radicals. Although the oxidation of trimesitylarsine (**2**) and the related arsines to the cation radicals gives reversible cyclic voltammograms, the arsenic-centered cation radicals are less stable than the phosphorus counterparts. Thus, decomposition takes place on the arsenic redox center after oxidation to the di(cation radical). On the other hand, the nitrogen radical center survives even after the decomposition on the arsenic center.

Although trimesitylphosphine (**1**) has a low oxidation potential, oxidants suitable for generation of the corresponding cation radical are still limited. Reaction of trimesitylphosphine with organic acceptors such as TCNE,[24] TCNQ, DDQ, and $TCNQF_4$ did not afford EPR signals of the corresponding cation radical. Only the anion radicals of the acceptors were detected by EPR, and **1** was probably converted to the closed shell adducts. The cationic oxidants such as thianthrenium perchlorate,[25] triphenylmethyl perchlorate, triphenylmethyl tetrafluoroborate, and tris(4-bromophenyl)methyl perchlorate, $AgBF_4$, $AgClO_4$, and H_2SO_4 also failed to generate EPR signals of $\mathbf{1}^{+\bullet}$. On the other hand, oxidation with tris(4-bromophenyl)aminium perchlorate[26] in dichloromethane gave a purple solution, and satisfactory EPR spectra (g = 2.0107 and $a(^{31}P)$ = 23.4 mT for the isotropic spectrum in solution and $g_\perp$ = 2.0094, $g_{||}$ = 2.0030, and $a_\perp(^{31}P)$ = 17.4, $a_{||}(^{31}P)$ = 40.8 mT for the anisotropic spectrum in frozen solution) were obtained. However, an excess amount of the oxidant resulted in the formation of the cation radical of tetramesityldiphosphane[27] (g = 2.0130, $a(^{31}P)$ = 16.5 mT), while the corresponding hexachloroantimonate did not work. Similarly, a dichloromethane solution of **2** was oxidized to the purple solution of the corresponding cation radical by tris(4-bromophenyl)aminium perchlorate, and isotropic and anisotropic spectra were obtained with g = 2.0378, $a(^{75}As)$ = 27.5 mT in solution and $g_\perp$ = 2.056, $g_{||}$ = 2.004, $a_\perp(^{75}As)$ = 18.7, $a_{||}(^{75}As)$ = 45.6 mT in frozen solution, respectively. Although **2** gave a reversible cyclic voltammogram, $\mathbf{2}^{+\bullet}$ was not as stable as expected and the EPR signal and the purple color of $\mathbf{2}^{+\bullet}$ gradually disappeared after the oxidation. Oxidation of aminophosphinobenzene **3bP** and aminoarsinobenzene **3bA** with tris(4-bromophenyl)aminium perchlorate in dichloromethane afforded a green solution and a brown solution, respectively. The EPR spectrum obtained by oxidation of **3bP** appeared as four lines at room temperature and can be interpreted as g = 2.0047, $a(^{14}N)$ = 0.73 mT, and $a(^{31}P)$ = 0.73 mT. **3bA** gave three lines at g = 2.0051 with $a(^{14}N)$ = 0.70 mT (Figure 6). Oxidation of **3bP** and **3bA** with silver perchlorate in dichloromethane, which oxidizes the triarylamines to the corresponding cation radicals, also afforded similar spectra, and these results as well as comparison with the value of the cation radicals of phenylphenothiazines ($a(^{14}N)$ = ca. 0.70 mT)[23] support formation of the cation radicals of the phenothiazine moieties. The magnitude of $a(^{31}P)$ of the cation radical of **3bP**, which is larger than that of phosphorus-substituted arylnitroxyls (0−0.34 mT),[28] suggests considerable unpaired electron delocalization on the phosphorus, probably due to intramolecular electron transfer from the phosphorus, whereas arsenic derivative **3bA** shows negligible coupling with ^{75}As despite larger atomic hyperfine coupling constants.[29] Although the fate of the triarylpnictogen moieties after oxidation is still ambiguous, the EPR spectra as well as the cyclic voltammograms suggest that the crowded pnictogen cation radical centers are still not stable enough to accommodate di(cation radicals), which can be observed by EPR and still need further stabilization.

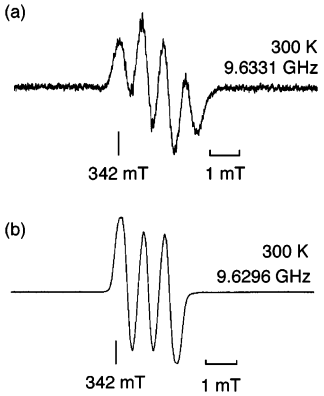

Figure 6. EPR spectra obtained after oxidation of (a) **3bP** and (b) **3bA** with tris(4-bromophenyl)aminium perchlorate in dichloromethane at 300 K.

