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Stereochemical Consequences of the Bismuth Atom Electron Lone Pair, a Comparison between MX_6E and MX_6 Systems. Crystal and Molecular Structures of Tris[*N*-(*P*,*P*-diphenylphosphinoyl)-*P*,*P*-diphenylphosphinimidato]bismuth(III), $[Bi\{(OPPh_2)_2N\}_3]$, -indium(III), $[In\{(OPPh_2)_2N\}_3]\cdot C_6H_6$, and -gallium(III), $[Ga\{(OPPh_2)_2N\}_3]\cdot CH_2Cl_2$

Verónica García-Montalvo,*[†] Raymundo Cea-Olivares,[†] Daniel J. Williams,[‡] and Georgina Espinosa-Pérez[†]

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior,
Ciudad Universitaria, México, 04510 DF, Mexico, and Department of Chemistry,
Kennesaw State College, Marietta, Georgia 30061

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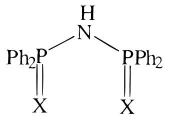
The tetraphenylimidodiphosphinate [*N*-(*P*,*P*-diphenylphosphinoyl)-*P*,*P*-diphenylphosphinimidate] ion forms stable tris-chelates with the Bi(III), In(III), and Ga(III) cations. The crystal and molecular structures of $[M\{(OPPh_2)_2N\}_3]$ (M = Ga, In, Bi) were determined by X-ray diffractometry. The geometry around the bismuth atom in compound **3** displays an approximately C_{3v} symmetry. This arrangement suggests the presence of a stereoactive lone pair of electrons, which is located in one of the triangular octahedral faces. Derivative **3** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 14.006(6)$ Å, $b = 14.185(4)$ Å, $c = 17.609(8)$ Å, $\alpha = 88.45(2)°$, $\beta = 79.34(2)°$, and $\gamma = 78.23(2)°$. The structures of the gallium(III) and indium(III) tris-chelate oxygen-based complexes (**1** and **2**, respectively) were compared with the bismuth analogue in order to determine the ligand steric bulk influence on the coordination sphere in the absence of the electron lone pair. Complex **1** crystallizes as the $[Ga\{(OPPh_2)_2N\}_3]\cdot CH_2Cl_2$ solvate in the triclinic space group $P\bar{1}$; $Z = 2$, $a = 13.534(4)$ Å, $b = 13.855(4)$ Å, $c = 18.732(7)$ Å, $\alpha = 95.48(2)°$, $\beta = 98.26(2)°$, and $\gamma = 97.84(2)°$. Crystal data for the benzene solvate of **2**, $[In\{(OPPh_2)_2N\}_3]\cdot C_6H_6$: triclinic space group $P\bar{1}$, $Z = 2$, $a = 13.542(9)$ Å, $b = 15.622(3)$ Å, $c = 18.063(5)$ Å, $\alpha = 98.21(1)°$, $\beta = 104.77(0)°$, and $\gamma = 92.260(0)°$.

Introduction

Over 30 years after the basic ideas of the valence shell electron pair repulsion (VSEPR) model were first proposed,[1,2] this model continues to have remarkable success explaining the geometry of main group compounds. According to the VSEPR scheme, the MX_6E main group complexes (M = main group element, X = ligand, E = electron lone pair) should have a seven-coordinated structure with the lone pair acting as a pseudoligand. However, some MX_6E species have a regular octahedral geometry, while others have a distorted structure. The geometry of the molecules which fall into the first category is often discussed in terms of an "inert pair of electrons". This chemically inert pair, often implied by the structures of complexes containing a heavy main group atom, has long posed a problem for theorists. At present, several possible explanations, ranging in sophistication from VSEPR to relativistic molecular orbital calculations, have been put forth for various observed structures.[3] Wheeler *et al.* presented a simple picture of the orbital reasons for the lone pair activity or inactivity in some group 15 halides.[3i] It is based on qualitative symmetry and overlap arguments. They found that the "inert pair effect" is favored for electropositive central atoms and electropositive ligands and that the interligand repulsion, the determinant of molecular structure according to VSEPR, also acts to inhibit the distortion.

In an effort to better understand the stereochemical consequences of the lone pair in MX_6E systems, we chose to investigate the structures of three main group metal complexes of the [*N*-(*P*,*P*-diphenylphosphinoyl)-*P*,*P*-diphenylphosphinimidate] ligand, **a**. The imidobis(diphenylphosphinechalcogenide) ligands, $[Ph_2P(X)NP(X)Ph_2]$ {X = O (**a**), S (**b**), Se (**c**)}, seem to be specially suited for testing the stereochemical influence of the electron lone pair in main group derivatives.



a X = O
b X = S
c X = Se

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* Author to whom correspondence should be addressed.

[†] Universidad Nacional Autónoma de México.

[‡] Kennesaw State College.

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They offer the opportunity to vary the donor atoms and possess a wide degree of ring flexibility and ring bite, as evidenced in complexes containing the oxygen ligand showing O···O bite ranging from 3.44 to 2.55 Å.[4]

In this study, we report results of successful single crystal X-ray studies of $[Bi\{(OPPh_2)_2N\}_3]$ (**3**) and the $[In\{(OPPh_2)_2N\}_3]\cdot C_6H_6$ solvate (**2**·C_6H_6). Additionally, we report the synthesis and the X-ray structures of the $[Ga\{(OPPh_2)_2N\}_3]$ solvate (**1**·CH_2Cl_2). The group 13 complexes are reported in order to determine the coordination mode of the imidodiphosphinate entity with these metals and assess the degree of ligand steric bulk influence on the coordination sphere in the absence of the electron lone pair.

Experimental Section

The ^{31}P NMR spectrum was measured on a Varian VXR 300s spectrometer operating at 121 MHz with δ (ppm) scale and using a solution of 85% H_3PO_4 as external reference. The FAB mass spectra were recorded on a 3-nitrobenzyl alcohol support in the positive ion mode on a Jeol JMS-SX102A instrument. The IR spectrum was recorded on a Perkin-Elmer 283B spectrometer, as KBr pellets. Microanalyses were performed by Galbraith Laboratories.

