Cationic Complexes of Antimony(III) and Bismuth(III) Stabilized by Intra- or Intermolecular Coordination

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Three cationic aryl−antimony and −bismuth complexes stabilized by intra- or intermolecular coordination have been prepared. Treatment of either $SbAr_2Cl$ or $BiAr_2Cl$ (Ar = 2-[(dimethylamino)methyl]phenyl, 2-(Me_2NCH_2)C_6H_4) with $TlPF_6$ afforded [$SbAr_2$][PF_6] (**1**) or [$BiAr_2$][PF_6] (**2**), respectively. A related complex, [$SbPh_2${$OP(NMe_2)_3$}$_2$][PF_6] (**5**), stabilized by intermolecular coordination, was prepared *via* the reaction of $SbPhCl_2$ with 2 equiv of $TlPF_6$ in the presence of an excess of $OP(NMe_2)_3$. The X-ray crystal structures of compounds **1**, **2**, and **5** are described; the coordination geometry at the group 15 element center in each new compound was found to be distorted trigonal bipyramidal.

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Introduction

In a recent series of papers[1−3] we have reported the first examples of a range of cationic, 4-coordinate, 10-electron diarylbismuth(III) and bis(organotransition metal)bismuth(III) monocations. By means of X-ray crystallography, it was established that the stereochemistry of cations of the general type $[BiR_2(L)_2]^+$ (where R = Ph, L = $OPPh_3$, $OP(NMe_2)_3$; R = mesityl, L = $OP(NMe_2)_3$)[1,2] conforms to expectation in the sense that the bismuth center adopts an equatorially vacant trigonal-bipyramidal coordination geometry with the L ligands and aryl groups in axial and equatorial sites, respectively. Most of the other known structurally characterized bismuth or antimony monocations feature the coordination of a dihalide unit, $[EX_2]^+$ (E = Sb, Bi; X = halide), by a polydentate oxygen or nitrogen donor ligand. Examples include the crown ether complexes $[SbCl_2(18\text{-crown-}6)]^+$,[4] $[BiCl_2(18\text{-crown-}6)]^+$,[5] $[BiBr_2(18\text{-crown-}6)]^+$,[6] and $[BiCl_2(MeCN)(18\text{-crown-}6)]^+$,[7] the polyether complexes $[BiBr_2(\text{hexa(ethylene glycol)})]^+$ and $[BiBr_2(\text{penta(ethylene glycol)})]^+$,[6] and a cation stabilized by an aza macrocyclic ligand, $[SbCl_2(Me_3[9]aneN_3)]^+$.[8] Each of the foregoing examples features a bent $[EX_2]^+$ moiety, as is also found in the arene complex $[BiCl_2(C_6Me_6)][AlCl_4]$.[9] Linear $[EX_2]^+$ coordination is possible, however, as exemplified by $[BiI_2\{OP(NMe_2)_3\}_4]^+$ [10] and $[BiI_2(py)_3(dppmO_2)]^+$ (py = pyridine, $dppmO_2$ = $Ph_2P(O)CH_2(O)PPh_2$).[2] Further pertinent examples of bismuth or antimony monocations include the dimeric species $[Bi_2(\mu\text{-}Cl)_2Cl_2(tu)_6]^{2+}$ (tu = thiourea)[11] and $[Sb_2Cl_2(NPPh_3)_2(CH_3CN)_4]^{2+}$ [12] and the octahedral catecholate cation $[Sb(O_2C_6H_4)(phen)_2]^+$ (phen = 1,10-phenanthroline).[13] Each of the monocations listed above involves some degree of base stabilization, and it is only very recently that $[Cp^*{}_2Sb]^+$ and $[Cp'''{}_2Sb]^+$ (Cp* = pentamethylcyclopentadienyl, Cp‴ = 1,2,4-tri-*tert*-butylcyclopentadienyl), the first examples of base-free stibocenium cations, have been reported.[14]

