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Preparation, Characterization, and Structural Systematics of Diphosphane and Diarsane Complexes of Gallium(III) Halides

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The diphosphane o-C₆H₄(PMe₂)₂ reacts with GaX₃ (X = CI, Br, or I) in a 1:1 molar ratio in dry toluene to give *trans*-[GaX₂{o-C₆H₄(PMe₂)₂}₂][GaX₄], the cations of which contain the first examples of six-coordinate gallium in a phosphane complex. The use of a 1:2 ligand/GaCl₃ ratio produced [GaCl₂{o-C₆H₄(PMe₂)₂}][GaCl₄], containing a pseudotetrahedral cation, and similar pseudotetrahedral [GaX₂{o-C₆H₄(PPh₂)₂}][GaX₄] complexes are the only products isolated with the bulkier o-C₆H₄(PPh₂)₂. On the other hand, Et₂P(CH₂)₂PEt₂, which has a flexible aliphatic backbone, formed [(X₃Ga)₂{ μ -Et₂P(CH₂)₂PEt₂}], in which the ligand bridges two pseudotetrahedral gallium centers. The diarsane, o-C₆H₄(AsMe₂)₂, formed [GaX₂{o-C₆H₄(AsMe₂)₂}][GaX₄], also containing pseudotetrahedral cations, and in marked contrast to the diphosphane analogue, no six-coordinate complexes form; a very rare example where these two much studied ligands behave differently towards a common metal acceptor. The complexes [(I₃Ga)₂{ μ -Ph₂As-(CH₂)₂AsPh₂}] and [GaX₃(AsMe₃)] are also described. The X-ray structures of *trans*-[GaX₂{o-C₆H₄(PMe₂)₂}][GaX₄], (X = CI, Br or I), [GaCl₂{o-C₆H₄(PPh₂)₂}][GaCl₄], [GaX₂{o-C₆H₄(AsMe₂)₂}][GaX₄] (X = CI or I), [(I₃Ga)₂{ μ -Ph₂-As(CH₂)₂AsPh₂}], and [GaX₃(AsMe₃)] (X = CI, Br or I) are reported, and the structural trends are discussed. The solution behavior of the complexes has been explored using a combination of ³¹P{¹H} and ⁷¹Ga NMR spectroscopy.

Introduction

The coordination chemistry of the p-block metals has been much less thoroughly investigated than that of the transition elements,^{1,2} and while detailed studies have been carried out on individual complexes or systems, the factors which control stoichiometries and structures often remain unclear.^{3,4} In general, p-block chemistry seems less amenable to "fine-tuning" of the metal center properties by ligand design than that of familiar d-block elements. However, the p-block metals have many technologically important applications and devising improved reagents for existing processes or developing new synthons depends upon an understanding of how the ligands control the metal-center chemistry, structure, and reactivity. In the case of gallium, the major applications lie

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in the electronics industries in compound semiconductors based on III–V materials: for example, GaN, GaP, and GaAs are used extensively in LED applications; GaSb is used in thermal imaging devices, while GaAs is also widely used in integrated circuits, displays, and solar cells.^{5,6} Other applications of gallium compounds are as gallium gadolinium garnet in bubble memory devices,⁶ and the lower Lewis acidity, compared to that of aluminum halides, has produced some applications for GaX₃ in organic transformations.⁷ The radioisotopes ⁶⁷Ga and ⁶⁸Ga have found uses in diagnosis and therapy;⁸ mostly, these are used as gallium complexes with O- or N-donor chelates, which resist hydrolysis in vivo and provide appropriate lipophilicity.

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A number of gallium(III) halide complexes with phosphane or arsane ligands have been reported, the vast majority being of the type $[GaX_3(ER_3)]$ (E = P or As) with pseudotetrahedral gallium.⁹⁻¹² Two other types identified are the $[(I_3 - I_3 -$ Ga)₂{ μ -Ph₂P(CH₂)₂PPh₂}]¹³ and the rare cationic [GaX₂{o- $C_6H_4(PPh_2)_2$][GaX₄] (X = Br or I).¹⁴ We have recently reported complexes with the triarsane, $MeC(CH_2AsMe_2)_3$, which adopts a number of coordination modes, but all are to four-coordinate gallium centers.¹⁵ Here, we report detailed structural and spectroscopic investigations on gallium(III) halide complexes with diphosphane and diarsane ligands, with the aim of understanding how the ligand architecture, electronic requirements, and steric requirements influence the stoichiometry and properties. The solution properties and interconversions have been probed by variable-temperature ³¹P{¹H} and ⁷¹Ga NMR spectroscopy.