Tris[*N*-(*P*,*P*-diphenylphosphinoyl)-*P*,*P*-diphenylphosphinimidato]gallium(III), $[Ga\{(OPPh_2)_2N\}_3]$ (1). An aqueous solution of $Ga(NO_3)_3$ (0.056 g, 0.219 mmol) in 5 mL of water was added to an aqueous solution of $K(OPPh_2NPPh_2O)$ (0.3 g, 0.657 mmol), prepared by previously described procedures,[5,6] in 3 mL of water. The white solid formed was filtered, washed with water, and dried in vacuo; yield 0.72 g (83%), mp >300 °C. ^{31}P-NMR ($CDCl_3$, ppm): δ 25.36 (s). IR (KBr, cm^{-1}): ν(PN), 1210 (vs, br); ν(PN)/δ(CH), 1176 (m); ν(P=O), 1088 (s), 1065 (s); ν(PN), 751 (w); γ(PNP), 555 (vs); δ(OPN), 427 (w-m). MS (FAB$^+$, CH_3Cl, for ^{69}Ga, *m/z*): 1318 [M^+], 1240 $[O_6P_6Ph_{11}N_3Ga^+]$, 901 $[O_4(PPh_2)_4N_2Ga^+]$, 562 $[Ph + O_2(PPh_2)_2NGa^+]$, 485 $[O_2(PPh_2)_2NGa^+]$, 416 $[(OPPh_2)_2N^+]$, 408 $[O_2P_2Ph_3NGa^+]$, 400 $[O(PPh_2)_2N^+]$. Anal. Calcd for $C_{72}H_{60}N_3P_6O_6Ga$: C, 62.46; H, 4.45; N, 2.99. Found: C, 62.24; H, 4.43; N, 2.83.

Tris[*N*-(*P*,*P*-diphenylphosphinoyl)-*P*,*P*-diphenylphosphinimidato]indium(III) (2) and -bismuth(III) (3). The synthesis and characterization of the In(III) and Bi (III) complexes have been previously reported by Cea-Olivares[7] and Williams,[8] respectively. MS for **2** (FAB$^+$, CH_3Cl, for ^{115}In, *m/z*): 1364 [M^+], 1286 $[O_6P_6Ph_{11}N_3In^+]$, 948 $[O_4(PPh_2)_4N_2In^+]$, 870 $[O_4P_4Ph_7N_2In^+]$, 608 $[Ph + O_2(PPh_2)_2NIn^+]$, 532 $[O_2(PPh_2)_2NIn^+]$, 454 $[O_2P_2Ph_3NIn^+]$, 416 $[(OPPh_2)_2N^+]$, 400 $[O(PPh_2)_2N^+]$. MS for **3** (FAB$^+$, CH_3Cl, *m/z*): 1458 [M^+], 1380 $[O_6P_6Ph_{11}N_3Bi^+]$, 1041 $[O_4(PPh_2)_4N_2Bi^+]$, 964 $[O_4P_4Ph_7N_2Bi^+]$, 702 $[Ph + O_2(PPh_2)_2NBi^+]$, 625 $[O_2(PPh_2)_2NBi^+]$, 548 $[O_2P_2Ph_3NIn^+]$, 416 $[(OPPh_2)_2N^+]$, 400 $[O(PPh_2)_2N^+]$.

X-ray Diffraction Studies. Suitable crystals were obtained by solvent diffusion from a dichloromethane/*n*-hexane mixture for **1** and for **3** and from a benzene/*n*-hexane mixture for **2**. Data collections were performed at room temperature on a Siemens P4 four-cycle diffractometer with graphite-monochromated Mo Kα radiation, using the $\omega-2\theta$ scan technique. Totals of 12 584, 12 657, and 12 345 (3° $< 2\theta <$ 50°) reflections were measured for **1**−**3**, respectively, from which 5477 (**1**), 10 415 (**2**), and 7850 [$F > 4.0\sigma(F)$] (**3**) were used for calculations. Three check reflections, monitored periodically during data collection, revealed a total loss of intensity of 13.8% and 26.3% for **1** and **2**, respectively. In all cases, data were corrected for background and Lorentz−polarization effects, and a semiempirical (ψ-scan) absorption correction was applied for **3**. Crystallographic data are summarized in Table 1. The structures of **1** and **3** were solved by the Patterson method, while that of **2** was solved by direct methods, using the Siemens SHELXTL-PLUS program (PC version)[9] and refined by full-matrix least-squares calculations. The numbers of refined parameters were 821 for **1**, 842 for **2**, and 782 for **3**. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated as a riding model with fixed isotropic $U = 0.06$. The structures of **1** and **2** showed solvent disorders. The atom coordinates are listed in Table 2, and summaries of selected bond distances and angles are listed in Tables 3 and 4.

Table 1. Crystallographic Data for $[Ga\{(OPPh_2)_2N\}_3]\cdot CH_2Cl_2$ (**1**), $[In\{(OPPh_2)_2N\}_3]\cdot C_6H_6$ (**2**), and $[Bi\{(OPPh_2)_2N\}_3]$ (**3**)

	1	**2**	**3**
formula	$C_{72}H_{60}N_3P_6O_6Ga\cdot CH_2Cl_2$	$C_{72}H_{60}N_3P_6O_6In\cdot C_6H_6$	$C_{72}H_{60}N_3P_6O_6Bi$
fw	1403.7	1435.87	1458.0
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
λ (Mo Kα), Å	0.710 73	0.710 73	0.710 73
T, °C	20	20	20
a, Å	13.534 (4)	13.542 (9)	14.006 (6)
b, Å	13.855 (4)	15.622 (3)	14.185 (4)
c, Å	18.732 (7)	18.063 (5)	17.609 (8)
α, deg	95.48 (2)	98.210 (10)	88.45 (2)
β, deg	98.26 (2)	104.77 (0)	79.34 (2)
γ, deg	97.84 (2)	92.260 (0)	78.23 (2)
V, $Å^3$	3420 (2)	3645 (4)	3366 (3)
Z	2	2	2
ρ_{calcd}, mg/cm^3	1.363	1.269	1.439
μ, mm^{-1}	0.675	0.507	2.815
$R(F_o)$,[a] %	7.28	4.28	5.64
$R_w(F_o)$,[b] %	6.74	6.73	6.58