Information on dications of the heavier group 15 elements is somewhat sparse. Of the three structurally authenticated dications, two of them, $[SbCl(15\text{-crown-}5)]^{2+}$ [7] and $[BiCl(MeCN)_2(18\text{-crown-}6)]^{2+}$,[7] involve coordination by a crown ether. The third example, $[BiPh\{OP(NMe_2)_3\}_4]^{2+}$,[2] features stabilization of the highly electrophilic $[BiPh]^{2+}$ moiety by coordination of four $OP(NMe_2)_3$ ligands. Interestingly, some structurally characterized bismuth and antimony trications have been previously reported, including the octahedral species $[Bi(dmpu)_6]^{3+}$ (dmpu = *N*,*N′*-dimethylpropylene urea),[15] $[Bi(tu)_6]^{3+}$,[16] and $[Bi(aptu)_6]^{3+}$ (aptu = 1-allyl-3-(2-pyridyl)thiourea-*S*)[17] and the crown ether complexes $[M(12\text{-crown-}4)_2(MeCN)]^{3+}$ (M = Sb, Bi).[18]

In the present contribution, we describe the synthesis and X-ray structures of three cationic aryl−bismuth

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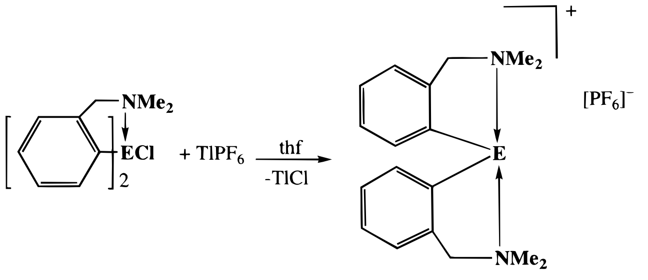
Scheme 1



E = Sb (**1**) and Bi (**2**)

and −antimony complexes stabilized by intra- or intermolecular coordination. Our motivation for the preparation and structural characterization of these cationic complexes of the heavier group 15 elements stemmed from two main considerations. First, we were interested in investigating the differences resulting from the presence of intra- versus intermolecular stabilization of the cations, and second, we wished to attempt the preparation of further examples of cationic compounds of the heavier group 15 elements with low coordination numbers.

Results and Discussion

The colorless crystalline compounds **1** and **2** were prepared *via* the reaction between $TlPF_6$ and the appropriate diarylelement monochloride in thf solution at room temperature (Scheme 1). Elemental analytical data, together with ^1H and ^{13}C NMR spectroscopic data for both **1** and **2**, were consistent with the anticipated formulas. However, in order to reveal the extent to which the NMe_2 groups were coordinated to the group 15 element centers, it was necessary to determine the structures of these compounds by X-ray crystallography. Although they are not isomorphous, both **1** and **2** crystallize in the monoclinic space group $P2_1/c$ or $P2_1/n$ with $Z = 4$. The solid-state structures of both compounds comprise $[EAr_2]^+$ (Ar = 2-[(dimethylamino)methyl]phenyl, 2-$(Me_2NCH_2)C_6H_4$) cations ($\mathbf{1}^+$, E = Sb; $\mathbf{2}^+$, E = Bi) and hexafluorophosphate anions (the $[PF_6]^-$ anion is disordered in the structure of **2**). In the case of **1**, the ion pairs are well-separated, as evidenced by the observation that the closest Sb···F contact is 4.806 Å. Interestingly, the closest interionic contact in **2** is much shorter (Bi···F = 3.49 Å). Examination of the structure of cation $\mathbf{1}^+$ (Figure 1) reveals that both amine arms are coordinated strongly to the Sb center, the two Sb−N bond lengths being identical within experimental error (2.414(3) Å). Overall, the coordination geometry of $\mathbf{1}^+$ is that of an equatorially vacant trigonal bipyramid in which the axial and equatorial sites are occupied by amine nitrogen atoms and the *ipso* carbon atoms of the aryl ligands, respectively, although all the bond angles are less than ideal trigonal-bipyramidal values (Table 1). Thus, the N(1)−Sb−N(2) bond angle is 163.72(1)° rather than 180° and the C(1)−Sb−C(10) bond angle of 95.7(1)° is considerably less than 120°. The former angular diminution results primarily from the constraints imposed by the bidentate ligands, whereas the latter is typical for heavier element complexes with this geometry and reflects the stereochemical activity of the equatorially disposed antimony lone pair. It is of interest to compare the structure of $\mathbf{1}^+$ with that of the precursor chloride, $SbAr_2Cl$ (**3**).[19] The most conspicuous difference is that only one of the amine arms is coordinated in the case of **3**. However, both species adopt equatorially vacant trigonal-bipyramidal structures, the interrelationship between them being that one of the amine arms in $\mathbf{1}^+$ is replaced by a chloride ligand in **3**. As expected, the Sb−N bond lengths in $\mathbf{1}^+$ (average 2.414(4) Å) are slightly shorter than those in **3** (2.463(2) Å) due to the more electrophilic nature of the antimony center in the cation.

