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Diphosphine and Diarsine Complexes of Germanium(II) Halides—Preparation, Spectroscopic, and Structural Studies

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The Ge(II) halide complexes [GeX_2(L—L)] (L—L = *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$; X = Cl, Br, I. L—L = $Et_2P(CH_2)_2PEt_2$; X = Cl or Br. L—L = *o*-$C_6H_4(AsMe_2)_2$; X = Br or I) and [GeCl(L—L)][$GeCl_3$] (L—L = *o*-$C_6H_4(AsMe_2)_2$) have been prepared and characterized by IR, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and microanalyses. The crystal structures of [GeX_2{*o*-$C_6H_4(PPh_2)_2$}] (X = Cl, Br, I) reveal discrete mononuclear units with a very asymmetric bidentate *o*-$C_6H_4(PPh_2)_2$ ligand and a bent GeX_2 unit. Those of [GeX_2{*o*-$C_6H_4(PMe_2)_2$}] show symmetrically coordinated diphosphine with loosely associated dimer arrangements, formed through long Ge···X bridges between adjacent monomer units. [$GeX_2\{R_2P(CH_2)_2PR_2\}$] (R = Me; X = Cl, Br, I. R = Et; X = Cl, Br) all show discrete monomer structures with 2-fold crystallographic symmetry and based upon four-coordinate Ge, with the diphosphine chelating and approximately linear GeX_2 units. [GeI_2{*o*-$C_6H_4(AsMe_2)_2$}] involves significant intermolecular Ge···I interactions, giving rise to a zigzag polymer chain. Finally, the structure of [GeCl{*o*-$C_6H_4(AsMe_2)_2$}]-[$GeCl_3$] shows pyramidal cations and anions both with crystallographic mirror symmetry, with the diarsine symmetrically chelating, and long Ge···Cl interactions give a loosely associated chain polymer with alternating cations and anions. Comparisons across this series of structurally diverse complexes are discussed.

Introduction

The chemistry of germanium compounds is a very topical area of research at present, with major activity in organogermanium chemistry and germanium coordination chemistry, including for example the development of low-valent compounds, such as, germylenes, multiply bonded species, radicals and clusters, stabilization of germanium cations, and new reagents for Ge-containing materials.[1,2]

The majority of germanium coordination complexes are based upon the Ge(IV) oxidation state.[3] We and others have examined the chemistry of the tetrahalides with both hard N/O- and soft P/S-donor ligands, including the first [GeF_4-(diphosphine)] and [GeF_4(dithioether)] complexes.[3–5] On the other hand, the tetrahalides $GeBr_4$ and $GeCl_4$ do not form complexes with thioether ligands, and they are reduced to [R_3PX][GeX_3] by phosphines.[5,6] However, two examples of Ge(IV) arsine complexes have been structurally characterized, *trans*-[$GeCl_4(AsR_3)_2$] (R = Me or Et), although curiously no adduct formation was observed with *o*-$C_6H_4(AsMe_2)_2$.[5,6]

Reports of the coordination chemistry of Ge(II) halides with neutral ligands are relatively few—structural data are now available for several series of complexes with O- and N-donor ligands and macrocycles, including neutral,[7] monocationic,[8] and dicationic species[8,9] in which the coordination number at Ge(II) varies between three and eight, as well as

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(1) (a) Marygaryan, A. M. *Photodetectors and Fiber Optics*; Academic Press: San Diego, CA, 2001; pp 369−458. (b) Shemkunas, M. P.; Petuskey, W. T.; Chizmeshya, A. V. G.; Leinenweber, K.; Wolf, G. H. *J. Mater. Res.* **2004**, *19*, 1392–1399.

(2) For example, see: (a) Parr, J. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Oxford, 2004; Vol *3*, pp 545−608. (b) Power, P. P. *Organometallics* **2007**, *26*, 4362–4372. (c) Power, P. P. *Appl. Organometal. Chem.* **2005**, *19*, 488–493. (d) Spike, G. H.; Power, P. P. *Chem. Commun.* **2007**, 85–87. (e) Richards, A. F.; Brynda, M.; Olmstead, M. M.; Power, P. P. *Organometallics* **2004**, *23*, 2841–2844. (f) Richards, A. F.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed.* **2003**, *42*, 4071–4074. (g) Dias, H. V. R.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67–86. (h) Braunschweig, H.; Hitchcock, P. B.; Lappert, M. F.; Pierssens, L. J. M. *Angew. Chem., Int. Ed.* **1994**, *33*, 1156–1158. (i) Saur, I.; Garcia Alonso, S.; Barrau, J. *Appl. Organometal. Chem.* **2005**, *19*, 414–428. (j) Mizuhata, Y.; Sasamori, T.; Tokitoh, N. *Chem. Rev.* **2009**, *109*, 3479–3511.

(3) (a) Willey, G. R.; Somasundaram, U.; Aris, D. R.; Errington, W. *Inorg. Chim. Acta* **2001**, *315*, 191–195. (b) Adley, A. D.; Bird, P. H.; Fraser, A. R.; Onyszchuk, M. *Inorg. Chem.* **1972**, *11*, 1402–1409. (c) Ejfler, J.; Szafert, S.; Jiao, H.; Sobota, P. *New J. Chem.* **2002**, *26*, 803–805. (d) Cheng, F.; Davis, M. F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Eur. J. Inorg. Chem.* **2007**, 2488–2495. (e) Cheng, F.; Davis, M. F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Eur. J. Inorg. Chem.* **2007**, 4897–4905.

(4) Davis, M. F.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Dalton Trans.* **2008**, 533–538.

(5) Davis, M. F.; Levason, W.; Reid, G.; Webster, M. *Dalton Trans.* **2008**, 2261–2269.

(6) Godfrey, S. M.; Mushtaq, I; Pritchard, R. G. *Dalton Trans.* **1999**, 1319–1323.

(7) (a) Denk, M. K.; Khan, M.; Lough, A. J.; Shuchi, K. *Acta Crystallogr., Sect. C* **1998**, *54*, 1830–1832. (b) Leites, L. A.; Zabula, A. V.; Bukalov, S. S.; Korlyukov, A. A.; Koroteev, P. S.; Maslennikova, O. S.; Egorov, M. P.; Nefedov, O. M. *J. Mol. Struct.* **2005**, *750*, 116–122. (c) Tian, X.; Pape, T.; Mitzel, N. W. *Heteroatom Chem.* **2005**, *16*, 361–363. (d) Cheng, F.; Dyke, J. M.; Ferrante, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Dalton Trans.* **2010**, DOI: 10.1039/b911016j.

N-heterocyclic carbene complexes.[8d,e] In terms of soft phosphine and arsine ligands, only the structures of the very distorted monomer, $[GeCl_2\{Ph_2P(CH_2)_2PPh_2\}]$,[10] and two pyramidal complexes, $[GeX_2(PPh_3)]$ (X = Cl or I), have been reported,[7b,11] and there are early reports of the preparations of GeI_2 complexes with some tertiary and secondary phosphine ligands, including the diphosphine complexes, $[GeI_2\{Ph_2P(CH_2)_2PPh_2\}]$ and $[(GeI_2)_2\{Ph_2P(CH_2)_2PPh_2\}]$,[12a] and $GeCl_2$ complexes with $AsPh_3$ and As^tBu_3, albeit without structural data.[12b] We reported a series of Ge(II) complexes with (soft) macrocyclic thioethers, which show extended chain and network structures based upon distorted six-coordinate geometries at germanium through Ge−X (X = Cl or Br) and long Ge−S bonds to S atoms of bridging (*exodentate*) thiacrowns.[13]

We describe here a systematic study of the synthesis and structural properties of Ge(II) halide (chloride, bromide, and iodide) complexes with neutral diphosphine and diarsine ligands, all of which can form five-membered chelate rings but have quite different steric and electronic properties. In comparison to complexes of the transition metal ions, within the p block it is much less well understood how small variations in ligand architecture, steric requirements, and donor properties influence their coordination complexes. For example, acceptors such as GaX_3 and InX_3 (X = Cl, Br, or I) form a diverse range of structure types with closely related diphosphine and diarsine ligands such as *o*-$C_6H_4(ER_2)_2$ (E = P or As; R = Me; E = P; R = Ph) and $R_2P(CH_2)_2PR_2$ (R = Me or Et).[14]