[a] $R(F_o) = \sum||F_o - F_c||/\sum|F_o|$. [b] $R_w(F_o) = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

Results and Discussion

The structure of gallium tris-chelate **1**, which was found to crystallize as the $[Ga\{(OPPh_2)_2N\}_3]\cdot CH_2Cl_2$ solvate, is illustrated in the ORTEP plot of Figure 1. Indium(III) compound **2** contains benzene molecules as crystallization solvent in a 1:1 ratio. Figure 2 shows the molecular structure and atomic labeling scheme of $[Bi\{(OPPh_2)_2N\}_3]$, **3**.

The structures are built from discrete $[M\{(OPPh_2)_2N\}_3]$ molecules (M = Ga, In, and Bi). Every metal is coordinated to the oxygen atoms from three bidentate ligands, forming six-membered chelate rings. In complexes **1** and **2**, the coordination geometry around the metal centers exhibits a slightly distorted octahedral arrangement, as compared to the distortion pattern observed in the analogous bismuth(III) compound (**3**) also herein described.[10] The ligands display a quite symmetrical chelating coordination mode on interacting with the gallium(III) and indium(III) cations. The average Ga−O and In−O bond distances are 1.973(13) and 2.127 (9) Å, respectively. The differences between the shortest {[**1**] 1.954 (5) and [**2**] 2.115

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(10) According to the dihedral angle (δ') criterion, it is established that the **1** and **2** tris-chelates lie near the D_{3d} limit in the path $O_h(D_{3d}) \leftrightarrow D_{3h}$ [ideal δ' angles: $O_h(D_{3d})$ 70.5, 70.5, 70.5° at b_1 and 70.5, 70.5, 70.5° at b_2. Ideal δ' angles: (D_{3h}) 0, 0, 0° at b_1 and 120, 120, 120° at b_2]. The observed δ' angles are 108.6, 70.7, 71.9° at b_1 and 71.0, 111.5, 70.9° at b_2 for **1**; 108.4, 71.0, 70.1° at b_1, and 71.5, 111.0, 72.5° at b_2 for **2**. The observed δ' angles for **3**: 81.4, 74.5, 111.1° at b_1 and 105.7, 59.9, 67.2° at b_2. Muetterties, E. L.; Guggenberger, L. J. *Inorg. Chem.* **1974**, *96*, 1748−1756.

Table 2. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)[a] for **1**·CH_2Cl_2, **2**·C_6H_6, and **3**

	1				**2**				**3**			
atom	*x*	*y*	*z*	*U*(eq)	*x*	*y*	*z*	*U*(eq)	*x*	*y*	*z*	*U*(eq)
M	1796(1)	1914(1)	2253(1)	29(1)	1682(1)	7264(1)	2007(1)	30(1)	1938(1)	2648(1)	3152(1)	38(1)
P(1)	1005(2)	3908(2)	1970(1)	36(1)	−168(1)	7480(1)	492(1)	37(1)	749(2)	733(2)	3048(1)	48(1)
P(2)	1081(2)	3392(2)	3388(1)	36(1)	1529(1)	8724(1)	855(1)	39(1)	2873(2)	192(2)	2980(2)	50(1)
P(3)	140(2)	14(2)	2070(1)	38(1)	3434(1)	6120(1)	1476(1)	43(1)	2630(2)	3552(2)	4791(2)	52(1)
P(4)	1805(2)	116(2)	3161(1)	42(1)	4159(1)	7551(1)	2685(1)	42(1)	4013(2)	3541(2)	3375(2)	50(1)
P(5)	4139(2)	2617(2)	2624(1)	40(1)	1033(1)	8404(1)	3442(1)	35(1)	2306(3)	2953(2)	1169(2)	59(1)
P(6)	3439(2)	1514(2)	1276(1)	40(1)	1076(5)	6597(1)	3479(1)	37(1)	878(3)	4487(2)	1984(2)	66(1)
N(1)	1045(5)	4170(4)	2816(3)	38(3)	350(3)	8429(2)	543(2)	43(1)	1816(7)	75(7)	2847(6)	57(4)
N(2)	682(5)	−299(5)	2799(3)	44(3)	4258(3)	6882(2)	1972(2)	52(1)	3701(7)	3408(8)	4282(5)	58(4)
N(3)	4295(5)	1877(5)	1949(4)	49(3)	1221(3)	7581(2)	3866(2)	44(1)	1629(11)	3985(8)	1260(6)	95(5)
O(1)	1229(4)	2905(4)	1715(3)	38(2)	280(2)	6961(2)	1130(2)	43(1)	681(6)	1706(5)	3404(4)	50(3)
O(2)	1238(4)	2369(3)	3117(3)	32(2)	2191(2)	8148(2)	1356(2)	40(1)	3006(6)	1204(5)	3174(4)	53(3)
O(3)	551(4)	1997(4)	1852(3)	37(2)	2326(2)	6211(2)	1476(2)	45(1)	1830(6)	3252(6)	4434(4)	61(3)
O(4)	2357(4)	894(4)	2790(3)	38(2)	3126(2)	7577(2)	2857(2)	40(1)	3301(6)	3321(6)	2874(4)	56(3)
O(5)	3078(4)	2827(4)	2643(3)	38(2)	1064(2)	8291(2)	2600(1)	36(1)	2275(6)	2312(5)	1874(4)	54(3)
O(6)	2345(4)	1500(4)	1381(3)	41(2)	1161(2)	6393(2)	2655(2)	41(1)	885(7)	3995(6)	2758(5)	70(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Distances (Å) for **1**·CH_2Cl_2, **2**·C_6H_6, and **3**