Conclusion

We have synthesized (phenothiazinoaryl)dimesitylphosphines and -arsines possessing crowded triarylphoshine or arsine moieties similar to the trimesityl derivatives and revealed redox properties. The (bromoaryl)dimesitylphosphine and -arsines, developed as key synthetic intermediates, are expected to be convenient synthetic intermediates for introduction of these crowded triarylpnictogen moieties. The (phenothiazinoaryl)-dimesitylphosphines and -arsines show two-step redox waves corresponding to oxidation at nitrogen and phosphorus or arsenic redox centers. However, the two-step redox systems are not reversible at room temperature even if the redox centers are connected through a 1,4-arylene linkage, which generally

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stabilizes such redox systems. Although trimesitylphosphine and -arsine are known to be reversible redox couples, further stability is required to construct two-step reversible redox systems. Synthesis and redox properties of the (phenothiazinoaryl)-phosphines and -arsines carrying more stabilized phosphorus or arsenic redox centers are under investigation.

Experimental Section

(3-Bromomesityl)dimesitylphosphine (5aP). A solution of 3-bromomesitylmagnesium bromide was prepared from magnesium (1.24 g, 51.0 mmol) and 2,4-dibromomesitylene (13.9 g, 50.1 mmol) in THF (100 mL). To a solution of phosphorus trichloride (6.5 mL, 74.6 mmol) in THF (50 mL) was added the solution of the aryl Grignard reagent over 20 min, and the mixture was stirred for 30 min at −78 °C. The mixture was warmed to room temperature, stirred for 12 h, and evaporated to remove the solvent and excess phosphorus trichloride. The residue was dissolved in THF (200 mL), and a solution of mesitylmagnesium bromide, which was prepared from magnesium (3.12 g, 128 mmol) and 2-bromomesitylene (19.0 mL, 124 mmol) in THF (100 mL), was added over 35 min at −78 °C. After being stirred for 12 h at room temperature, the mixture was washed with a saturated NaCl solution and dried over $MgSO_4$. The drying agent was removed by filtration, and the solvent was evaporated to give crude **5aP**. The crude product was chromatographed over silica gel (eluent: hexane) to afford **5aP** (11.9 g, 25.4 mmol) in 51% yield. **5aP**: colorless crystals, mp 161.5−162.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.88 (1H, d, J_{PH} = 3.4 Hz), 6.82 (4H, d, J_{PH} = 3.2 Hz), 2.40 (3H, s), 2.34 (3H, s), 2.28 (6H, s), 2.06 (12H, s), 2.02 (3H, s); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 142.47 (d, J_{PC} = 17.8 Hz), 141.49 (d, J_{PC} = 18.8 Hz), 141.12 (d, J_{PC} = 18.2 Hz), 137.93 (s), 137.78 (s), 135.01 (d, J_{PC} = 22.2 Hz), 131.06 (d, J_{PC} = 18.1 Hz), 130.99 (d, J_{PC} = 3.4 Hz), 129.80 (d, J_{PC} = 3.6 Hz), 126.80 (d, J_{PC} = 2.9 Hz), 24.31 (s), 23.48 (d, J_{PC} = 19.5 Hz), 22.78 (d, J_{PC} = 16.5 Hz), 22.58 (d, J_{PC} = 15.4 Hz), 20.93 (s); ^{31}P NMR (81 MHz, $CDCl_3$) δ −30.2 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 468 (M^+ + 2; 36), 466 (M^+; 34), 453 (M^+ + 2 − Me; 100), 451 (M^+ − Me; 94), 387 (M^+ − Br; 7.4), 267 (M^+ − 1 − Br − Mes; 11), 252 (M^+ − 1 − Br − Mes − Me; 32), 119 (Mes^+; 28); HRMS (70 eV, EI) found *m*/*z* 466.1431, calcd for $C_{27}H_{32}PBr$, M, 466.1425. Anal. Calcd for $C_{27}H_{32}PBr$: C, 69.38; H, 6.90. Found: C, 70.43; H, 7.00.