Results and Discussion

The reaction of $[GeCl_2(dioxane)]$ with 1 mol equiv of the neutral P- or As-donor ligand L−L (L−L = *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$, or $Et_2P(CH_2)_2PEt_2$) in an anhydrous CH_2Cl_2 solution resulted in the formation of the neutral $[GeCl_2(L{-}L)]$ as moisture-sensitive white solids in good yield. The reaction of $[GeCl_2(dioxane)]$ with *o*-$C_6H_4(AsMe_2)_2$ in a 2:1 ratio gives the ionic $[GeCl\{o\text{-}C_6H_4(AsMe_2)_2\}][GeCl_3]$ in high yield, and this is also the product isolated from a 1:1 molar ratio (contrast reaction of $GeBr_2$ or GeI_2 with *o*-$C_6H_4(AsMe_2)_2$, which gives the neutral $[GeX_2(o\text{-}C_6H_4(AsMe_2)_2)]$, below).

The Ge(II) bromo and iodo complexes, $[GeX_2(L{-}L)]$ (X = Br; L−L = *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$, $Et_2P(CH_2)_2PEt_2$, or *o*-$C_6H_4(AsMe_2)_2$. X = I; L−L = $C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$, or *o*-$C_6H_4(AsMe_2)_2$) were also isolated as white or light-yellow solids in good yield by the direct reaction of $GeBr_2$ or GeI_2 with the ligand in anhydrous MeCN. On the other hand, $Ph_2As(CH_2)_2AsPh_2$ does not displace dioxane from $[GeCl_2(dioxane)]$ in anhydrous CH_2Cl_2, consistent with the much weaker σ-donor properties of the Ph-substituted diarsine, although we note that the corresponding diphosphine gives $[GeCl_2\{Ph_2P(CH_2)_2PPh_2\}]$.[10] The complexes $[GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}]$ (X = Cl, Br, I) and $[GeCl_2\{Et_2P(CH_2)_2PEt_2\}]$ (X = Cl, Br) are readily soluble in non-donor solvents such as CH_2Cl_2, whereas $[GeX_2\{Me_2P(CH_2)_2PMe_2\}]$ (X = Cl, Br, I) are only moderately soluble, and for $[GeX_2\{o\text{-}C_6H_4(PMe_2)_2\}]$ (X = Cl, Br, I), $[GeX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$ (X = Br, I), and $[GeCl\{o\text{-}C_6H_4(AsMe_2)_2\}][GeCl_3]$, the solubility in CH_2Cl_2 is poor.

Table 1. $^{31}P\{^1H\}$ NMR Spectroscopic Data[a]

complex	$\delta^{31}P\{^1H\}$/ppm	Δ/ppm[b]
$[GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}]$	+4.5 (183 K: +3.2)	+17.5
$[GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}]$	−4.8 [c]	+8.7
$[GeI_2\{o\text{-}C_6H_4(PPh_2)_2\}]$	−10.5 (183 K: −7.2)	+2.5
$[GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	+21.6 (193 K: +22.4)	+76.6
$[GeBr_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	+13.2 (193 K: +14.4)	+68.3
$[GeI_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	+0.4 (183 K: +2.5)	+55.5
$[GeCl_2\{Me_2P(CH_2)_2PMe_2\}]$	+17.4 (193 K: +20.5)	+65.4
$[GeBr_2\{Me_2P(CH_2)_2PMe_2\}]$	+11.8 (193 K: +13.0)	+59.8
$[GeI_2\{Me_2P(CH_2)_2PMe_2\}]$	+0.7 (183 K: +1.5)	+48.7
$[GeCl_2\{Et_2P(CH_2)_2PEt_2\}]$	+35.7 (183 K: +37.2)	+55.0
$[GeBr_2\{Et_2P(CH_2)_2PEt_2\}]$	+29.4 (193 K: +29.3)	+48.7

[a] Spectra recorded in a CH_2Cl_2 solution at 298 K. [b] Δ = δ(complex) − δ(ligand) at 298 K. [c] Significantly broadened but unshifted at 223 K; no resonance observed at 183 K.

The ^1H NMR spectra of these new complexes (CD_2Cl_2) are simple, with resonances to high frequency of uncomplexed L−L, and consistent with symmetrical coordination of the diphosphine or diarsine. Variable-temperature $^{31}P\{^1H\}$ NMR spectroscopic measurements on the diphosphine complexes (Table 1) show a singlet resonance to high frequency of the ligand itself, and in all cases this is essentially unchanged on cooling to below 200 K. All of the ligands investigated involve a C_2-linking group between the P atoms and, hence, if bidentate in solution, would give rise to a five-membered chelate ring. The magnitude of the coordination shifts, Δ, (Table 1) varies considerably with the nature of the phosphine, with the largest Δ values observed for the stronger σ-donor phosphines with terminal alkyl substituents. This suggests that, for L−L = *o*-$C_6H_4(PMe_2)_2$, $Me_2P(CH_2)_2PMe_2$, and $Et_2P(CH_2)_2PEt_2$, the solution structures of $[GeX_2(L{-}L)]$ involve chelating L−L, whereas for L−L = *o*-$C_6H_4(PPh_2)_2$, the ligand is probably monodentate in solution and undergoing rapid exchange of the “free” and coordinated P atoms even at 200 K (the $^{31}P\{^1H\}$ NMR spectrum of the reported $[GeCl_2\{Ph_2P(CH_2)_2PPh_2\}]$, which involves very asymmetric diphosphine coordination in the solid state is also a single resonance, attributed to fast equilibration of the P atoms in solution).[10] Large, positive shifts are frequently (although not always) observed for diphosphine complexes containing five-membered chelate rings.[15] Consistent with this (although not definitive evidence), variable-temperature

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(8) (a) Rupar, P. A.; Staroverov, V. N.; Ragogna, P. J.; Baines, K. M. *J. Am. Chem. Soc.* **2007**, *129*, 15138–15139. (b) Reger, D. L.; Coan, P. S. *Inorg. Chem.* **1996**, *35*, 258–260. (c) Rupar, P. A.; Bandyopadhyay, R.; Cooper, B. F. T.; Stinchcombe, M. R.; Ragogna, P. J.; Macdonald, C. L. B.; Baines, K. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5155–5158. (d) Rupar, P. A.; Jennings, M. C.; Baines, K. M. *Organometallics* **2008**, *27*, 5043–5051. (e) Arduengo, A. J., III; Dim, H. V. R.; Calabrese, J. C; Davidson, F. *Inorg. Chem.* **1993**, *32*, 1541–1542.

(9) (a) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. *Science* **2008**, *322*, 1360–1363. (b) Cheng, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5152–5154.

(10) Bruncks, N.; Du Mont, W. W.; Pickardt, J.; Rudolph, G. *Chem. Ber.* **1981**, *114*, 3572–3580.

(11) Inoguchi, Y.; Okui, S.; Mochida, K.; Itai, A. *Bull. Chem. Soc. Jpn.* **1985**, 974–977.

(12) (a) King, R. B. *Inorg. Chem.* **1963**, *2*, 199–200. (b) du Mont, W.-W.; Rudolph, G. *Z. Naturforsch., B* **1981**, *36*, 1215–1218.

(13) Cheng, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Chem. Commun.* **2008**, 5508–5510.

(14) (a) Cheng, F.; Davis, M. F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.* **2007**, *46*, 7215–7223. (b) Cheng, F.; Friend, S. I.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Inorg. Chem.* **2008**, *47*, 9691–9700.

(15) Garrou, P. *Chem. Rev.* **1981**, *81*, 229–266.