Experimental Section

General Procedures. All the reactions and manipulations were performed in an inert atmosphere (N₂) glovebox or with Schlenk techniques. The solvents toluene, diethyl ether, and hexane were dried by distillation over sodium/benzophenone, and dichloromethane was dried by distillation from CaH₂. Infrared spectra were measured as Nujol mulls between CsI plates on a Perkin-Elmer PE983 spectrometer. Raman spectra were recorded from powdered solid samples using a Perkin-Elmer FT-Raman 2000R with a Nd:YAG laser. ¹H NMR spectra were recorded in CDCl₃ solution on a Bruker AV300; ³¹P{¹H} (161.9 MHz) and ⁷¹Ga (122.0 MHz) NMR spectra were recorded on a Bruker DPX400 and referenced to 85% H₃PO₄ and [Ga(H₂O)₆]³⁺, respectively. GaCl₃ and GaI₃ were obtained from Aldrich and used as received. GaBr₃ (Aldrich) was sublimed in vacuo at 70 °C. The ligands o-C₆H₄-(PMe₂)₂, o-C₆H₄(PPh₂)₂, o-C₆H₄(AsMe₂)₂, Ph₂P(CH₂)₂PPh₂ and Ph₂-As(CH₂)₂AsPh₂ were prepared by literature methods,¹⁶⁻¹⁹ while the other ligands were obtained from Aldrich or Strem and used as received. The complexes were made by similar routes and therefore only representative examples are described. [GaX₃(PPh₃)] complexes were made as described.11

[GaI₂{o-C₆H₄(PMe₂)₂}₂][GaI₄]. GaI₃ (0.266 g, 0.590 mmol) was added to a solution of o-C₆H₄(PMe₂)₂ (0.117 g, 0.590 mmol) in toluene (15 cm³) at room temperature. After it was heated at 80 °C for 2 h, the mixture was returned to room temperature, and the solvent was reduced in vacuo to ~5 cm³. The resulting white precipitate was filtered off and dried in vacuo. Yield: 0.32 g, 85%.

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Anal. Calcd for $C_{20}H_{32}Ga_{2}I_{6}P_{4}$: C, 18.5; H, 2.5. Found: C, 18.7; H, 2.4. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.6–7.8 (m, [4H], C₆H₄), 1.74 (s, [12H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ –457 (br). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ –43.0 (s). IR (cm⁻¹, Nujol): ν 216 (s), 205 (m). Raman (cm⁻¹): 217 (s).

[GaCl₂{*o***-C₆H₄(PMe₂)₂]₂][GaCl₄].** This was prepared in a manner similar to that described above as a white solid. Yield: 82%. Anal. Calcd for C₂₀H₃₂Cl₆Ga₂P₄: C, 32.1; H, 4.3. Found: C, 32.2; H, 4.2. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.6−7.8 (m, [4H], C₆H₄) 1.75 (s, [12H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 251 (s). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ -40.8 (s). IR (cm⁻¹, Nujol): *v* 372 (vs), 339 (m), 252 (m), 203 (m). Raman (cm⁻¹): 372 (w), 344 (s), 332 (m), 238 (s), 197 (m).

[GaBr₂{o-C₆H₄(PMe₂)₂]₂][GaBr₄]. This was prepared in a manner similar to that described above as a white solid. Yield: 90%. Anal. Calcd for C₂₀H₃₂Br₆Ga₂P₄: C, 23.7; H, 3.2. Found: C, 23.3; H, 3.1. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.6–7.8 (m, [4H], C₆H₄), 1.73 (s, [12H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 63.5 (s). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ –41.2 (s). IR (cm⁻¹, Nujol): ν 315 (w), 272 (vs), 250 (w). Raman (cm⁻¹): 333 (m), 273 (m), 239 (m), 210 (vs).

[GaCl₂{*o***-C₆H₄(PMe₂)₂}][GaCl₄].** This was prepared in a manner similar to that described above as a white solid by reaction of the ligand and GaCl₃ in a 1:2 molar ratio in hot toluene. Yield: 85%. Anal. Calcd for C₁₀H₁₆Cl₆Ga₂P₂: C, 21.8; H, 2.9. Found: C, 22.0; H, 2.9. ¹H NMR (300 MHz, CD₂Cl₂): insoluble. ⁷¹Ga NMR (see text) (MeCN/5% CD₃CN): δ 251 (s). ³¹P{¹H} NMR (MeCN/5% CD₃CN): δ -52.2 (br, [P]). ^{-4.0} (br, [P]). ³¹P⁻¹H coupled NMR (MeCN/5% CD₃CN): δ -52.2 (br, [P]), -4.0 (d, [P] ¹J_{PH} = 545 Hz). IR (cm⁻¹, Nujol): ν 410 (s), 380 (vs), 362 (s).