(3-Bromomesityl)dimesitylarsine (5aA). A solution of mesitylmagnesium bromide was prepared from magnesium (1.76 g, 72.5 mmol) and 2-bromomesitylene (11.0 mL, 71.9 mmol) in THF (180 mL). To a solution of arsenic trichloride (3.0 mL, 35.6 mmol) in THF (200 mL) was added a solution of the Grignard reagent over 15 min, and the mixture was stirred for 10 min at −78 °C. To the resultant pale yellow suspension was added a solution of the Grignard reagent, prepared from magnesium (2.60 g, 107 mmol) and 2,4-dibromomesitylene (29.7 g, 107 mmol) in THF (240 mL), in 15 min, and the mixture was stirred for 30 min at −78 °C. The mixture was warmed to room temperature, stirred for 12 h, and evaporated. The residue was extracted with ether, washed with saturated NH_4Cl solution and saturated NaCl solution, and dried over anhydrous $MgSO_4$. After removal of the drying agent by filtration and evaporation of the solvent, the residue was chromatographed over silica gel (eluent: hexane) to afford **5aA** (5.18 g, 10.1 mmol) in 29% yield and **2** (1.85 g, 4.28 mmol) in 12% yield. **5aA**: colorless prisms (EtOH), mp 142.5−143.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (1H, s), 6.83 (4H, s), 2.414 (3H, s), 2.405 (3H, s), 2.29 (6H, s), 2.17 (12H, s), 2.15 (3H, s); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 142.59, 141.69, 141.28, 139.17, 137.79, 137.59, 135.62, 130.81, 129.60, 126.67, 24.14, 24.1 1, 23.05, 22.87, 20.78; LRMS (70 eV, EI) *m*/*z* (rel intensity) 512 (M^+ + 2; 100), 510 (M^+; 97), 313 (Mes_2As^+; 17), 119 (Mes^+; 38); HRMS (70 eV, EI) found *m*/*z* 510.0948, calcd for $C_{27}H_{32}AsBr$, M, 510.0903. Anal. Calcd for $C_{27}H_{32}AsBr$: C, 63.42; H, 6.31; Br, 15.63. Found: C, 63.72; H, 6.31; Br, 15.48.

(3-Iodomesityl)dimesitylphosphine (5bP). To a solution of **5aP** (1.00 g, 2.14 mmol) in THF (20 mL) was added butyllithium (1.75 mL in hexane, 2.91 mmol) at −78 °C. After being stirred for 20 min, a solution of iodine (962 mg, 3.79 mmol) in THF (15 mL) was added, and the mixture was warmed to room temperature. Excess iodine was quenched with saturated $NaHSO_3$ solution, and the organic layer was extracted with ether, washed with saturated $NaHCO_3$ solution and saturated NaCl solution, and dried over $MgSO_4$. After removal of the drying agent by filtration and evaporation of the solvent, the crude mixture was chromatographed over silica gel (eluent: hexane) to afford **5bP** (938 mg, 1.82 mmol) in 85% yield. **5bP**: colorless crystals; mp 161.5−163.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.86 (1H, d, J_{PH} = 3.0 Hz), 6.79 (4H, d, J_{PH} = 3.2 Hz), 2.44 (3H, s), 2.42 (3H, s), 2.26 (6H, s), 2.03 (12H, s), 2.00 (3H, s); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 144.72 (d, J_{PC} = 18.7 Hz), 142.42 (d, J_{PC} = 17.8 Hz), 142.06 (d, J_{PC} = 18.3 Hz), 137.77 (s), 134.16 (d, J_{PC} = 23.2 Hz), 131.23 (d, J_{PC} = 18.2 Hz), 130.18 (d, J_{PC} = 3.3 Hz), 129.81 (d, J_{PC} = 3.6 Hz), 108.42 (d, J_{PC} = 1.6 Hz), 30.36 (s), 30.03 (d, J_{PC} = 19.8 Hz), 22.79 (d, J_{PC} = 16.5 Hz), 22.54 (d, J_{PC} = 15.2 Hz), 20.94 (s); ^{31}P NMR (81 MHz, $CDCl_3$) δ −28.2 (s); LRMS (70 eV, El) *m*/*z* (rel intensity) 514 (M^+; 49), 499 (M^+ − Me; 100), 387 (M^+ − I; 14), 119 (Mes; 9); HRMS (70 eV, EI) found *m*/*z* 514.1284, calcd for $C_{27}H_{32}PI$, M, 514.1287. Anal. Calcd for $C_{27}H_{32}PI$: C, 63.04; H, 6.27; I, 24.67. Found: C, 63.37; H, 6.34; I, 25.53.

(3-Iodomesityl)dimesitylarsine (5bA). Iodination of **5aA** in a manner similar to the preparation of **5bP** afforded **5bA** in 97% yield. **5bA**: colorless crystals, mp 144.0−144.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 (1H, s), 6.82 (4H, s), 2.52 (3H, s), 2.46 (3H, s), 2.28 (6H, s), 2.16 (12H, s), 2.15 (3H, s); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 145.00, 142.64, 142.33, 141.80, 138.36, 137.67, 135.92, 130.03, 129.69, 108.39, 30.71, 30.23, 23.14, 22.90, 20.87; LRMS (70 eV, EI) *m*/*z* (rel intensity) 558 (M^+; 100), 543 (M^+ − Me; 4), 439 (M^+ − Mes; 3), 313 (Mes_2As^+; 11), 193 ($MesAs^+$ − 1; 9), 119 (Mes^+; 15); HRMS (70 eV, EI) found *m*/*z* 558.0795, calcd for $C_{27}H_{32}AsI$, M, 558.0765. Anal. Calcd for $C_{27}H_{32}AsI$: C, 57.85; H, 5.77; I, 22.73. Found: C, 58.08; H, 5.78; I, 22.67.