	1	**2**	**3**
M−O(1)	1.954(5)	2.126(3)	2.392(8)
M−O(2)	1.968(5)	2.138(3)	2.281(7)
M−O(3)	1.971(5)	2.115(3)	2.404(8)
M−O(4)	1.983(5)	2.144(3)	2.273(9)
M−O(5)	1.996(5)	2.120(3)	2.256(7)
M−O(6)	1.959(5)	2.126(3)	2.337(8)
N(1)−P(1)	1.582(6)	1.594(4)	1.577(9)
N(1)−P(2)	1.591(7)	1.578(4)	1.583(11)
N(2)−P(3)	1.581(7)	1.595(4)	1.574(10)
N(2)−P(4)	1.579(7)	1.577(4)	1.593(9)
N(3)−P(5)	1.608(7)	1.585(4)	1.568(12)
N(3)−P(6)	1.576(6)	1.577(4)	1.577(11)
P(1)−O(1)	1.511(6)	1.517(3)	1.509(8)
P(2)−O(2)	1.511(5)	1.520(3)	1.539(9)
P(3)−O(3)	1.514(6)	1.513(3)	1.517(10)
P(4)−O(4)	1.508(6)	1.509(3)	1.528(10)
P(5)−O(5)	1.505(6)	1.518(3)	1.519(8)
P(6)−O(6)	1.519(6)	1.512(3)	1.516(9)
O(1)···O(2)	2.797(7)	3.028(3)	3.164(8)
O(3)···O(4)	2.824(7)	2.977(3)	3.127(9)
O(5)···O(6)	2.818(7)	2.990(3)	3.021(8)
O(1)···O(3)	2.715(7)	3.003(3)	3.655(8)
O(1)···O(6)	2.701(7)	2.985(3)	3.468(8)
O(3)···O(6)	2.722(7)	2.947(3)	3.515(8)
O(2)···O(4)	2.773(7)	2.961(3)	3.153(8)
O(2)···O(5)	2.781(7)	3.008(3)	3.034(8)
O(4)···O(5)	2.768(7)	2.997(3)	2.966(8)
O(1)···O(5)	2.797(7)	3.028(3)	3.383(8)
O(2)···O(3)	2.797(7)	3.028(3)	3.655(8)
O(4)···O(6)	2.797(7)	3.028(3)	3.361(8)

Table 4. Selected Bond Angles (deg) for **1**·CH_2Cl_2, **2**·C_6H_6, and **3**

	1	**2**	**3**
O(1)−M−O(2)	90.9(2)	90.5(1)	84.4(3)
O(1)−M−O(3)	88.0(2)	90.2(1)	99.6(3)
O(1)−M−O(4)	179.2(2)	177.7(1)	171.1(2)
O(1)−M−O(5)	92.7(2)	91.9(1)	92.5(3)
O(1)−M−O(6)	87.4(2)	89.2(1)	94.0(3)
O(2)−M−O(3)	92.6(2)	92.6(1)	101.3(3)
O(2)−M−O(4)	89.4(2)	87.6(1)	86.9(3)
O(2)−M−O(5)	88.8(2)	90.0(1)	82.0(3)
O(2)−M−O(6)	178.2(2)	179.3(1)	163.4(3)
O(3)−M−O(4)	91.2(2)	88.7(1)	83.8(3)
O(3)−M−O(5)	178.3(2)	176.7(1)	167.7(3)
O(3)−M−O(6)	87.8(2)	88.0(1)	95.3(3)
O(4)−M−O(5)	88.0(2)	89.3(1)	84.4(3)
O(4)−M−O(6)	92.3(2)	92.8(1)	93.8(3)
O(5)−M−O(6)	90.7(2)	89.5(1)	81.6(3)
P(1)−N(1)−P(2)	124.3(4)	126.2(2)	133.0(7)
P(3)−N(1)−P(4)	124.3(4)	127.2(3)	128.9(7)
P(5)−N(1)−P(6)	122.5(5)	127.4(2)	130.0(7)
M−O(1)−P(1)	131.2(3)	127.1(2)	125.3(4)
M−O(2)−P(2)	129.5(3)	126.5(2)	129.0(5)
M−O(3)−P(3)	130.6(3)	128.5(2)	128.8(4)
M−O(4)−P(4)	128.2(3)	125.0(2)	132.0(4)
M−O(5)−P(5)	127.4(3)	126.5(2)	132.0(4)
M−O(6)−P(6)	129.3(3)	126.9(2)	132.0(5)
N(1)−P(1)−O(1)	117.0(3)	118.0(2)	116.5(5)
N(1)−P(2)−O(2)	117.2(3)	116.8(2)	118.1(5)
N(2)−P(3)−O(3)	117.4(3)	117.5(2)	117.2(5)
N(2)−P(4)−O(4)	116.1(3)	117.6(2)	116.4(5)
N(3)−P(5)−O(5)	116.2(3)	117.0(2)	117.1(5)
N(3)−P(6)−O(6)	118.6(4)	117.5(2)	118.0(5)

(3) Å} and the longest {[**1**] 1.996 (5) and [**2**] 2.144 (3) Å} M−O bond distances are only 0.042 Å for **1** and 0.024 Å for **2**. Some additional structural similarities are observed when O−In−O bond angles are compared with the corresponding O−Ga−O bond angles (Table 4). The largest difference between O−M−O bond angles is only 2.6°, and the average value of these differences is 1.2(7)°.