[GaI₃{\mu-Et₂P(CH₂)₂PEt₂}GaI₃]. A solution of Et₂P(CH₂)₂PEt₂ (0.075 g, 0.364 mmol) in toluene (5 cm³) was added dropwise to a stirred solution of GaI₃ (0.327 g, 0.726 mmol) in toluene (20 cm³) at room temperature. After it was heated at 80 °C for 2 h, the mixture was returned to room temperature, and the solvent was reduced to about 6 cm³ in vacuo. The white precipitate was filtered off and dried in vacuo. Yield: 0.31 g, 77%. Anal. Calcd for C₁₀H₂₄-Ga₂I₆P₂: C, 10.9; H, 2.2. Found: C, 11.6; H, 2.2. ¹H NMR (300 MHz, CDCl₃): δ 2.47 (d, [4H], CH₂), 2.22–2.00 (m, [8H], CH₂), 1.45–1.29 (m, [12H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ –132 (br). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ –27.6 (s). IR (cm⁻¹, Nujol): ν 240 (s), 229 (s). Raman (cm⁻¹): 230 (s).

[GaCl₃{ μ -Et₂P(CH₂)₂PEt₂}GaCl₃]. This was prepared in a manner similar to that described above. Yield: 79%. Anal. Calcd for C₁₀H₂₄Cl₆Ga₂P₂: C, 21.5; H, 4.3. Found: C, 20.7; H, 4.6. ¹H NMR (300 MHz, CDCl₃): δ 2.26 (d, [4H], CH₂), 2.13–1.96 (m, [8H], CH₂), 1.44–1.23 (m, [12H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 274 (br). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ -2.0 (s). IR (cm⁻¹, Nujol): ν 376 (s), 350 (m). Raman (cm⁻¹): 381 (m), 353 (s).

[GaBr₃{ μ -Et₂P(CH₂)₂PEt₂}GaBr₃]. This was prepared in a manner similar to that described above. Yield: 81%. Anal. Calcd for C₁₀H₂₄Br₆Ga₂P₂: C, 14.6; H, 3.0. Found: C, 14.3; H, 3.2. ¹H NMR (300 MHz, CDCl₃): δ 2.35 (d, [4H], CH₂), 2.17–1.95 (m, [8H], CH₂), 1.39–1.20 (m, [12H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 163 (br). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ -7.7 (s). IR (cm⁻¹, Nujol): ν 292 (s), 251 (w). Raman (cm⁻¹): 295 (m), 249 (s).

[GaCl₂{ $o-C_6H_4(PPh_2)_2$ }][GaCl₄]. A solution of $o-C_6H_4(PPh_2)_2$ (0.29 g, 0.65 mmol) in toluene (25 cm³) was added dropwise to a stirred solution of GaCl₃ (0.23 g, 1.31 mmol) in toluene (4 cm³) at room temperature. The solution was heated to 80 °C for 2 h, and then it was cooled to room temperature. The resultant white

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Complexes of Gallium(III) Halides