(4-Bromoduryl)dimesitylphosphine (6aP). Preparation of dichloro(duryl)phosphine followed by addition of mesitylmagnesium bromide in a manner similar to the preparation of **5aP** afforded **6aP** in 56% yield. **6aP**: colorless prisms (EtOH−benzene); mp 214.0−215.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.79 (4H, d, J_{PH} = 3.1 Hz), 2.37 (6H, s), 2.26 (6H, s), 2.14 (6H, s), 2.02 (12H, s); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 142.24 (d, J_{PC} = 17.6 Hz), 139.55 (d, J_{PC} = 18.1 Hz), 137.50 (s), 136.19 (d, J_{PC} = 18.3 Hz), 133.92 (d, J_{PC} = 4.0 Hz), 131.61 (d, J_{PC} = 18.4 Hz), 130.09 (s), 129.73 (d, J_{PC} = 3.5 Hz), 22.73 (d, J_{PC} = 16.1 Hz), 21.66 (d, J_{PC} = 1.7 Hz), 20.93 (d, J_{PC} = 19.6 Hz), 20.89 (s); ^{31}P NMR (81 MHz, $CDCl_3$) δ −31.6 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 482 (M^+ + 2; 47), 480 (M^+; 44), 467 (M^+ + 2 − Me; 95), 465 (M^+ − Me;100), 401 (M^+ − Br; 10), 119 (Mes^+; 16); HRMS (70 eV, EI) found *m*/*z* 480.1575, calcd for $C_{28}H_{34}PBr$, M, 480.1581. Anal. Calcd for $C_{28}H_{34}PBr$: C, 69.85; H, 7.12; Br, 16.60. Found: C, 70.24; H, 7.23; Br, 16.10.

(4-Bromoduryl)dimesitylarsine (6aA). Successive addition of mesitylmagnesium bromide (2 equiv) and 4-bromodurylmagnesium bromide to a solution of arsenic trichloride in a manner similar to the preparation of **5aA** afforded **6aA** in 27% yield. **6aA**: colorless prisms (EtOH), mp 216.0−217.0 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.79 (4H, s), 2.38 (6H, s), 2.26 (6H, s), 2.23 (6H, s), 2.12 (12H, s); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ 142.56, 141.19, 139.69, 137.46, 136.14, 134.03, 129.96, 129.59, 23.05, 21.80, 21.63, 20.82; LRMS (70 eV, EI) *m*/*z* (rel intensity) 526 (M^+ + 2; 100), 524 (M^+; 99), 446 (M^+ + 1 − Br; 21), 406 (M^+ + 2 − Mes − 1; 7),

404 ($M^+ - Mes^+ - 1$; 7), 313 (Mes_2As^+; 18), 119 (Mes; 15); HRMS (70 eV, EI) found *m*/*z* 524.1047, calcd for $C_{28}H_{34}AsBr$, M, 524.1060.

(4-Iododuryl)dimesitylphosphine (6bP). Iodination of **6aP** in a manner similar to the preparation of **5bP** afforded **6bP** in 68% yield. **6bP**: colorless solid, mp 221.0−221.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.79 (4H, d, J_{PH} = 3.3 Hz), 2.48 (6H, s), 2.26 (6H, s), 2.18 (6H, s), 2.03 (12H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 142.30 (d, J_{PC} = 17.8 Hz), 138.84 (d, J_{PC} = 18.0 Hz), 137.56 (s), 137.50 (d, J_{PC} = 3.8 Hz), 137.43 (d, J_{PC} = 18.7 Hz), 131.64 (d, J_{PC} = 18.4 Hz), 129.77 (d, J_{PC} = 3.5 Hz), 113.14 (s), 28.38 (d, J_{PC} = 1.9 Hz), 22.77 (d, J_{PC} = 16.1 Hz), 21.72 (d, J_{PC} = 19.6 Hz), 20.92 (s); ^{31}P NMR (81 MHz, $CDCl_3$) δ −31.5 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 528 (M^+; 100), 513 ($M^+ - Me$; 92); HRMS (70 eV, EI) found *m*/*z* 528.1447, calcd for $C_{28}H_{34}PI$, M, 528.1443. Anal. Calcd for $C_{28}H_{34}PI$: C, 63.64; H, 6.48; I, 24.02. Found: C, 63.84; H, 6.47; I, 23.82.