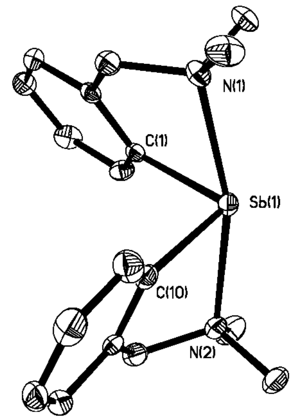


Figure 1. View of the structure of $\mathbf{1}^+$ showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted.

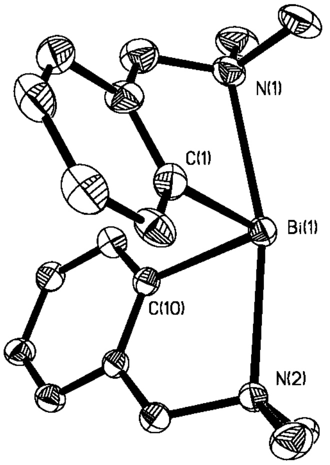


Figure 2. View of the molecular structure of the cation $\mathbf{2}^+$ showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted.

Even though **1** and the bismuth analogue, **2**, are not isomorphous, the structures of the cations are very similar (Figure 2 and Table 1) and the comments that were made concerning the pattern of bond angles in $\mathbf{1}^+$ are pertinent to $\mathbf{2}^+$ also. The structural interrelationships between $\mathbf{2}^+$ and the precursor chloride, $BiAr_2Cl$ (**4**),[19] are also similar to those of the analogous antimony species. As anticipated, the Bi−N bond lengths in $\mathbf{2}^+$ (average 2.500(1) Å) are slightly shorter than those in **4**[19] (2.570(5) Å). Interestingly, the Bi−N bond length in $\mathbf{2}^+$ is identical with that in the dihalide $BiArI_2$[19] (2.503(4) Å) within experimental error.

In general, the geometries of $\mathbf{1}^+$ and $\mathbf{2}^+$ are similar to those of the type $[BiR_2(L)_2]^+$ which feature monodentate aryl ligands (R) and two-electron donors (L)[1,2] in the sense that they all possess an equatorially vacant

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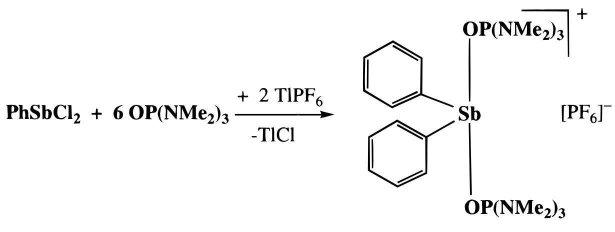
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Compounds 1, 2, and 5

1		2		5	
Sb(1)−C(1)	2.164(4)	Bi(1)−C(1)	2.259(4)	Sb(1)−C(1)	2.140(8)
Sb(1)−C(10)	2.165(4)	Bi(1)−C(10)	2.253(2)	Sb(1)−C(7)	2.138(1)
Sb(1)−N(1)	2.412(3)	Bi(1)−N(1)	2.509(1)	Sb(1)−O(1)	2.236(7)
Sb(1)−N(2)	2.416(4)	Bi(1)−N(2)	2.491(1)	Sb(1)−O(2)	2.231(7)
C(1)−Sb(1)−C(10)	95.7(1)	C(1)−Bi(1)−C(10)	91.6(5)	C(1)−Sb(1)−C(7)	95.6(4)
C(1)−Sb(1)−N(1)	74.4(1)	C(1)−Bi(1)−N(1)	73.0(5)	C(1)−Sb(1)−O(1)	84.5(5)
C(10)−Sb(1)−N(1)	94.2(1)	C(10)−Bi(1)−N(1)	95.8(4)	C(7)−Sb(1)−O(1)	88.8(3)
C(1)−Sb(1)−N(2)	94.5(1)	C(1)−Bi(1)−N(2)	95.4(5)	C(1)−Sb(1)−O(2)	87.9(5)
C(10)−Sb(1)−N(2)	74.8(1)	C(10)−Bi(1)−N(2)	74.3(4)	C(7)−Sb(1)−O(2)	84.1(3)
N(1)−Sb(1)−N(2)	163.72(1)	N(1)−Bi(1)−N(2)	164.8(4)	O(1)−Sb(1)−O(2)	169.1(3)

Scheme 2



(5)

trigonal-bipyramidal geometry. In the cases of 1^+ and 2^+, the angular distortions are more pronounced because of the constraints of bidentate ligation.