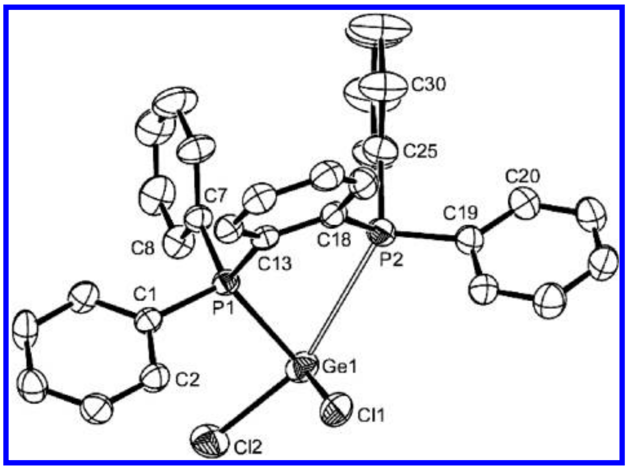

Figure 1. View of the structure of the [$GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$] monomer with the atom numbering scheme adopted. Phenyl rings are numbered cyclically starting at the *ipso* C atom. Ellipsoids are drawn at the 30% probability level, and H atoms are omitted for clarity.

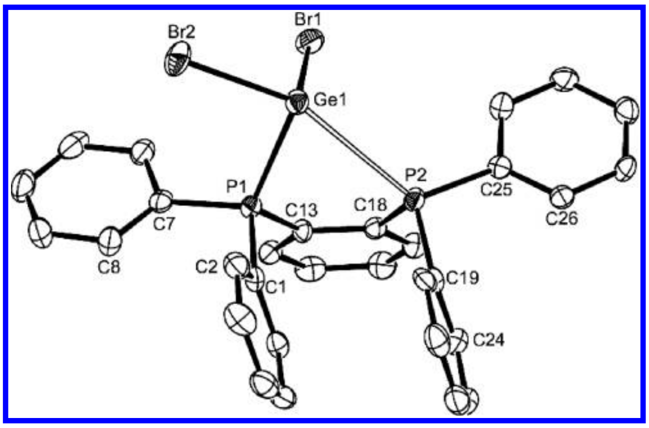

Figure 2. View of the structure of the [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] monomer with the atom numbering scheme adopted. Phenyl rings are numbered cyclically starting at the *ipso* C atom. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The same atom numbering scheme applies for [$GeI_2\{o\text{-}C_6H_4(PPh_2)_2\}$].

$^{31}P\{^1H\}$ NMR spectra of [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] with added $o\text{-}C_6H_4(PPh_2)_2$ show a broad singlet resonance even at 200 K, consistent with rapid ligand exchange. In contrast, those of [$GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}$] and [$GeCl_2\{Et_2P(CH_2)_2PEt_2\}$] with added ligand show broad, averaged resonances at 298 K, which separate on cooling (by 243 K) into two sharp singlets with chemical shifts identical to those of the individual [$GeCl_2$(L−L)] and "free" L−L. These proposed solution structures are also consistent with the structures observed in the solid state (X-ray crystallography), below.

X-Ray Crystallographic Studies. In view of the paucity of structural data available for Ge(II) halide complexes with phosphines (vide supra) and the absence of any structurally characterized Ge(II) arsine complexes in the literature, we have undertaken crystal structure determinations on a series of the new complexes reported herein, including examples with each ligand type. These are described below and followed by a comparison of the structures observed: the effect of halide type, P versus As donor ligands, aryl versus alkyl substituents, and saturated versus aromatic interdonor linkages.

Table 2. Selected Bond Lengths [Å] and angles [deg] for [$GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}$] (X = Cl, Br, I)

compound	X = Cl	X = Br	X = I
Ge1−P1	2.5153(13)	2.5259(13)	2.511(2)
Ge1−P2	3.1958(15)	3.1167(14)	3.068(2)
Ge1−X1	2.2753(15)	2.4635(7)	2.6733(11)
Ge1−X2	2.3195(16)	2.5057(8)	2.7663(11)
P1−Ge1−P2	66.58(4)	67.15(3)	68.40(6)
X1−Ge1−P1	89.47(5)	89.09(3)	90.03(6)
X2−Ge1−P1	90.12(5)	92.92(3)	93.74(6)
X1−Ge1−X2	95.82(5)	97.36(3)	97.55(3)
X1−Ge1−P2	83.49(5)	85.45(3)	85.61(5)
X2−Ge1−P2	156.67(5)	159.89(3)	161.93(5)

The complexes [$GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}$] (X = Cl, Br, or I) adopt very similar structures (although only for X = Br and I are they isomorphous), based upon discrete mononuclear units (Figures 1 and 2, Table 2) with two halide ligands and a very asymmetric bidentate $o\text{-}C_6H_4(PPh_2)_2$ ligand, with the Ge−P distance differing by ca. 0.6 Å. Alternatively, the structure may be described as a pyramidal PX_2 coordination environment at Ge(II), with the diphosphine effectively monodentate, with the second P-donor atom interacting weakly, giving [3 + 1] coordination. [In this work, we use the notation [X + Y] coordination to differentiate between short and long contacts; for example, [3 + 1] means three short and one long Ge−L bond.] The P−Ge···P chelate angles are very acute, 66.58(4)° (Cl), 67.15(3)° (Br), and 68.40(6)° (I), with the GeX_2 unit bent, 95.82(5)° (Cl), 97.36(3)° (Br), and 97.55(3)° (I). The P···P distance in [$GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}$] does not vary significantly with X (ca. 3.18 Å), and two of the Ph rings (one on each P) are nearly parallel (angles between the C6 planes = 15.4(1) (X = Cl), 4.8(2) (X = Br), and 3.2(4)° (X = I)). The distances between the C atoms of one ring and the best plane through the other C_6 ring also vary with X (3.42−4.22 (X = Cl), 3.21−3.48 (X = Br),; 3.21−3.39 Å (X = I)).

Many complexes involving the *o*-phenylene diphosphine, $o\text{-}C_6H_4(PPh_2)_2$, have been described and invariably involve essentially symmetric chelation. Therefore, the very asymmetric chelation (or *pseudo*-monodentate coordination) as in the Ge(II) complexes in this work is extremely unusual.

[$GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}$], which incorporates the less sterically demanding and much stronger σ-donor diphosphine, shows (Figure 3, Table 3) a loosely associated dimer, having 2-fold crystallographic symmetry, formed through long Ge···Cl bridges between adjacent monomer units. Notably, the Ge atom is coordinated to an approximately symmetrically chelating diphosphine (P−Ge−P = 80.01(4)°), one terminal Cl2 (2.704(1) Å), and two asymmetrically bridging Cl atoms (Ge1−Cl1 = 2.494(1), Ge1···Cl1a = 3.481(1) Å, where a = $1 - x, y, 3/2 - z$). The Ge1···Ge1a distance across the Ge_2Cl_2 unit is 3.64 Å, considerably shorter than twice the van der Waals radius for Ge (4.0 Å),[16] and the Ge_2Cl_2 unit is not planar (the angle between the two $GeCl_2$ planes is 104.04(3)°). The bromo analog, [$GeBr_2\{o\text{-}C_6H_4(PMe_2)_2\}$]

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(16) See the Web site www.ccdc.cam.ac.uk/products/csd/radii/ for values used by the CCDC and literature references: Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverria, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832−2838.