(4-Iododuryl)dimesitylarsine (6bA). Iodination of **6aA** in a manner similar to the preparation of **5bP** afforded **6bA** in 93% yield. **6bA**: colorless plates (EtOH−dichloromethane), mp 211.0−211.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 (4H, s), 2.48 (6H, s), 2.271 (6H, s), 2.266 (6H, s), 2.13 (12H, s); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 142.60, 142.52, 139.05, 137.64, 137.52, 136.18, 129.63, 113.09, 28.36, 23.10, 22.63, 20.86; LRMS (70 eV, EI) *m*/*z* (rel intensity) 572 (M^+; 100), 313 (M^+ − DurylI; 9), 119 (Mes^+; 7); HRMS (70 eV, EI) found *m*/*z* 572.0927, calcd for $C_{28}H_{34}AsI$, M, 572.0922.

Bis(4-bromoduryl)mesitylphosphine (7). Preparation of chlorodidurylphosphine followed by addition of mesitylmagnesium bromide in a manner similar to the preparation of **5aP** afforded **7** in 15% yield. **7**: colorless prisms (EtOH−benzene); mp 216.0−217.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.82 (2H, d, J_{PH} = 3.3 Hz), 2.40 (12H, s), 2.28 (3H, s), 2.14 (12H, s), 2.03 (6H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 141.97 (d, J_{PC} = 17.9 Hz), 139.21 (d, J_{PC} = 18.3 Hz), 137.64 (s), 136.28 (d, J_{PC} = 18.9 Hz), 134.11 (d, J_{PC} = 3.9 Hz), 131.91 (d, J_{PC} = 17.9 Hz), 130.17 (s), 129.87 (d, J_{PC} = 3.5 Hz), 22.86 (d, J_{PC} = 15.7 Hz), 21.74 (d, J_{PC} = 1.7 Hz), 20.92 (s), 20.89 (d, J_{PC} = 19.1 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ −27.9 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 576 ($M^+ + 4$; 32), 574 ($M^+ + 2$; 59), 572 (M^+; 31), 561 ($M^+ + 4 - Me$; 52), 559 ($M^+ + 2 - Me$; 100), 557 ($M^+ - Me$; 52), 493 ($M^+ + 2 - Br$; 19), 493 ($M^+ - Br$; 21), 119 (Mes^+; 13).

Tris(4-bromoduryl)phosphine (8). Addition of 3 equiv of 4-bromodurylmagnesium bromide in THF to a THF solution of phosphorus trichloride at −78 °C in a manner similar to the preparation of **5aP** afforded **8** almost quantitatively. **8**: colorless plates (EtOH−benzene), mp 262.0−262.5 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.39 (18H, s), 2.11 (18H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 138.87 (d, J_{PC} = 18.4 Hz), 136.54 (d, J_{PC} = 18.9 Hz), 134.26 (s), 130.20 (s), 21.75 (s, Me-*m*), 20.91 (d, J_{PC} = 18.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ −24.4 (s); ^{31}P NMR (81 MHz, $CDCl_3$/THF) δ −25.1 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 670 ($M^+ + 6$; 40), 668 ($M^+ + 4$; 100), 666 ($M^+ + 2$; 91), 664 (M^+; 39), 655 ($M^+ + 6 - Me$; 38), 653 ($M^+ + 4 - Me$; 93), 651 ($M^+ + 2 - Me$; 90), 649 ($M^+ - Me$; 26), 589 ($M^+ + 4 - Br$; 25), 587 ($M^+ + 2 - Br$; 49), 585 ($M^+ - Br$; 20); HRMS (70 eV, EI) found *m*/*z* 664.0106, calcd for $C_{30}H_{36}PBr_3$, M, 664.0105.

Bis(3-bromomesityl)mesitylarsine (9). Successive addition of 3-bromomesitylmagnesium bromide (1.0 equiv) and mesitylmagnesium bromide (3 equiv) to a solution of arsenic trichloride in a manner similar to the preparation of **5aA** afforded **2** (27%), **5aA** (9%), and **9** (14%). **9**: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.94 (2H, s), 6.87 (2H, s), 2.46 (6H, s), 2.44 (6H, s), 2.32 (3H, s), 2.20 (6H, s), 2.18 (6H, s); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 142.46, 141.61, 141.14, 139.02, 138.13, 137.91, 135.53, 131.03, 129.84, 126.87, 24.20, 24.19, 23.13, 22.95, 20.85; LRMS (70 eV, EI) *m*/*z* (rel intensity) 592 ($M^+ + 4$; 54), 590 ($M^+ + 2$; 100), 588 (M^+; 49), 512 ($M^+ + 2 - Br$; 6), 510 ($M^+ - Br$; 5), 119 (Mes^+; 16); HRMS (70 eV, EI) found *m*/*z* 588.0033, calcd for $C_{27}H_{31}AsBr_2$, M, 588.0008.