Since it had proved possible[2] to isolate a bismuth dication by treatment of $BiPhBr_2$ with $TlPF_6$ in the presence of an excess of $OP(NMe_2)_3$, a similar approach seemed appropriate in our quest for a comparable antimony dication. However, as shown in Scheme 2, the reaction of $SbPhCl_2$[20] with $TlPF_6$ and $OP(NMe_2)_3$ afforded an antimony monocation salt of formula $[SbPh_2\{OP(NMe_2)_3\}_2][PF_6]$ (**5**) rather than the targeted dication salt $[SbPh\{OP(NMe_2)_3\}_x][PF_6]_2$. Clearly, an aryl−halide redistribution reaction is involved in the formation of **5**. Such reactions are, in fact, commonly encountered in the solution chemistry of arylantimony and arylbismuth halides.[21] Preliminary characterization of **5** was provided both by a satisfactory elemental analysis and by integration of the phenyl and $OP(NMe_2)_3$ ^1H NMR resonances, but in order to confirm the structural assignment, an X-ray crystallographic study was carried out. Compound **5** crystallizes in the orthorhombic space group $Pna2_1$ with $Z = 4$ and consists of $[SbPh_2\{OP(NMe_2)_3\}_2]^+$ (5^+) and hexafluorophosphate anions; there are no unusually short interionic contacts. While they are not isomorphous, the structure of **5** bears a close resemblance to those of $[BiPh_2\{OP(NMe_2)_3\}_2][PF_6]$ (**6**)[2] and $[BiPh_2\{OP(NMe_2)_3\}_2][BF_4]$ (**7**).[2] Like those of 1^+ and 2^+, the geometry of 5^+ at the group 15 center is equatorially vacant trigonal bipyramidal (Figure 3 and Table 1), the equatorial and axial sites being occupied by phenyl groups and $OP(NMe_2)_3$ ligands, respectively. Interestingly, the C−Sb−C bond angle (95.6(4)°) and the average Sb−C bond length (2.139(8) Å) in 5^+ are very similar to those in 1^+ (95.7(1)° and 2.164(4) Å), even though the aryl groups are bidentate in the latter. However, as expected, the axial bond angle in 5^+ (169(3)°) is somewhat closer to 180° than that in 1^+ (163.72(1)°). Finally, in comparing the structure of 5^+ with those of the related bismuth cations 6^+ and 7^+, one finds considerable variation in the E−O−P bond angles. For example, in the case of 5^+ these angles differ by over 5° (140.1(5) and 134.0(4)° for Sb(1)−O(1)−P(1) and Sb(1)−O(2)−P(2), respectively). As pointed out previously,[2] such differences reflect a relatively soft E−O−P angular deformation potential and a consequent sensitivity to crystal-packing forces.

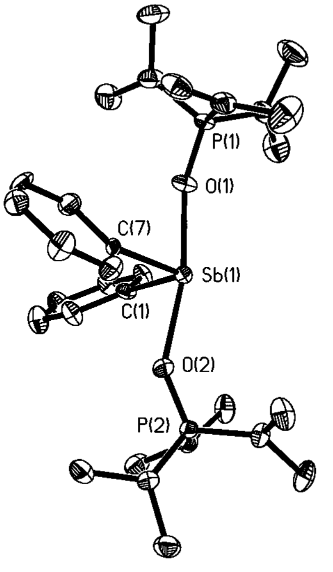


Figure 3. View of the molecular structure of the cation 5^+ showing the atom-numbering scheme. Ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted.