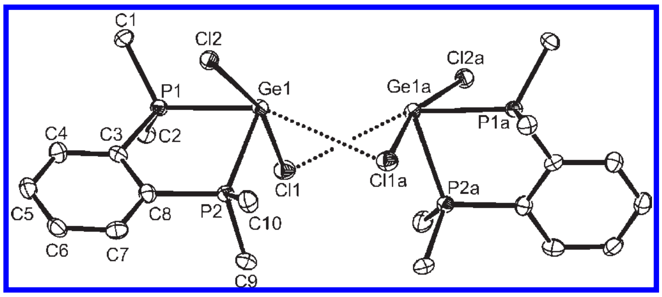

Figure 3. View of the structure of the weakly associated [GeCl$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}]$_2$ dimer with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = −*x*, *y*, 1/2 − *z*.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for [GeX$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] (X = Cl, Br, I)

compound	X = Cl	X = Br	X = I
Ge1−P1	2.4709(11)	2.4805(9)	2.481(2)
Ge1−P2	2.4390(11)	2.4498(10)	2.456(2)
Ge1−X1	2.4942(11)	2.6521(6)	2.8211(12)
Ge1−X2	2.7040(11)	2.8529(6)	3.0749(12)
P1−Ge1−P2	80.01(4)	80.19(3)	79.79(7)
X1−Ge1−X2	164.35(4)	166.513(17)	172.31(4)
P1−Ge1−X1	88.99(4)	89.58(3)	89.44(6)
P1−Ge1−X2	79.86(4)	80.69(3)	83.28(6)
P2−Ge1−X1	87.66(4)	88.83(3)	94.71(6)
P2−Ge1−X2	79.66(4)	80.37(3)	81.57(6)

(Table 3), is isomorphous with the chloride complex, with Ge1···Br1a = 3.539(1) and Ge1···Ge1a = 3.818(1) Å. The iodo complex [GeI$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] shows (Figure 4, Table 3) a similar monomer unit with the *o*-C$_6$H$_4$(PMe$_2$)$_2$ chelating and the GeI$_2$ unit essentially linear (172.31(4)°); however, while the adjacent monomers align to give a precisely planar rhombic Ge$_2$I$_2$ arrangement, the intermolecular Ge1···I1a distance is 3.92 Å, just within the sum of the van der Waals radii (3.98 Å).[16]

The crystals of [GeX$_2${Me$_2$P(CH$_2$)$_2$PMe$_2$}] (X = Cl or Br) are isomorphous and show (Figure 5, Table 4) a discrete monomer structure with 2-fold crystallographic symmetry and based upon four-coordinate Ge, with the diphosphine chelating (P−Ge−P ca. 80°), and approximately linear GeX$_2$ units (168.79(3)° (Cl), 171.81(2)° (Br), 174.57(3)° (I)).

While not isomorphous with the chloro and bromo analogs, the structure of [GeI$_2${Me$_2$P(CH$_2$)$_2$PMe$_2$}] shows a similar coordination environment at Ge. Closer inspection of the packing in the unit cell reveals the very weakly associated centrosymmetric dimer shown in Figure 6 (Table 5), similar to that in [GeI$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] above; while the Ge1···I1a distance (3.851(1) Å) is at the upper limit for an interaction (sum of the van der Waals radii of Ge and I = 3.98 Å),[16] the directionality of the rhombic Ge$_2$I$_2$ core does suggest that this is a genuine, albeit weak, intermolecular interaction.

The compounds [GeX$_2${Et$_2$P(CH$_2$)$_2$PEt$_2$}] (X = Cl or Br) are isomorphous, and their molecular structures (Figure 7, Table 6) are based upon discrete monomer units with 2-fold crystallographic symmetry, which are very similar to those of their methyl analogues, [GeX$_2${Me$_2$P(CH$_2$)$_2$PMe$_2$}] (X = Cl or Br) above, again with the diphosphine approximately symmetrically chelating and with nearly linear GeX$_2$ units.

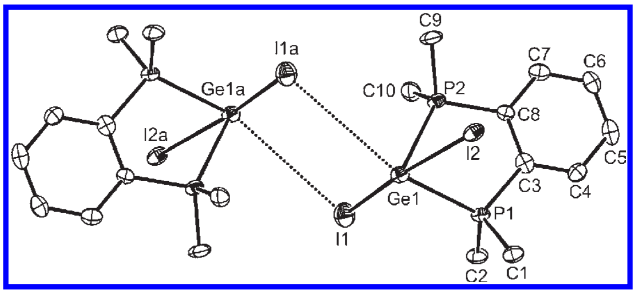

Figure 4. View of the structure of [GeI$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] with the atom numbering scheme adopted and showing the long Ge···I contacts between the adjacent monomer units. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = 1 − *x*, −*y*, 1 − *z*.

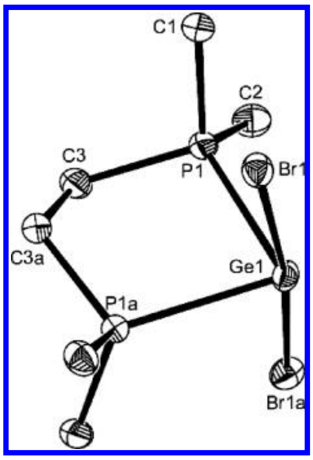

Figure 5. View of the structure of [GeBr$_2${Me$_2$P(CH$_2$)$_2$PMe$_2$}] with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The atom numbering scheme used is the same for [GeCl$_2${Me$_2$P(CH$_2$)$_2$PMe$_2$}]. Symmetry operation: a = −*x*, *y*, 1/2 − *z*.

Table 4. Selected Bond Lengths [Å] and Angles [deg] for [GeX$_2${Me$_2$P(CH$_2$)$_2$PMe$_2$}] (X = Cl, Br)

compound	X = Cl	X = Br
Ge1−P1	2.4495(6)	2.4628(7)
Ge1−X1	2.5858(7)	2.7335(5)
P1−Ge1−P1a[a]	81.63(3)	81.56(3)
P1−Ge1−X1	83.69(2)	89.091(19)
P1−Ge1−X1a[a]	87.83(2)	84.702(19)
X1−Ge1−X1a[a]	168.79(3)	171.806(16)

[a] Symmetry operation: a = −*x*, *y*, 1/2 − *z*.

The crystal structure of [GeI$_2${*o*-C$_6$H$_4$(AsMe$_2$)$_2$}] (Figure 8a and b, Table 7) shows that the monomer unit has a similar arrangement as in [GeI$_2${*o*-C$_6$H$_4$(PMe$_2$)$_2$}] above, with I1−Ge1−I2 = 165.88(3)° and As1−Ge1−As2 = 79.75(3)°, although closer inspection of the crystal packing reveals significant intermolecular Ge1···I1b (3.476(1) Å) and Ge1···I2a (3.352(1) Å) interactions, giving rise to a zigzag polymer chain, as illustrated in Figure 8b, and a highly distorted [As$_2$I$_2$ + I$_2$] donor set at each Ge atom. A similar polymeric chain structure is present in [GeCl$_2$(2,2′-bipy)]$_n$ and [GeBr$_2$(1,10-phen)]$_n$.[7d]

The structure of [GeCl{*o*-C$_6$H$_4$(AsMe$_2$)$_2$}][GeCl$_3$] shows (Figure 9a, Table 8) pyramidal cations and anions, both with crystallographic mirror symmetry, and with the

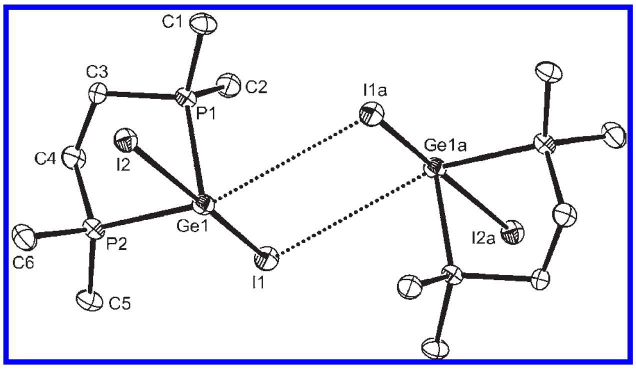

Figure 6. View of the structure of the very weakly associated $[GeI_2\{Me_2P(CH_2)_2PMe_2\}]_2$ dimer with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = 1 − *x*, 2 − *y*, −*z*.