The MO_2P_2N chelate rings (M = Ga, In, and Bi) are arranged in boat conformation with the metal and nitrogen atoms at the apices. There are some phenyl−phenyl contacts, presumably due to the bulky nature of this ligand and to the size of the central atoms. These contacts occur mainly between phenyl groups on the same phosphorus atom and also between the equatorial phenyl groups situated on the same chelate ring. This contrasts with the observed situation in some bis-chelates with the analogous sulfur ligand **b**, where the chair and boat conformations with the metal and the nitrogen atoms at the apices give unfavorable 1,3 axial−axial arrangements of phenyl groups situated on the same ring.[11] The closest C···C nonbonded distances between phenyl carbons (all of which are within the range of the sum of the van der Waals radii)[12] are presented in Table 5, a few intramolecular distances shorter than the van der Waals radii sum (C−O, C−N, or C−P) being also present. There are no particularly short intermolecular contacts. The crystal packing is determined by normal van der Waals forces. The resulting distortion pattern observed around the gallium and indium atoms may be accounted for by the presence of all the intramolecular interactions mentioned above. In the case of the bismuth atoms of **3**, this does not appear to be the unique factor.

The average bond distances and angles (including those around the phosphorus atom, in exocyclic position) found in

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(11) (a) Siiman, O.; Gray, H. B. *Inorg. Chem.* **1974**, *13*, 1185. (b) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1971**, *10*, 1778.

(12) Pauling, L. *The Nature of the Chemical Bond*; 3rd. ed.; Cornell University Press; Ithaca, N.Y., 1960.

Table 5. Short C···C Nonbonded Distance Found in **1**·CH$_2$Cl$_2$, **2**·C$_6$H$_6$, and **3**

1		2		3	
C(1)···C(7)	2.925(20)	C(1)···C(7)	2.861(9)	C(1)···C(7)	2.868(14)
C(1···C(12)	3.141(22)			C(1)···C(12)	3.404(15)
C(13)···C(19)	2.885(19)	C(13)···C(19)	2.851(9)	C(13)···C(19)	2.846(17)
C(13)···C(24)	3.374(20)	C(13)···C(20)	3.320(9)	C(6)···C(7)	3.201(16)
C(14)···C(19)	3.334(19)	C(14)···C(19)	3.210(10)		
C(25)···C(31)	2.842(20)	C(25)···C(31)	2.852(7)	C(25)···C(31)	2.840(15)
C(25)···C(36)	3.385(20)	C(25)···C(32)	3.380(8)	C(25)···C(32)	3.365(18)
C(37)···C(43)	2.803(21)	C(37)···C(43)	2.827(8)	C(37)···C(43)	2.863(17)
C(37)···C(48)	3.249(23)	C(37)···C(44)	3.403(8)	C(37)···C(44)	3.080(18)
C(38)···C(43)	3.165(22)			C(38)···C(44)	3.435(17)
C(38)···C(59)	3.439(22)			C(30)···C(31)	3.275(15)
C(49)···C(55)	2.805(20)	C(49)···C(55)	2.881(7)	C(49)···C(55)	2.825(19)
C(49)···C(60)	3.406(20)	C(49)···C(56)	3.367(7)		
C(54)···C(55)	3.267(21)			C(50)···C(55)	3.463(21)
C(61)···C(67)	2.858(18)	C(61)···C(67)	2.916(8)	C(61)···C(67)	2.899(18)
C(66)···C(67)	3.357(21)	C(61)···C(72)	3.291(9)		

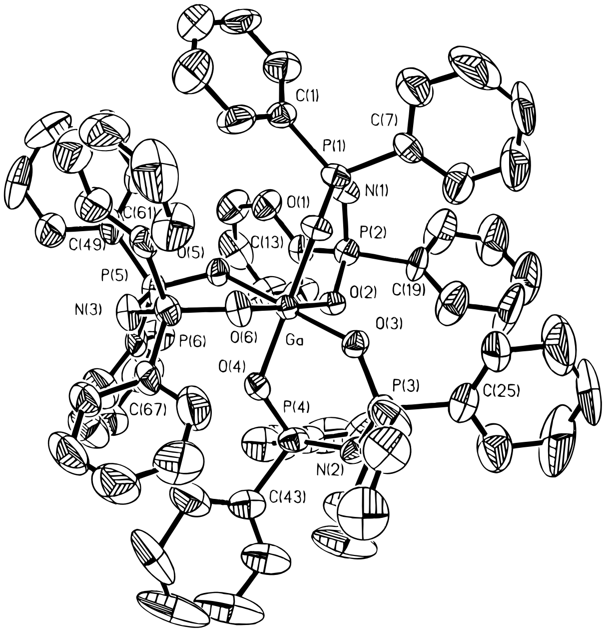

Figure 1. ORTEP plot of $[\mathrm{Ga}\{(\mathrm{OPPh}_2)_2\mathrm{N}\}_3]\cdot\mathrm{CH}_2\mathrm{Cl}_2$ with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

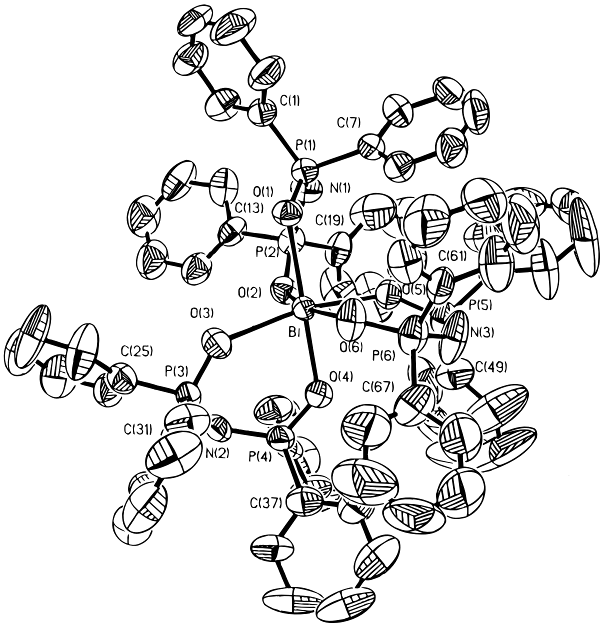

Figure 2. ORTEP plot of $[\mathrm{Bi}\{(\mathrm{OPPh}_2)_2\mathrm{N}\}_3]$, **3**, with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

the chelate rings agree well with corresponding dimensions found in previous structure determinations (Table 6).[4] The average P−N and P−O bond distances are consistent with a π-delocalized structure involving the five ligand atoms in the chelate ring, as it has been noted in cyclic phosphazenes.[13] The chelate ring angles in Table 6 vary somewhat due to variation in size of the central atom and overall structure. The variation in the average P−N−P ($\Delta = 7°$), M−O−P ($\Delta = 24.7°$), and O−P−N ($\Delta = 8.4°$) angles demonstrates the flexibility of the ligand and its ability to fulfill the requirements imposed by the central atom, whereas it also indicates that the O···O bite can be greater or smaller than the range observed in the table.