In conclusion, it has been demonstrated that antimony(III) and bismuth(III) monocations can be synthesized when stabilized by either intra- or intermolecular coordination by Lewis basic moieties. However, the attempt to prepare a dicationic complex of antimony(III) was unsuccessful due to complications that arose on account of a facile redistribution reaction.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free dinitrogen or argon atmosphere using standard Schlenk techniques or an Innovative Technology System One-M drybox. Unless otherwise stated, all solvents were dried over sodium and distilled from sodium benzophenone ketyl under argon prior to use. The reagents $SbAr_2Cl$,[19] $BiAr_2Cl$,[19] and $SbPhCl_2$[20] were prepared according to literature methods. All other reagents were procured commercially and used without further purification. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Physical Measurements. Mass spectra (CIMS) were run on a MAT 4023 instrument, and NMR spectra were recorded on a GE QE-300 spectrometer (^1H, 300.19 MHz; ^{13}C, 75.48 MHz). NMR spectra are referenced to C_6D_6, which was dried over sodium−potassium alloy and distilled prior to use; ^1H and ^{13}C chemical shifts are reported relative to $Si(CH_3)_4$ (0.00 ppm). Melting points were obtained in sealed glass capillaries under argon and are uncorrected.

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Table 2. Crystal Data and Details of Intensity, Measurement, and Structure Refinement for 1, 2, and 5

	1	2	5
formula	$C_{18}H_{24}F_6N_2PSb$	$C_{18}H_{24}F_6N_2PBi$	$C_{28}H_{54}F_6N_6O_3P_3Sb$
fw	535.11	622.34	851.43
temp, K	153(2)	298(2)	153(2)
λ, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$Pna2_1$
a, Å	11.926(5)	7.5114(7)	16.6783(1)
b, Å	14.094(4)	27.224(3)	14.9964(1)
c, Å	12.787(4)	10.519(1)	15.5319(1)
β, deg	103.39(3)	92.033(9)	90°
V, Å^3	2091.0(12)	2149.7(4)	3884.8(5)
Z	4	4	4
d(calcd), g/cm^3	1.700	1.923	1.456
abs coeff, cm^{-1}	14.54	83.32	8.99
cryst size, mm	0.14 × 0.14 × 0.11	0.59 × 0.31 × 0.19	0.51 × 0.39 × 0.26
θ range, deg	2.10−27.51	2.45−24.96	2.25−27.50
total no. of rflns	9565	4901	8291
no. of obsd rflns	4797	3749	4954
no. of ref params	261	261	441
GOF on F^2	0.994	1.074	1.016
wR2/R1 [$I > 2\sigma(I)$][a]	0.0716/0.0382	0.1475/0.0500	0.1268/0.0574

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\mathrm{Max}(0,F_o^2)/3 + 2F_c^2/3]$.

Preparations. Compound 1. A sample of $SbAr_2Cl$ (2.145 g, 5.04 mmol) was dissolved in 30 mL of thf to give a pale yellow solution. A solution of $TlPF_6$ (1.76 g, 5.04 mmol) in thf (25 mL) was added dropwise at room temperature, which led to the immediate formation of a white precipitate. The reaction mixture was stirred for 30 min and then filtered through Celite, resulting in a colorless solution which was reduced *in vacuo* to a volume of approximately 10 mL. Cooling of this solution to −20 °C overnight afforded a 79% yield of colorless, crystalline **1** (mp 220−222 °C). Anal. Calcd for $C_{18}H_{24}N_2SbF_6P$: C, 40.40; H, 4.52; N, 5.23. Found: C, 40.20; H, 4.50; N, 5.14. ^1H NMR (C_6D_6): δ 2.76 (s, 12H, NMe_2), 4.10 (s, 4H, CH_2), 7.11−7.68 (m, 8H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.3 (s, CH_3), 68.9 (s, CH_2), 130.0 (s, CH, C_6H_4), 137.3 (s, CH, C_6H_4), 144.5 (s, CH, C_6H_4), 147.6 (s, CH, C_6H_4); *ipso* carbons not detected.