Table 5. Selected Bond Lengths [Å] and Angles [deg] for $[GeI_2\{Me_2P(CH_2)_2PMe_2\}]$

Ge1−P1	2.463(2)	Ge1−P2	2.514(2)
Ge1−I1	2.8685(12)	Ge1−I2	3.0787(13)
P1−Ge1−P2	80.95(7)	P1−Ge1−I1	91.40(6)
P2−Ge1−I1	87.63(6)	P1−Ge1−I2	84.52(5)
P2−Ge1−I2	88.19(6)	I1−Ge1−I2	174.57(3)

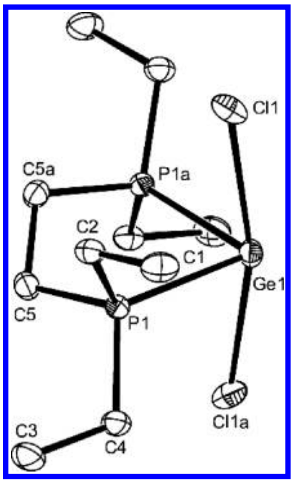

Figure 7. View of the structure of $[GeCl_2\{Et_2P(CH_2)_2PEt_2\}]$ with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Symmetry operation: a = −*x*, *y*, 1/2 − *z*. The atom numbering scheme used is the same for $[GeBr_2\{Et_2P(CH_2)_2PEt_2\}]$.

Table 6. Selected Bond Lengths [Å] and Angles [deg] for $[GeX_2\{Et_2P(CH_2)_2PEt_2\}]$ (X = Cl, Br)

compound	X = Cl	X = Br
Ge1−P1	2.4672(5)	2.4694(5)
Ge1−X1	2.5803(5)	2.7340(4)
P1−Ge1−P1a[a]	81.55(2)	81.60(3)
P1−Ge1−X1	87.100(15)	88.107(15)
P1−Ge1−X1a[a]	81.768(15)	83.276(15)
X1−Ge1−X1a[a]	165.30(2)	168.619(14)

[a] Symmetry operation: a = −*x*, *y*, 1/2 − *z*.

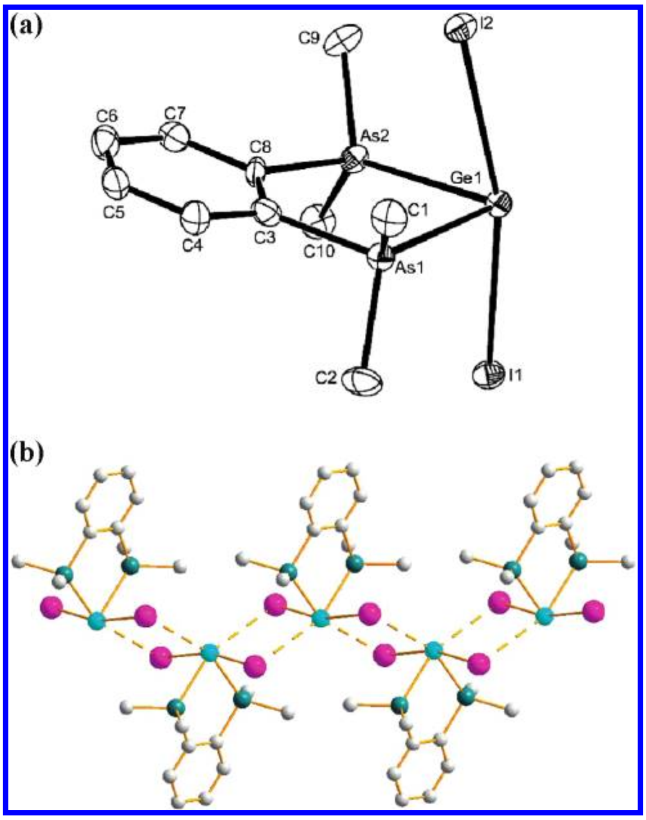

Figure 8. (a) View of the structure of $[GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$ showing the numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. (b) View of the chain structure of $[GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}]_n$ formed through long Ge···I contacts. Turquoise = Ge; pink = I; teal = As; gray = C.

Table 7. Selected Bond Lengths [Å] and Angles [deg] for $[GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$

Ge1−I1	2.8763(10)	Ge1−I2	3.0888(10)
Ge1−As1	2.6210(11)	Ge1−As2	2.6313(11)
As1−Ge1−As2	79.75(3)	As1−Ge1−I1	87.32(3)
As2−Ge1−I1	89.85(3)	As1−Ge1−I2	81.15(3)
As2−Ge1−I2	80.14(3)	I1−Ge1−I2	165.88(3)

diarsine symmetrically chelating (cation, Ge1−Cl1 = 2.373(1) Å, Ge1−As1 = 2.5847(5), As1−Ge1−As1a = 80.75(2)°; anion, Ge−Cl = 2.311(2), 2.294(1) Å). Atoms Cl3 and Cl3b also exhibit weak interactions with Ge1 (3.44 Å), giving a loosely associated chain polymer with alternating cations and anions, and leading to an overall $[As_2Cl + Cl_2]$ coordination at Ge1 (Figure 9b). These are the first reported examples of arsine complexes of germanium(II).

Structural Comparisons. Structural data are presented here for several series of Ge(II) halide complexes with diphosphine and diarsine ligands, allowing quite detailed comparisons to be made. In terms of coordination number and environments present in $[GeX_2(L{-}L)]$, we find [3 + 1] coordination ($PX_2 + P$) for L−L = $o\text{-}C_6H_4(PPh_2)_2$ irrespective of X (likely due to the steric requirements of the Ph rings); essentially [4] coordination (P_2X_2) for L−L = $R_2P(CH_2)_2PR_2$ (R = Me or Et) irrespective of X and for $[GeI_2\{o\text{-}C_6H_4(PMe_2)_2\}]$; and [4 + 2] coordination ($P_2X_2 + X_2$) for $[GeX_2\{o\text{-}C_6H_4(PMe_2)_2\}]$ (X = Cl, Br), which form weak halide-bridged dimers, and for $[GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$, which forms a zigzag chain structure. For a given diphosphine, the Ge−P bond distances are essentially independent of the halide, indicating very similar Lewis acidities for the GeX_2 fragments. In the discrete monomer structures, $[GeX_2\{o\text{-}C_6H_4(PPh_2)_2\}]$, we observe a bent X−Ge−X unit resulting from the pyramidal GeX_2P core, whereas in the four-coordinate $[GeX_2\{R_2P(CH_2)_2PR_2\}]$, the X−Ge−X are approximately linear.

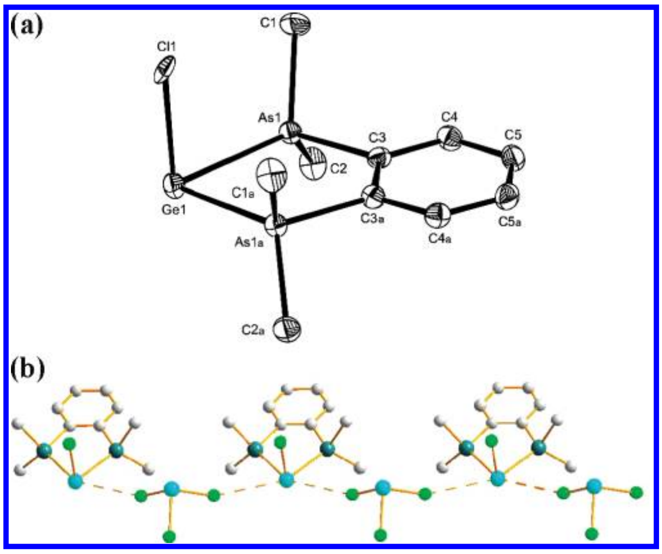

Figure 9. (a) View of the structure of the cation in [GeCl{*o*-C_6H_4-$(AsMe_2)_2$}][$GeCl_3$] with the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The cation (and the anion) has crystallographic mirror symmetry. Symmetry operation: a = *x*, 1/2 − *y*, *z*. (b) View of the chain structure showing alternating, weakly associated [GeCl{*o*-$C_6H_4(AsMe_2)_2$}]$^+$ cations and [$GeCl_3$]$^-$ anions. Turquoise = Ge; green = Cl; teal = As; gray = C.