We now make reference to compound **3**, in which the coordination geometry around bismuth imitates the trigonal C_{3v} distortion noted in several six-coordinated group 15 compounds.[3i,14−17] The ligands coordinate to the bismuth atom asymmetrically, a fact which results in two distinct sets of Bi−O bond lengths with the distances of one set longer than the other. A similar pattern has been noted before, and it is considered evidence for the presence of a stereoactive lone pair.[3i,14] Figure 3 shows the coordination sphere around the bismuth atom with the phenyl rings omitted. The distortion pattern around the bismuth atom in compound **3** suggests the presence of a lone pair. The shorter bond distances, set a [Bi−O(2), 2.281(7) Å; Bi−O(4), 2.273(9) Å; and Bi−O(5), 2.256(7) Å], correspond to those oriented in the direction opposite to the lone pair and the longer bond distances (set b) are those adjacent to the lone

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(17) (a) Bartell, L. S.; Gavin, R. M. *J. Chem. Phys.* **1968**, *48*, 2460. (b) Russell, D. R.; Poore, M. C. *J. Chem. Soc., Chem. Commun.* **1971**, 18. (c) Iven, M. L.; Irving, H. M. N.; Nassimbeni, L. R.; Hutton, A. T. *Acta Crystallogr.* **1982**, *B38*, 2140. (d) Massiani, M. C.; Papiernik, R.; Hubert-Pfalzgraf, L. G. *Polyhedron* **1991**, *10*, 437. (e) Hegetschweiler, K.; Ghisletta, M.; Gramlich, V. *Inorg. Chem.* **1993**, *32*, 2699. (f) Reger, D. L.; Hulf, M. F.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 579. (g) Reger, D. L. *Synth. Lett.* **1992**, 469.

Table 6. Average Interatomic Distances (Å) and Angles (deg) in Some Chelate Rings Containig the Ligand $\{(OPPh_2)_2N\}$

compound	M−O	P−O	P−N	P−C	O···O bite	O−M−O bite	M−O−P	O−P−N	P−N−P	O−P−C	N−P−C	C−P−C
$[Sn\{(OPPh_2)_2N\}_2]$	2.24(11)	1.521(7)	1.587(6)		3.045	85.64(4)	131.3(2)	117.4(5)	126.7(2)			
$[Sn\{(OPPh_2)_2N\}_2I2]$[a]	2.073(4)	1.540(4)	1.581(9)		2.921	89.55(1)	130.6(2)	115.9(4)	126.3(3)			
$[Sn\{(OPPh_2)_2N\}_2R_2]$[b]	2.203(5)	1.523(3)	1.586(2)		3.074	88.5(2)	130.5(3)	118.0(4)	130.4(4)	107.9(5)	109.1(6)	103.7(6)
$[K(Crw\text{-}8)\{(OPPh_2)_2N\}]$[c]	2.870(4)	1.499(4)	1.588(3)	1.819(1)	3.444	73.5(1)	115.9(2)	119.0(3)	129.3(3)	109.2(2)		104.2(2.0)
$[Mo\{(OPPh_2)_2N\}(Cl)_2(O)_2]$[d]	2.206(5)	1.499(1)	1.656(12)	1.767(13)	2.785	78.3(3)	140.6(5)	110.6(5)	123.2(6)			
$[Mo\{(OPPh_2)_2N)\}(Cl)(O)]$[d]	2.06(5)	1.530(7)	1.582(13)	1.796(7)	2.811	86.0(2)	136.1(3)	116.7(3)	125.7(4)			
$[Mo\{(OPPh_2)_2N)\}_2O]$[d]	2.09(8)	1.522(12)	1.581(9)	1.801(3)	2.788	83.4(1)	137.7(1)	116.7(1)	125.3(2)			
$[ReO\{(OPPh_2)_2N)\}ClPPh_3]$[e]	2.062(8)	1.534(4)	1.587(4)	1.795(6)	2.813	86.0(2)	134.4(3)	115.6(2)	123.8(3)	107.7(2.4)	108.4(1.9)	
$[V\{(OPPh_2)_2N)\}_2O]$[f]	1.982(3)	1.525(4)	1.588(2)	1.801(5)	2.759	88.2(1)	135.9(1)	115.8(7)	130.7(1)			
$[Ga\{(OPPh_2)_2N\}_3]\cdot CH_2Cl_2$[g]	1.973(13)	1.511(4)	1.586(10)	1.802(8)	2.812(1)	91.5(9)	129.3(1.4)	117.1(7)	123.7(4)	108.4(1.9)	108.8(1.1)	104.4(1.5)
$[In\{(OPPh_2)_2N\}_3]\cdot C_6H_6$[g]	2.127(9)	1.515(4)	1.584(7)	1.799(7)	2.99(2)	89.6(7)	126.7(1.0)	117.3(4)	127.0(4)	107.8(1.6)	108.7(2.0)	106.0(1.1)
$[Bi\{(OPPh_2)_2N\}_3]$[g]	2.33(5)	1.520(6)	1.578(4)	1.799(11)	3.10(6)	83.3(1.0)	129.8(2.5)	117.2(9)	130.6(1.8)	108.3(1.0)	108.8(2.0)	104.9(9)

[a] See ref 4a. [b] See ref 4f. [c] See ref 4e. [d] See ref 4c. [e] See ref 4d. [f] See ref 4b. [g] This study.