Compound 2. A sample of $BiAr_2Cl$ (0.193 g, 0.376 mmol) was dissolved in thf (15 mL) to give a pale yellow solution. A solution of $TlPF_6$ (0.131 g, 0.376 mmol) in thf (10 mL) was added dropwise at room temperature, which led to the immediate formation of a white precipitate. The reaction mixture was stirred overnight and then filtered through Celite, resulting in a colorless solution which was reduced *in vacuo* to a volume of approximately 5 mL. Hexanes (20 mL) were then added as an overlayer, and solvent diffusion over a period of days at −20 °C resulted in the formation of a white crystalline solid. This solid was redissolved in CH_2Cl_2 (5 mL) and hexanes (15 mL) was added as an overlayer. Solvent diffusion over a period of days at −20 °C afforded a 65% yield of colorless, crystalline **2** (mp 232−234 °C). Anal. Calcd for $C_{18}H_{24}N_2BiF_6P$: C, 34.74; H, 3.90; N, 4.50. Found: C, 34.65; H, 3.60; N, 4.00. HRMS: calcd for $[BiAr_2]^+$ m/z 477.174 337, found 477.172 686. ^1H NMR (C_6D_6): δ 2.83 (s, 12H, NMe_2), 4.25 (s, 4H, CH_2), 7.45 (t, 2H, C_6H_4), 7.62 (t, 2H, C_6H_4), 7.72 (m, 2H, C_6H_4), 8.05 (m, 2H, C_6H_4). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.3 (s, CH_3), 68.9 (s, CH_2), 130.0 (s, CH, C_6H_4), 137.3 (s, CH, C_6H_4), 144.5 (s, CH, C_6H_4), 147.6 (s, CH, C_6H_4); *ipso* carbons not detected.

Compound 5. A sample of hmpa (0.1 mL, 0.575 mmol) was added dropwise to a stirred solution of $SbPhCl_2$ (0.127 g, 0.287 mmol) in thf (5 cm^3) at room temperature, which resulted in a colorless reaction mixture. A solution of $TlPF_6$ (0.113 g, 0.287 mmol) in thf (6 mL) was then added, which resulted in the immediate formation of a white precipitate. The reaction mixture was stirred for 30 min and then filtered through Celite, resulting in a pale yellow solution, which was reduced *in vacuo* to a volume of approximately 5 mL. Cooling of the resulting solution to −20 °C overnight afforded a 50% yield of colorless, crystalline **5** (mp 172−176 °C). Anal. Calcd for $C_{24}H_{46}SbF_6N_6O_2P_3$: C, 36.99; H, 5.95; N, 10.78. Found: C, 36.24; H, 5.67; N, 10.60. HRMS: calcd for $[SbPh_2\{OP(NMe_2)_3\}_2]^+$ m/z 633.219 576, found 633.220 628. ^1H NMR (CD_2Cl_2): δ 2.32 (d, 36H, $OP(NMe_2)_3$), 7.54 (t, 2H, C_6H_5), 7.68 (t, 2H, C_6H_5), 8.22 (d, 2H, C_6H_5). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 36.4 (s, $OP(NMe_2)_3$), 130.0 (s, C, C_6H_5), 133.0 (s, CH, C_6H_5), 134.1 (s, CH, C_6H_5), 150.0 (s, C, C_6H_5).

X-ray Crystallography. Crystallographic data and details of the data collection procedures and structure refinement for **1**, **2**, and **5** are presented in Table 2. Crystals of **2** were grown by solvent diffusion of CH_2Cl_2 and hexanes at −20 °C, whereas **1** and **5** were grown from thf solutions stored at −20 °C. Data sets for **1** and **5** were collected on a Siemens P4 diffractometer at −100 °C, whereas an Enraf-Nonius CAD4 diffractometer was used for the collection of data for **2** at 25 °C. Graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) was used for all structures. Accurate unit cell parameters were determined by recentering 25 optimal high-angle reflections. Three standard reflections were measured every 1800 s during data collection, and no decreases in intensities were noted. Corrections were applied for Lorentz−polarization and absorption (SHELXA[22] for **2** and **5**, face-indexed for **1**) effects. The structures were solved for the heavy atoms by direct methods. The $[PF_6]^-$ anion is disordered in compound **2** (and to some extent in compound **5**); however, this disorder in the anions does not constitute a major problem in the characterization of the cations, which represent the focal point of this work. Subsequent difference syntheses gave all other non-hydrogen atomic positions and these were refined by full-matrix least squares on F^2 using the Siemens SHELXL PLUS 5.0 (PC) software package.[22] All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were included at calculated positions (C−H = 0.96 Å) and were refined using a riding model and a general isotropic thermal parameter.

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Supporting Information Available: Listings of bond distances, bond angles, atomic coordinates, and thermal parameters for **1**, **2**, and **5** (25 pages). Ordering information is given on any current masthead page.

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[22] Sheldrick, G. M. SHELXTL PC Version 5.0; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1994.