Table 8. Selected Bond Lengths [Å] and Angles [deg] for [GeCl{*o*-C_6H_4-$(AsMe_2)_2$}][$GeCl_3$]

Ge1−As1	2.5847(5)	Ge2−Cl2	2.3108(15)
Ge1−Cl1	2.3734(13)	Ge2−Cl3	2.2941(10)
As1−Ge1−As1a[a]	80.75(2)	Cl3−Ge2−Cl3b[a]	95.46(5)
Cl1−Ge1−As1	88.21(3)	Cl3−Ge2−Cl2	94.73(4)

[a] Symmetry operations: a = *x*, 1/2 − *y*, *z*; b = *x*, 3/2 − *y*, *z*.

The series [GeX_2{*o*-$C_6H_4(PPh_2)_2$}] (X = Cl, Br, I) adopts a very similar structure to that of [$GeCl_2${$Ph_2P(CH_2)_2PPh_2$}],[10] involving the much more flexible $Ph_2P(CH_2)_2PPh_2$ ligand, which shows Ge−Cl = 2.236(2) and 2.332(2) Å, although the shorter of the two Ge−P distances in that complex (2.314(2) Å) is ca. 0.2 Å shorter than those in [GeX_2{*o*-$C_6H_4(PPh_2)_2$}] (ca. 2.52 Å), while the long Ge···P distance (3.340(2) Å) is ca. 0.2 Å longer, possibly a consequence of the difference in flexibility of the ligand backbones. The Ge−P distances also compare well with those for [$GeX_2(PPh_3)$] (X = Cl, 2.51 Å; X = I, 2.503(4), 2.510(5) Å for the two independent molecules).

The Ge−P distances show a greater dependence upon the nature of the terminal substituent. Most notably, comparing the series [GeX_2{*o*-$C_6H_4(PPh_2)_2$] with [GeX_2{*o*-$C_6H_4(PMe_2)_2$}], we find a decrease in Ge−P in the latter by ca. 0.05 Å (despite the increased coordination number which, in the absence of other factors, would usually lead to lengthening of the bond). This is consistent with the increased σ-donor ability of the Me-substituted phosphine. The same pattern is observed in the structures of [GeX_2{$R_2P(CH_2)_2PR_2$}], which also contain alkyl-substituted (strong σ-donor) phosphines.

Uniquely for the $GeCl_2$/*o*-$C_6H_4(AsMe_2)_2$ system, only the ionic [GeCl{*o*-$C_6H_4(AsMe_2)_2$}][$GeCl_3$] was obtained, although it may simply be the least soluble species in the (labile) reaction system.

A comparison of the Ge−P versus Ge−As distances in the direct analogs [GeI_2{*o*-$C_6H_4(EMe_2)_2$}] (E = P or As) shows that the difference is essentially as expected on the basis of the donor covalent radii.[16]

The only other structurally characterized germanium arsine complexes are *trans*-[$GeCl_4(AsR_3)_2$] (R = Me or Et),[5,6] for which Ge−As = 2.472(1) (Me) and 2.4904(9) Å (Et) and Ge−Cl = 2.307(4) and 2.341(4) Å (Me) and 2.330(2) and 2.323(1) Å (Et). Thus, both Ge−As and Ge−Cl are slightly longer in the Ge(II) species. Similarly, while we cannot compare $GeCl_4$ phosphine complexes with the Ge(II) systems here, since none have been structurally characterized (due to their rapid decomposition into Ge(II) and chlorophosphonium(V) salts),[6] structural data are available for [GeF_4{*o*-$C_6H_4(PMe_2)_2$}] (Ge−P = 2.427(1) Å), which compares with the range 2.4390(11)−2.481(2) Å in the [GeX_2{*o*-$C_6H_4(PMe_2)_2$}].

Conclusions

This work presents the first extended series of Ge(II) halide complexes involving neutral diphosphine and diarsine ligands. The structural studies have identified the range of motifs present which appear to be subtly dependent upon the ligand donor type and steric and electronic properties, although mostly independent of the halide present. The diversity of the structures and coordination numbers observed within this quite closely related series of diphosphine and diarsine ligands suggests that the germanium center does not have a strong stereochemical preference; hence, small differences in steric and electronic properties and possibly crystal packing may play a significant role in determining the geometries adopted. We have not found evidence for more than one structure type for a specific L−L and X. In view of the larger energy gap between the s and p orbitals in germanium compared to silicon and carbon,[17] the observed structures can be rationalized using germanium 4p orbitals and a three-center−four-electron bonding model, leaving the Ge-based "lone pair" occupying the stabilized 4s orbital.

Experimental Section

[$GeCl_2$(1,4-dioxane)] was prepared by the literature method,[18] and $GeBr_2$ and GeI_2 were obtained from Aldrich and used as received. The ligands $Me_2P(CH_2)_2PMe_2$ and $Et_2P(CH_2)_2PEt_2$ were obtained from Aldrich, while *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, and $Ph_2As(CH_2)_2AsPh_2$ were made according to literature methods and stored under N_2 in a glovebox.[19−21] All reactions were conducted using Schlenk, vacuum line, and glovebox techniques and under a dry dinitrogen atmosphere. IR spectra were recorded from Nujol mulls on a Perkin-Elmer Spectrum 100 spectrometer and Raman spectra using a Perkin-Elmer FT Raman 2000R with a Nd:YAG laser. The bands below 360 cm^{-1} in each complex are listed below. ^1H NMR spectra were recorded from solutions in $CDCl_3$ or CD_2Cl_2 solutions on a Bruker AV300 and $^{31}P\{^1H\}$ NMR spectra on a Bruker DPX400 and referenced to 85% H_3PO_4. Microanalytical results were from Medac Ltd.

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(17) See: Nagendran, S.; Roesky, H. W. *Organometallics* **2008**, *27*, 457−492 and references therein.

(18) Denk, M. K.; Herrman, W. A. German Patent DE 4214281 A1, **1993**.

(19) McFarlane, H. C. E.; McFarlane, W. *Polyhedron* **1983**, *2*, 303–304.

(20) Kyba, E. P.; Liu, S. T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877–1879.

(21) Feltham, R. D.; Nyholm, R. S.; Kasenally, A. *J. Organomet. Chem.* **1967**, *7*, 285–288.

[$GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$]. 1,2-Bis(diphenylphosphino)benzene (0.223 g, 0.50 mmol) was added to a solution of [$GeCl_2$(1,4-dioxane)] (0.115 g, 0.50 mmol) in CH_2Cl_2 (15 mL) at room temperature with stirring, giving a clear solution. After 30 min, the solvent was removed in vacuo to leave a white solid which was washed with diethyl ether and dried in vacuo. Colorless crystals were obtained by slow evaporation of the solvent from the dichloromethane solution. Yield: 0.28 g, 95%. Anal. Calcd for $C_{30}H_{24}Cl_2GeP_2$: C, 61.1; H, 4.1. Found: C, 60.7; H, 4.0. ^1H NMR (CD_2Cl_2, 298 K): δ 7.28−7.55 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 4.5 (s). IR (Nujol, cm^{-1}): 317(s), 269(s, br), 240(sh). Raman (cm^{-1}): 318(s), 262(s), 217(s).

[$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$]. 1,2-Bis(diphenylphosphino)benzene (0.223 g, 0.50 mmol) was added to a solution of $GeBr_2$ (0.115 g, 0.50 mmol) in CH_3CN (15 mL) at room temperature with stirring, which gave a clear solution. After 30 min, the solvent was removed in vacuo to leave a white solid, which was washed with diethyl ether and dried in vacuo. Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution. Yield: 0.30 g, 88%. Anal. Calcd for $C_{30}H_{24}Br_2GeP_2$: C, 53.1; H, 3.6. Found: C, 52.9; H, 3.8. ^1H NMR (CD_2Cl_2, 298 K): δ 7.20−7.55 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ −4.8. IR (Nujol, cm^{-1}): 327(m), 289(w), 257(w).