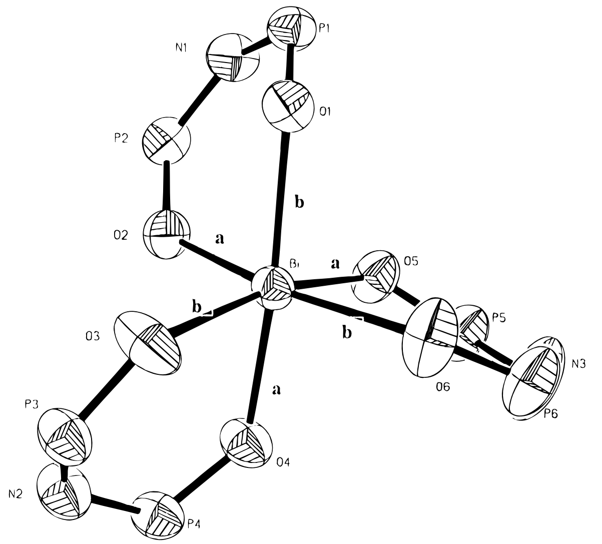

Figure 3. 50% probability plot showing geometry around bismuth atom with the phenyl rings omitted. The Bi−O bonds, denoted by letters, identify the two distinct set of distances; the longer bonds corresponding to set b are Bi−O(1), Bi−O(3), and Bi−O(6) and the shorter bonds [set a] consist of Bi−O(2), Bi−O(4), and Bi−O(5).

pair [Bi−O(1), 2.392(8) Å; Bi−O(3), 2.404(8) Å; and Bi−O(6), 2.337(8) Å]. This speculation is supported by the opening of the O−Bi−O bond angles straddling the lone pair, which averages 96.3 (2.0)°, 11.9° larger than the average [84.4 (2.5)°] associated with the short set (set a). Moreover, the O···O nonbonded distances [O(1)···O(3), 3.655(5) Å; O(1)···O(6), 3.467(5) Å; and O(3)···O(6), 3.513(5) Å] of the trigonal face O(1)−O(3)−O(6) are larger than those of the other faces, particularly the face opposite to the lone pair [O(2)···O(4), 3.157(5) Å; O(2)···O(5), 2.964(5) Å; and O(4)···O(5), 3.041(5) Å]. Notably even the O(2)···O(5) length is shorter than the 3.04 Å van der Waals radii sum[18] (Table 3). In addition, there exists the possibility that the lone pair is displaced toward the O(2)···O(3) edge, as evidenced by one of the longer O···O distances [3.6551(5) Å] and the corresponding O−Bi−O bond angle [O(2)−Bi−O(3), 101.5(2)°], the largest angle observed in the coordination sphere. This pattern is in agreement with the result obtained by Wheeler *et al.* They found that the electron lone pair on the central atom in distorted MX_6E^{3-} molecules (M = Bi or Sb; X = I or Cl)[3i] is hybridized toward longer bonds and larger angles, in accordance with the VSEPR model.

In Table 7 are listed some useful gauges employed by Lawton[14] for measuring the extent of deformation of the central MX_6E group (M = metal, X = donor atom, E = lone pair). All of the MX_6E cores present an approximately C_{3v} symmetry.[14−16] It is important to point out that this distortion does not necessarily prove stereochemical activity of a lone pair but that the resulting geometry is imposed both by the formation of four-membered chelate rings of the S_2COR, S_2CNR_2, $S_2P(OR)_2$, and S_2PR_2 ligands and by the rigid nature of the S_2COR, and S_2CNR_2 ligands.[19,20] In our compound **3**, the bending deformation[21] ($R_y = 0.87$), comparable with that found in both arsenic compounds, is larger than the stretching deformation ($R_x = 0.95$), which is within the range of those exhibited by the other bismuth compounds.[14,15a,c]

In marked contrast to the results obtained by comparing the structures of both analogous compounds of indium(III), **2**, and

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(18) Bondi, A. J. *J. Phys. Chem.* **1964**, *68*, 441.

(19) Zukerman-Schpector, J.; Haiduc, I.; Silvestru C.; Cea-Olivares, R. *Polyhedron* **1995**, *21*, 3087.

Table 7. Dimensions of the MX_6E Group (X = S or O) Involving Trivalent As, Sb, and Bi in Some Chelate Compounds [Average Interatomic Distances (Å) and Angles (deg)][a]

compound	av M−X[b] (Å)				av X−M−X[b] (deg)			
	X_a	X_b	Δ	$R_x = X_a/X_b$[c]	X_a−M-X_a	X_b−M-X_b	Δ	$R_y = \angle_a/\angle_b$[c]
$[As(S_2COEt)_3]$[d]	2.28	2.94	0.66	0.78	92.0	107.6	15.6	0.86
α-$[As(S_2COMe)_3]$[e]	2.30	3.00	0.70	0.76	90.7	111.1	20.4	0.82
β-$[As(S_2COMe)_3]$[e]	2.30	2.96	0.66	0.77	91.2	109.8	18.6	0.83
$[As(S_2CNEt_2)_3]$[d]	2.35	2.84	0.49	0.83	89.7	104.2	14.5	0.86
$[Sb(S_2COEt)_3]$[d]	2.52	3.00	0.48	0.84	87.5	113.1	25.6	0.77
$[Sb(S_2P(OMe)_2)_3]$[f]	2.53	3.01	0.48	0.84	88.4	106.2	17.8	0.83
$[Sb(S_2P(OEt)_2)_3]$[g]	2.60	2.83	0.23	0.91	94.1	100.9	6.8	0.93
$[Sb(S_2P(O^iPro)_2)_3]$[f]	2.52	3.02	0.49	0.83	87.5	106.6	19.1	0.82
$[Sb(S_2P(OEt)_2)_3]$[h]	2.53	3.05	0.52	0.83	87.0	102.9	15.9	0.84
$[Bi(S_2PEt_2)_3]$[i]	2.75	2.82	0.06	0.97	95.5	98.6	3.1	0.97
$[Bi(S_2PEt_2)_3]\cdot C_6H_6$[j]	2.78	2.79	0.01	0.99	93.2	93.0	-0.2	1.00
$[Bi(S_2P(O^iPro)_2)_3]$[d]	2.70	2.87	0.17	0.94	91.2	99.9	8.7	0.91
$[Bi\{(OPPh_2)_2N\}_3]$[k]	2.27	2.38	0.11	0.95	84.4	96.3	11.9	0.87