Dimesityl(3-phenothiazinomesityl)phosphine (3bP). A mixture of phenothiazine (101 mg, 0.509 mmol), **5bP** (243 mg, 0.473 mmol), K_2CO_3 (275 mg, 1.99 mmol), copper powder (67.4 mg, 1.06 mmol), 18-crown-6 (13.7 mg, 0.0518 mmol), and 1,2,4-trichlorobenzene (3 mL) was degassed by pumping and refluxed for 84 h under argon atmosphere. After being cooled to room temperature, the inorganic salts were removed by passing through a short alumina column (eluent: dichloromethane). The solvent was removed by evaporation, and the residue was chromatographed over silica gel (eluent: hexane−triethylamine = 100:1, hexane−dichloromethane−triethylamine = 700:100:7) to give **3bP** (144 mg, 0.246 mmol) in 52% yield. **3bP**: colorless solid, mp 175.0−176.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (lH, d, J_{PH} = 3.5 Hz), 6.85 (2H, dd, J_{HH} = 7.4 Hz, J_{HH} = 1.4 Hz), 6.80 (4H, brs), 6.76 (2H, td, J_{HH} = 7.7 Hz, J_{HH} = 1.5 Hz), 6.70 (2H, td, J_{HH} = 7.4 Hz, J_{HH} = 1.0 Hz), 5.84 (2H, dd, J_{HH} = 8.1 Hz, J_{HH} = 0.8 Hz), 2.26 (6H, s), 2.19 (3H, s), 2.18 (3H, s), 2.11 (12H, s), 2.01 (3H, s); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 143.10 (d, J_{PC} = 14.1 Hz), 142.98 (d, J_{PC} = 12.1 Hz), 142.43 (d, J_{PC} = 16.0 Hz), 141.18 (s), 138.03 (s), 137.80 (s), 135.89 (d, J_{PC} = 21.6 Hz), 135.79 (s), 132.16 (brs), 130,93 (d, J_{PC} = 17.8 Hz), 129.83 (brs), 127.04 (s), 126.24 (s), 121.94 (s), 118.26 (s), 113.89 (s), 22.75 (d, J_{PC} = 16.2 Hz), 20.91 (s), 18.06 (s), 17.12 (d, J_{PC} = 14.9 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ −33.4 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 585 (M^+; 100), 570 ($M^+ - Me$; 44), 198 (phenothiazine$^+$; 11); HRMS (70 eV, EI) found *m*/*z* 585.2624, calcd for $C_{39}H_{40}NPS$, M, 585.2619.

Bis(4-*tert*-butylphenyl)[3-(dimesitylarsino)mesityl]amine (3aA). The Ullmann coupling of **5bA** with bis(4-*tert*-butylphenyl)amine in refluxing 1,2-dichlorobenzene for 120 h in a manner similar to the preparation of **3bP** afforded **3aA** in 91% yield. **3aA**: colorless crystals; mp 280.5−281.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (4H, md, J_{HH} = 8.9 Hz), 6.92 (1H, s), 6.85 (4H, md, J_{HH} = 8.9 Hz), 6.76 (4H, s), 2.23 (6H, s), 2.21 (3H, s), 2.15 (12H, s), 1.97 (3H, s), 1.88 (3H, s), 1.29 (18H, s); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 143.34, 142.98, 142.86, 142.69, 141.53, 141.43, 139.20, 137.83, 137.40, 135.82, 131.59, 129.52, 125.56, 118.61, 34.00, 31.42, 23.07, 23.06, 20.81, 18.72, 18.67; HRMS (70 eV, EI) found *m*/*z* 711.3787, calcd for $C_{47}H_{58}AsN$, M, 711.3785. Anal. Calcd for $C_{47}H_{58}AsN$: C, 79.30; H, 8.21; N, 1.97. Found: C, 79.14; H, 8.32; N, 2.01.