[$GeI_2\{o\text{-}C_6H_4(PPh)_2\}$]. The same method as for [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, yielding a pale yellow solid. Yield: 0.35 g, 91%. Pale yellow crystals were obtained by slow evaporation of the solvent from a dichloromethane solution. Anal. Calcd for $C_{30}H_{24}GeI_2P_2$: C, 46.5; H, 3.1. Found: C, 46.7; H, 3.1. ^1H NMR (CD_2Cl_2, 298 K): δ 7.15−7.55 (m). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ −10.5.

[$GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}$]. The same method as for [$GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using o-$C_6H_4(PMe_2)_2$, yielding a white solid. Yield: 0.14 g, 85%. Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution. Anal. Calcd for $C_{10}H_{16}Cl_2GeP_2$: C, 35.4; H, 4.2. Found: C, 35.0; H, 4.6. ^1H NMR (CD_2Cl_2, 298 K): δ 7.76 (m, [4H], o-C_6H_4), 2.02 (d, [12H] J = 12 Hz, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 21.6 (s). IR (Nujol, cm^{-1}): 341(m), 302(s), 281(w), 225(m). Raman (cm^{-1}): 342(s), 250(s), 217(s).

[$GeBr_2\{o\text{-}C_6H_4(PMe_2)_2\}$]. The same method as for [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using o-$C_6H_4(PMe_2)_2$; the white precipitate was collected by filtration and washed with CH_2Cl_2. Yield: 0.15 g, 71%. Anal. Calcd for $C_{10}H_{16}Br_2GeP_2\cdot CH_2Cl_2$: C, 25.6; H, 3.5. Found: C, 25.4; H, 3.8. ^1H NMR (CD_2Cl_2, 298 K): δ 7.68 (m, [4H], o-C_6H_4), 2.04 (d, [12H] J = 12 Hz, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 13.2 (s). IR (Nujol, cm^{-1}): 339(m), 302(s), 288(w). Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution.

[$GeI_2\{o\text{-}C_6H_4(PMe_2)_2\}$]. 1,2-Bis(dimethylphosphino)benzene (0.100 g, 0.50 mmol) was added to a solution of GeI_2 (0.163 g, 0.50 mmol) in CH_3CN (3 mL) at room temperature with stirring, which immediately precipitated a white solid. After stirring for 30 min, the solid was collected by filtration, washed with a small amount of CH_3CN solvent, and dried in vacuo. Yield: 0.18 g, 70%. Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution. Anal. Calcd for $C_{10}H_{16}GeI_2P_2$: C, 22.8; H, 3.1. Found: C, 22.8; H, 3.1. ^1H NMR (CD_2Cl_2, 298 K): δ 7.69 (m, [4H], o-C_6H_4), 2.18 (d, [12H] J = 12 Hz, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 0.4 (s). IR (Nujol, cm^{-1}): 338(w), 301(m), 234(w).

[$GeCl_2\{Et_2P(CH_2)_2PEt_2\}$]. The same method as for [$GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using $Et_2P(CH_2)_2PEt_2$, yielding a white solid. Yield: 0.16 g, 92%. Colorless crystals were obtained by slow evaporation of the solvent from a dichloromethane solution. Anal. Calcd for $C_{10}H_{24}Cl_2GeP_2\cdot 1/4CH_2Cl_2$: C, 33.2; H, 6.7. Found: C, 33.5; H, 7.1. ^1H NMR (CD_2Cl_2, 298 K): δ 2.20 (m, [8H], CH_2), 1.15 (m, [12H], Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 35.7 (br s). IR (Nujol, cm^{-1}): 282(w), 233(m), 229(m).

[$GeBr_2\{Et_2P(CH_2)_2PEt_2\}$]. The same method as for [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using $Et_2P(CH_2)_2PEt_2$, yielding a white solid. Yield: 0.20 g, 93%. Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution. Anal. Calcd for $C_{10}H_{24}Br_2GeP_2$: C, 27.4; H, 5.5. Found: C, 27.5; H, 5.5. ^1H NMR (CD_2Cl_2, 298 K): δ 2.23 (m, [8H], CH_2), 1.15 (m, [12H] Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 29.4 (s). IR (Nujol, cm^{-1}): 278(w), 226(w).

[$GeCl_2\{Me_2P(CH_2)_2PMe_2\}$]. The same method as for [$GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using $Me_2P(CH_2)_2PMe_2$, yielding a white solid. Yield: 0.13 g, 90%. Colorless crystals were obtained by slow evaporation of the solvent from a dichloromethane solution. Anal. Calcd for $C_6H_{16}Cl_2GeP_2\cdot 1/2CH_2Cl_2$: C, 23.2; H, 5.2. Found: C, 23.1; H, 5.0. ^1H NMR (CD_2Cl_2, 298 K): δ 2.26 (d, [4H] $^2J_{P,H}$ = 12 Hz, CH_2), 1.72 (d, [12H] $^2J_{P,H}$ = 12 Hz, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 17.4 (s). IR (Nujol, cm^{-1}): 350(m), 327(w), 309(m), 265(br m).

[$GeBr_2\{Me_2P(CH_2)_2PMe_2\}$]. The same method as for [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using $Me_2P(CH_2)_2PMe_2$, yielding a white solid. Yield: 0.16 g, 88%. Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution. Attempts to obtain satisfactory microanalytical data on different samples consistently gave %C and %H values lower than expected, possibly due to some ligand loss during drying of the samples in vacuo. However, the spectroscopic and crystallographic data provide unambiguous evidence for the existence of this compound and strongly suggest only one phosphine-containing species is produced. ^1H NMR (CD_2Cl_2, 298 K): δ 2.27 (d, [4H] $^2J_{P,H}$ = 12 Hz, CH_2), 1.83 (d, [12H] $^2J_{P,H}$ = 12 Hz, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 11.8 (s). IR (Nujol, cm^{-1}): 345(m), 264(m).

[$GeI_2\{Me_2P(CH_2)_2PMe_2\}$]. 1,2-Bis(dimethylphosphino)ethane (0.075 g, 0.50 mmol) was added to a solution of GeI_2 (0.163 g, 0.50 mmol) in CH_3CN (5 mL) at room temperature. After stirring for 30 min, the volatiles were removed in vacuo to leave the white residue. Yield: 0.19 g, 92%. Colorless crystals were obtained by slow evaporation of the solvent from an acetonitrile solution. Anal. Calcd for $C_6H_{16}GeI_2P_2$: C, 15.1; H, 3.4. Found: C, 15.4; H, 3.6. ^1H NMR (CD_2Cl_2, 298 K): δ 2.31 (d, [4H] $^2J_{P,H}$ = 12 Hz, CH_2), 1.97 (d, [12H] $^2J_{P,H}$ = 12 Hz, Me). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 0.7 (s). IR (Nujol, cm^{-1}): 320(br w).

[$GeCl\{o\text{-}C_6H_4(AsMe_2)_2\}$][$GeCl_3$]. 1,2-Bis(dimethylarsino)benzene (0.140 g, 0.50 mmol) was added to a solution of [$GeCl_2$(1,4-dioxane)] (0.230 g, 1.00 mmol) in CH_2Cl_2 (15 mL) at room temperature with stirring, which gave precipitation of a white solid. After stirring for 30 min, the solvent was removed in vacuo. The white solid residue was washed with diethyl ether and dried in vacuo. Yield: 0.22 g, 75%. Colorless crystals were obtained by slow evaporation of the solvent from a dichloromethane solution. Anal. Calcd for $C_{10}H_{16}As_2Cl_4Ge_2$: C, 21.0; H, 2.8. Found: C, 21.6; H, 2.8. ^1H NMR (CD_2Cl_2, 298 K): δ 7.44 (m, [2H] o-C_6H_4), 7.31 (m, [2H] o-C_6H_4), 1.30 (s, [12H] Me). IR (Nujol, cm^{-1}) 343(m), 329(m),* 309(w), 271(vs)*. Raman (cm^{-1}): 355(m), 328(m),* 305(m), 255(s),* 216(m) (* = [$GeCl_3$]$^-$).