[a] All data are weighted averages. [b] Donor atom denoted by *X*. [c] See ref 21. [d] Data taken from ref 14. [e] See ref 16a. [f] See ref 16d. [g] See ref 15d. [h] See ref 19. [i] See ref 15a. [j] See ref 15c. [k] This study.

gallium(III), **1**, the comparison between the structures of compounds **2** and **3** brings forth important differences. In addition to the distinct coordination mode displayed in the bismuth compounds, the corresponding O−M−O bond angles differ significantly (Table 4). The largest difference observed between compound **2** and compound **3** is 15.9°, and the average value of these differences is 6.5(4.0)°. The model fitting for the bismuth and indium complexes is shown in Figure 4.

A close look at the phenyl ring positions reveals additional structural differences. In the bismuth compound, the phenyl groups oriented in the direction of the lone pair are arranged in such a way as to allow an enlargement of the trigonal face O(1)−O(3)−O(6), thus providing more space for the lone pair. In contrast, the aromatic groups in the corresponding face of the indium compound (Figure 3) are not arranged in such a fashion. The deviation from the idealized crystal coordinates for model atoms, illustrated in Figure 3, is strikingly larger for C(1)−C(12), C(25)−C(30), C(31)−C(36), C(61)−C(66), and C(67)−C(72), which belong to the phenyl rings located toward the trigonal face O(1)−O(3)−O(6).

The structures of the above reported Ga(III) and In(III) complexes, which act as MX_6 control systems, demonstrate that the steric bulk of the ligand does not appear to be the only driving force for the whole observed distortion pattern in compound **3**.

On the other hand, the trigonal distortion detected in **3** stands in contrast to the enigmatic distortion pattern observed in the sulfur-based analogue, $[Bi\{(SPPh_2)_2N\}_3]$,[7,22] for which the steric crowding in the valence shell may be expected to be smaller than in **3**. This result is consistent with the frontier orbital arguments that for highly electropositive central atoms and electropositive ligands, the small HOMO-$1a_1$ gap tempers the distortion and favors the inert pair effect.[3i] Further studies into the donor atom substitution effects on the geometry of the corresponding selenium-based analogue, $[Bi\{(SePPh_2)_2N\}_3]$, are in progress.

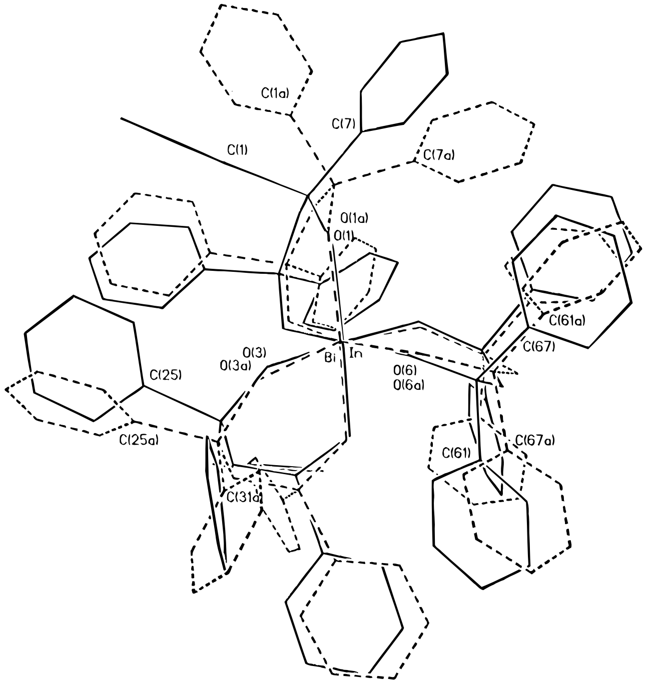

Figure 4. Model fitting view of $[In\{(OPPh_2)_2N\}_3]\ C_6H_6$ (**2**) [solid line] and $[Bi\{(OPPh_2)_2N\}_3]$ (**3**) [dashed line].

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates for each compound (39 pages). Ordering information is given on any current masthead page.

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(20) The comparison of the structures of group 13 and group 15 complexes containing S_2COR, S_2CNR_2, $S_2P(OR)_2$, and S_2PR_2 ligands indicates that the small differences observed in the coordination geometry may be rationalized without invoking a stereoactive lone pair. For example, the distortions in the indium(III) complexes are caused by the small bite of such ligands: (a) Svensson, G., Albertsson, J. *Acta Chem. Scand. 1989*, *43*, 511. (b) Coggon, P.; Lebeda, J. D.; McPhail, A. T.; Palmer, R. A. *J. Chem. Soc., Chem. Commun.* **1970**, 78. (c) Hauser, P. J.; Bordner, J.; Schreiner, A. F. *Inorg. Chem.* **1973**, *12*, 1347. (d) Bhattacharya, S.; Seth, N.; Gupta, V. D.; Nöth, H.; Thomann, M. *Z. Naturforsch.* **1994**, *49b*, 193.

(21) The stretching deformation is defined as $R_x = X_a/X_b$, where X_a and X_b refer to the average bond distances of donor atoms forming M−X short bonds, set a (X_a), and long bonds, set b (X_b). The bending deformation is defined as $R_y = \angle_a/\angle_b$, where $\angle_a$ is the average value of the X_a−M−X_a bond angles and $\angle_b$ is the average bond angle of the X_b−M−X_b set.

(22) Williams, D. J.; Quicksall, C. O.; Barkigia, K. W. *Inorg. Chem.* **1982**, *21*, 2097.