Dimesityl(3-phenothiazinomesityl)arsine (3bA). The Ullmann coupling of **5bA** with phenothiazine in refluxing 1,2,4-trichlorobenzene for 70 h in a manner similar to the preparation of **3bP** afforded **3bA** in 40% yield. **3bA**: colorless solid, mp 97.0−98.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (1H, s), 6.85 (2H, dd, J_{HH} = 7.5 Hz, J_{HH} = 1.6 Hz), 6.79 (4H, s), 6.75 (2H, td, J_{HH} = 7.7 Hz, J_{HH} = 1.6 Hz), 6.70 (2H, td, J_{HH} = 7.4 Hz, J_{HH} = 1.3 Hz), 5.82 (2H, dd, J_{HH} = 8.2 Hz, J_{HH} = 1.2 Hz), 2.29 (3H, s), 2.25 (3H, s), 2.18 (12H, s), 2,17 (3H, s), 2.07 (3H, s); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 143.37, 143.29, 142.64, 141.12, 140.17, 137.96, 137.67, 135.73, 135.50, 132.03, 129.69, 127.03, 126.23, 121.93, 118.22, 113.85, 23.19, 23.11, 20.83, 17.95, 17.86; LRMS (70 eV, EI) *m*/*z* (rel intensity) 629 (M^+; 100), 510 ($M^+ - Mes$; 4), 198 (phenothiazine$^+$; 11), 119 (Mes^+; 5); HRMS (70 eV, EI) found *m*/*z* 629.2098, calcd for $C_{39}H_{40}NSAs$, M, 629.2098.

Bis(4-methoxyphenyl)[3-(dimesitylarsino)mesityl]amine (3cA). The Ullmann coupling of **5bA** with bis(4-methoxyphenyl)amine in refluxing 1,2-dichlorobenzene for 133 h in a manner similar to the preparation of **3bP** afforded **3cA** in 69% yield. **3cA**: colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.89 (1H, s), 6.81 (4H, md, J_{HH} = 9.4 Hz), 6.75 (4H, s), 6.72 (4H, md, J_{HH} = 9.4 Hz), 3.76 (6H, s), 2.23 (6H, s), 2.18 (3H, s), 2.13 (12H, s), 1.97 (3H, s), 1.92 (3H, s); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ 153.34, 142.92, 142.66,

141.45, 141.40, 140.05, 139.23, 137.71, 137.43, 135.77, 131.71, 129.55, 120.05, 114.26, 55.49, 23.11, 22.64, 20.84, 18.72, 18.55; LRMS (70 eV, EI) *m*/*z* (rel intensity) 659 (M^+; 100).

Dimesityl(4-phenothiazinoduryl)phosphine (4bP). The Ullmann coupling of **6bP** with phenothiazine for 72 h in a manner similar to the preparation of **3bP** afforded **4bP** in 42% yield. **4bP**: colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (2H, dd, J_{HH} = 7.5 Hz, J_{HH} = 1.6 Hz), 6.83 (4H, d, J_{PH} = 3.2 Hz), 6.77 (2H, td, J_{HH} = 7.7 Hz, J_{HH} = 1.6 Hz), 6.72 (2H, td, J_{HH} = 7.4 Hz, J_{HH} = 1.3 Hz), 5.81 (2H, dd, J_{HH} = 8.1 Hz, J_{HH} = 1.2 Hz), 2.28 (6H, s), 2.16 (6H, s), 2.11 (12H, s), 2.10 (6H, s); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 142.34 (d, J_{PC} = 16.9 Hz), 141.59 (s), 140.91 (d, J_{PC} = 18.0 Hz), 137.650 (s), 137.647 (d, J_{PC} = 19.6 Hz), 137.31(s), 134.07 (d, J_{PC} = 4.1 Hz), 131.76 (d, J_{PC} = 18.6 Hz), 129.85 (s), 127.11 (s), 126.29 (s), 121.98 (s), 118.41 (s), 114.30 (s), 22.79 (d, J_{PC} = 16.1 Hz), 20.93 (s), 19.87 (d, J_{PC} = 18.1 Hz), 15.44 (d, J_{PC} = 1.5 Hz); ^{31}P NMR (81 MHz, $CDCl_3$) δ −32.0 (s); LRMS (70 eV, EI) *m*/*z* (rel intensity) 559 (M^+; 100). 584 (M^+ − Me; 49), 331 (M^+ − Mes_2P + 1; 9), 198 (phenothiazine$^+$; 12); HRMS (70 eV, EI) found *m*/*z* 599.2764, calcd for $C_{40}H_{42}NPS$, M, 599.2776.

Bis(4-*tert*-butylphenyl)[4-(dimesitylarsino)duryl]amine (4aA). The Ullmann coupling of **6bA** with bis(4-*tert*-butylphenyl)amine in refluxing 1,2-dichlorobenzene for 186 h in a manner similar to the preparation of **3bP** afforded **4aA** in 70% yield. **4aA**: colorless crystals, mp 131.5−133.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (4H, d, J_{HH} = 8.6 Hz), 6.88 (4H, d, J_{HH} = 8.6 Hz), 6.81 (4H, s), 2.27 (6H, s), 2.18 (12H, s), 2.17 (6H, s), 1.94 (6H, s), 1.30 (18H, s); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 143.60, 142.73, 142.69, 140.77, 140.23, 137.35, 136.64, 134.38, 129.60, 125.63, 118.60, 34.04, 31.46, 23.13, 20.87, 20.63, 15.75.