[$GeBr_2\{o\text{-}C_6H_4(AsMe_2)_2\}$]. The same method as for [$GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$] above is used, but using o-$C_6H_4(AsMe_2)_2$, yielding a white solid. Yield: 0.18 g, 72%. Colorless crystals were obtained by slow evaporation of the solvent from a CH_2Cl_2 solution. Anal. Calcd for $C_{10}H_{16}As_2Br_2Ge\cdot CH_2Cl_2$: C, 21.9; H, 3.0. Found: C, 21.7; H, 3.3. ^1H NMR (CD_2Cl_2, 298 K): δ 7.51 (m, [2H] o-C_6H_4), 7.44 (m, [2H] o-C_6H_4), 1.54 (s, [12H] Me). IR (Nujol, cm^{-1}): 356(s), 270(s), 253(s).

[$GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}$]. 1,2-Bis(dimethylarsino)benzene (0.140 g, 0.50 mmol) was added to a solution of GeI_2 (0.163 g, 0.50 mmol) in CH_3CN (3 mL) at room temperature with stirring, which gave precipitation of a white solid and a solution color

Table 9. Crystallographic Parameters[a]

compound	$[GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}]$	$[GeBr_2\{o\text{-}C_6H_4(PPh_2)_2\}]$	$[GeI_2\{o\text{-}C_6H_4(PPh_2)_2\}]$	$[GeCl_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	$[GeBr_2\{o\text{-}C_6H_4(PMe_2)_2\}]$
formula	$C_{30}H_{24}Cl_2GeP_2$	$C_{30}H_{24}Br_2GeP_2$	$C_{30}H_{24}GeI_2P_2$	$C_{10}H_{16}Cl_2GeP_2$	$C_{10}H_{16}Br_2GeP_2$
M	589.92	678.84	772.82	341.66	430.58
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)
a [Å]	10.438(3)	10.578(3)	11.0465(18)	28.542(4)	29.441(4)
b [Å]	14.335(4)	14.164(3)	14.192(3)	7.4696(10)	7.5466(10)
c [Å]	18.996(5)	18.588(3)	18.503(3)	14.101(3)	14.395(2)
α [deg]	90	90	90	90	90
β [deg]	90	98.068(15)	97.270(12)	109.928(10)	110.646(7)
γ [deg]	90	90	90	90	90
U [Å^3]	2842.1(13)	2757.4(10)	2877.5(9)	2826.3(8)	2992.9(7)
Z	4	4	4	8	8
μ(Mo Kα) [mm^{-1}]	1.396	4.143	3.339	2.740	7.571
total no. reflns	27455	36845	30988	15378	18434
R_{int}	0.095	0.108	0.084	0.073	0.050
unique reflns	6451	6287	6526	3243	3413
no. of params	317	316	316	140	140
R_1 [$I_o > 2\sigma(I_o)$]	0.052	0.048	0.068	0.046	0.032
R_1 [all data]	0.116	0.094	0.095	0.068	0.041
wR_2 [$I_o > 2\sigma(I_o)$]	0.091	0.096	0.143	0.092	0.062
wR_2 [all data]	0.109	0.111	0.160	0.104	0.066

compound	$[GeI_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	$[GeCl_2\{Me_2P(CH_2)_2PMe_2\}]$	$[GeBr_2\{Me_2P(CH_2)_2PMe_2\}]$	$[GeI_2\{Me_2P(CH_2)_2PMe_2\}]$
formula	$C_{10}H_{16}GeI_2P_2$	$C_6H_{16}Cl_2GeP_2$	$C_6H_{16}Br_2GeP_2$	$C_6H_{16}GeI_2P_2$
M	524.56	293.62	382.54	476.52
cryst syst	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a [Å]	15.369(3)	9.7602(15)	9.809(2)	7.586(2)
b [Å]	7.717(2)	10.533(2)	10.834(3)	7.648(2)
c [Å]	14.814(3)	12.113(2)	12.324(3)	12.419(4)
α [deg]	90	90	90	74.683(15)
β [deg]	116.741(10)	110.909(10)	109.803(3)	81.153(15)
γ [deg]	90	90	90	74.691(15)
U [Å^3]	1569.0(5)	1163.3(3)	1232.2(5)	667.5(3)
Z	4	4	4	2
μ(Mo Kα) [mm^{-1}]	6.064	3.313	9.180	7.113
total no. reflns	15015	7459	6301	12806
R_{int}	0.048	0.042	0.027	0.050
unique reflns	3569	1345	1402	3042
no. of params	140	53	53	104
R_1 [$I_o > 2\sigma(I_o)$]	0.053	0.024	0.019	0.045
R_1 [all data]	0.070	0.028	0.023	0.056
wR_2 [$I_o > 2\sigma(I_o)$]	0.110	0.052	0.047	0.098
wR_2 [all data]	0.119	0.054	0.049	0.104

compound	$[GeCl_2\{Et_2P(CH_2)_2PEt_2\}]$	$[GeBr_2\{Et_2P(CH_2)_2PEt_2\}]$	$[GeI_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$	$[GeCl\{o\text{-}C_6H_4(AsMe_2)_2\}][GeCl_3]$
formula	$C_{10}H_{24}Cl_2GeP_2$	$C_{10}H_{24}Br_2GeP_2$	$C_{10}H_{16}As_2GeI_2$	$C_{10}H_{16}As_2Cl_4Ge_2$
M	349.72	438.64	612.48	573.05
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)	$Pnma$ (no. 62)
a [Å]	12.116(1)	12.343(2)	9.1163(10)	18.572(2)
b [Å]	10.146(1)	10.339(2)	8.8655(10)	9.8246(10)
c [Å]	13.548(1)	13.732(2)	20.265(3)	9.9071(10)
α [deg]	90	90	90	90
β [deg]	114.188(1)	114.261(2)	101.324(7)	90
γ [deg]	90	90	90	90
U [Å^3]	1519.2(2)	1597.6(5)	1606.0(3)	1807.6(3)
Z	4	4	4	4
μ(Mo Kα) [mm^{-1}]	2.550	7.093	9.815	7.532
total no. reflns	10691	8945	19228	16937
R_{int}	0.026	0.024	0.057	0.026
unique reflns	1740	1830	3679	2167
no. of params	69	69	140	90
R_1 [$I_o > 2\sigma(I_o)$]	0.022	0.019	0.045	0.029
R_1 [all data]	0.025	0.021	0.063	0.031
wR_2 [$I_o > 2\sigma(I_o)$]	0.051	0.044	0.084	0.077
wR_2 [all data]	0.053	0.045	0.094	0.078

[a] Common items: temperature = 120 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°; $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

change from yellow to pale pink. After stirring for 30 min, the solvent was removed by filtration. The white solid residue was washed with a small amount of CH_3CN and dried in vacuo. Yield: 0.19 g, 63%. Colorless crystals were obtained by slow evaporation of the solvent from an acetronitrile solution. Anal. Calcd for $C_{10}H_{16}As_2GeI_2$: C, 19.6; H, 2.6. Found: C, 18.9; H, 2.6. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.51 (m, [4H] o-C_6H_4), 1.69 (s, [12H] Me). IR (Nujol, cm^{-1}): 355(m), 248(w), 223(w).

X-Ray Crystallography. Details of the crystallographic data collection and refinement parameters are given in Table 9. Crystals suitable for single-crystal X-ray analysis were obtained as described above. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo Kα radiation (λ = 0.71073 Å) and either a graphite monochromator or confocal mirrors, with the crystals held at 120 K in a nitrogen gas stream. Structure solution and refinement were mostly straightforward (except as described below),[22-24] with H atoms introduced into the models in idealized positions using the default C−H distance. The fit to the data for $[GeCl_2\{o\text{-}C_6H_4(PPh_2)_2\}]$ in the noncentrosymmetric space group was slightly improved by the inclusion of the SHELX TWIN/BASF commands in the model. Selected bond lengths and angles are given in Tables 2−8.

CCDC 724637−724641 and CCDC 749461−749468 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information Available: CIF files for the crystal structures described. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997.

(23) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

(24) Flack, H. D. *Acta Crystallogr., Sect. A* **1983**, *39*, 876–879.