Dimesityl(4-phenothiazinoduryl)arsine (4bA). The Ullmann coupling of **6bA** with phenothiazine in refluxing nitrobenzene for 1.5 h in a manner similar to the preparation of **3bP** afforded **4bA** in 37% yield. **4bA**: colorless solid; mp 116−118 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.93 (2H, dd, J_{HH} = 7,5 Hz, J_{HH} = 1.5 Hz), 6.86 (4H, s), 6.81 (2H, td, J_{HH} = 7.7 Hz, J_{HH} = 1.4 Hz), 6.75 (2H, td, J_{HH} = 7.4 Hz, J_{HH} = 1.2 Hz), 5.86 (2H, dd, J_{HH} = 8.1 Hz, J_{HH} = 1.1 Hz), 2.31 (6H, s), 2.28 (6H, s), 2.23 (12H, s), 2.14 (6H, s); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 142.61, 142.52, 141.58, 140.99, 137.55, 137.24, 136.27, 134.14, 129.69, 127.08, 126.27, 121.97, 118.42, 114.32, 23.14, 20.86, 20.63, 15.45; LRMS (70 eV, EI) *m*/*z* (rel intensity) 643 (M^+; 100), 524 (M^+ − Mes; 4), 198 (phenothiazine$^+$; 6); HRMS (70 eV, EI) found *m*/*z* 643.2271, calcd for $C_{40}H_{42}NSAs$, M, 643.2254.

X-ray Crystallography. All measurements were made on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The data were collected at a temperature of 23 °C using the ω−2θ scan technique to a maximum 2θ value of 50.0°. An empirical absorption correction based on azimuthal scans of several reflections was applied. The structure was solved by direct methods (SIR92),[30] expanded using Fourier techniques (DIRDIF94),[31] and refined by full matrix least squares on F^2 for all unique reflections. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Structure solution, refinement, and graphical representation were carried out using the teXsan package.[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Data Centre as supplementary publication nos. CCDC-26082 and -26083 for **8** and **6bA**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystal Data for 6bA. $C_{28}H_{34}AsI$, M = 572.40, colorless prism grown from ethanol−chloroform, crystal dimensions 0.75 × 0.45 × 0.15 mm^3. Triclinic, space group $P\bar{1}$ (#2), a = 10.764(1) Å, b = 14.461(2) Å, c = 8.748(1) Å, α = 103.961(9)°, β = 101.889(9)°, γ = 97.284(9)°, V = 1270.6(3) Å^3, Z = 2, ρ_{calcd} = 1.496 g cm^{-3}, μ = 2.566 mm^{-1}, F(000) = 576.00. Number of reflections measured was 4727 ($2\theta_{max}$ = 50.0°) of which 4466 were unique, with R_{int} = 0.026, and 3599 were larger than threshold [$I > 2.00\sigma(I)$]. Number of variables was 271. R = 0.070, R_w = 0.146, and goodness of fit S = 1.94 for all. R_1 = 0.047 for [$I > 2.00\sigma(I)$]. Maximum and minimum peaks on the final difference Fourier map corresponded to 0.83 and −1.23 e Å^{-3}, respectively.

Crystal Data for 8. $C_{30}H_{36}PBr_3$, M = 667.30, colorless prism grown from ethanol−benzene, crystal dimensions 0.70 × 0.30 × 0.10 mm^3. Monoclinic, space group $P2_1/c$ (#14), a = 9.812(2) Å, b = 21.432(3) Å, c = 13.712(2) Å, β = 100.06(1)°, V = 2839.4(8) Å^3, Z = 4, ρ_{calcd} = 1.561 g cm^{-3}, μ = 4.349 mm^{-1}, F(000) = 1344.00. Number of reflections measured = 5491 ($2\theta_{max}$ = 50.0°) of which 5015 were unique with R_{int} = 0.022, and 3356 were larger than threshold [$I > 2.00\sigma(I)$]. Number of variables was 307. R = 0.068, R_w = 0.114, and goodness of fit S = 1.36 for all. R_1 = 0.050 for [$I > 2.00\sigma(I)$]. Maximum and minimum peaks on the final difference Fourier map corresponded to 1.17 and −0.91 e Å^{-3}, respectively.

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Supporting Information Available: Experimental details, ^{1}H NMR spectra, cyclic voltammograms of **3aA**, **3cA**, and **4aA**, EPR spectra of cation radicals of **1**, **2**, **3bP**, and **3bA**, and crystallographic information files (CIF) of **6bA** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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