Table	1.	Summary	of	Crystallographic	Data ^a

	$[GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaCl_4]$	$[GaBr_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaBr_4]\textbf{\cdot}CH_2Cl_2$	$[GaI_2\{o-C_6H_4(PMe_2)_2\}_2][GaI_4] \cdot nCH_2Cl_2$
formula fw cryst syst	C ₂₀ H ₃₂ Cl ₆ Ga ₂ P ₄ 748.48 monoclinic	C ₂₁ H ₃₄ Br ₆ Cl ₂ Ga ₂ P ₄ 1100.16 orthorhombic	C _{20.4} H _{32.8} Cl _{0.8} Ga ₂ I ₆ P ₄ 1331.15 orthorhombic
space group	<i>C</i> 2/ <i>c</i> (No. 15)	Pnma (No. 62)	<i>Pnma</i> (No. 62)
a (Å)	13.2556(16)	14.688(3)	15.223(2)
$b(\mathbf{A})$	14.536(2)	22.978(4)	23.406(4)
$C(\mathbf{A})$	10.594(2)	10.4931(18)	11.0027(10)
β (deg)	104 131(8)	90	90
γ (deg)	90	90	90
$V(Å^3)$	3100.6(7)	3541.5(11)	3920.4(9)
Ζ	4	4	4
D_{calcd} (g cm ⁻³)	1.603	2.063	2.255
μ (Mo K α) (mm ⁻¹)	2.472	8.636	6.328
F(000) D1h [I > 2 $\sigma(D)$	1504	2104	2435.2
$KI^{\circ}[I \ge 2O(I)]$ wR2 [all data]	0.020	0.041	0.050
witt2 [all uata]			
	$[GaCl_2\{o-C_6H_4(PPh_2)_2\}][GaCl_4]$	$[(GaBr_3)_2 \{Et_2P(CH_2)_2PEt_2\}]$	$[(Gal_3)_2\{Et_2P(CH_2)_2PEt_2\}]$
formula	$C_{30}H_{24}Cl_6Ga_2P_2$	$C_{10}H_{24}Br_6Ga_2P_2$	$C_{10}H_{24}Ga_2I_6P_2$
TW arrivet exect	/98.57 trialinia	825.13 trialinia	1107.07 trialinia
space group	$P\overline{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\overline{1}$ (No. 2)
a(Å)	10139(2)	7 4000(16)	7 7763(18)
$b(\mathbf{A})$	10.593(3)	7.4685(16)	7.818(2)
c (Å)	16.028(4)	10.805(2)	10.993(3)
α (deg)	72.765(12)	85.619(12)	86.676(15)
β (deg)	87.616(12)	88.087(12)	82.577(15)
γ (deg)	89.878(12)	77.456(12)	80.447(18)
$V(A^3)$	1642.6(7)	581.1(2)	653.1(3)
Z -3	2	1	1
D_{calcd} (g cm ⁻³)	1.615	2.338	2.815
$\mu(NO K0)(IIIII)$	2.240	386	9.208
$R_{1b}^{b}[I > 2\sigma(I)]$	0.048	0.037	0.038
wR2 [all data]	0.102	0.071	0.089
. ,	$[GaCl_2{o-C_6H_4(AsMe_2)_2}][GaCl_4]$	$[GaI_2{o-C_6H_4(AsMe_2)_2}][GaI_4]$	$[(GaI_3)_2{Ph_2As(CH_2)_2AsPh_2}]$
formula	C10H16AS2CleGa2	C10H16As2Ga2I6	C26H24AS2Ga2I6
fw	638.21	1186.91	1387.13
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/m$ (No. 11)	<i>Pnma</i> (No. 62)	$P2_1/n$ (No. 14)
a (Å)	9.941(2)	15.935(4)	10.1666(10)
b (A)	10.111(3)	11.374(2)	15.4125(15)
$c(\mathbf{A})$	10.206(2)	14.319(3)	23.181(2)
α (deg) β (deg)	90	90	90
μ (deg)	91.505(10)	90	99.030(3)
$V(Å^3)$	1025.7(4)	2595 4(9)	3587 1(6)
Z	2	4	4
D_{calcd} (g cm ⁻³)	2.066	3.038	2.568
μ (Mo K α) (mm ⁻¹)	6.597	11.736	8.512
F(000)	612	2088	2504
$\mathrm{R1}^{b}\left[I \geq 2\sigma(I)\right]$	0.067	0.073	0.045
wR2 [all data]	0.146	0.150	0.091

^{*a*} Temp = 120 K; wavelength(Mo K α) = 0.71073 Å; θ (max) = 27.5°. ^{*b*} R1 = Σ ||*F*_o| - |*F*_c||/ Σ |*F*_o|; wR2 = [$\Sigma w(F_o^2 - F_c^2)^2 / \Sigma wF_o^4$]^{1/2}.

precipitate was filtered off and dried in vacuo. Yield: 0.27 g, 53%. Anal. Calcd for $C_{30}H_{24}Cl_6Ga_2P_2$: C, 45.1; H, 3.0. Found: C, 44.8; H, 3.2. ¹H NMR (300 MHz, CDCl₃): δ 8.01–7.31 (m, Ph). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 251 (br). ³¹P{¹H} NMR (CH₂Cl₂/5% CD₂Cl₂): δ -18.9 (br). IR (cm⁻¹, Nujol): ν 404 (m), 385 (s), 370 (s). Raman (cm⁻¹): 402 (w), 388 (m), 374 (m), 346 (s).

 $[GaX_2{o-C_6H_4(PPh_2)_2}][GaX_4]$ (X = Br or I). These compounds were made as described.¹⁴

 $[GaCl_{2}{o-C_{6}H_{4}(AsMe_{2})_{2}}][GaCl_{4}]$. A solution of $o-C_{6}H_{4}$ -(AsMe₂)₂ (0.163 g, 0.57 mmol) in toluene (5 cm³) was added dropwise to a stirred solution of GaCl₃ (0.200 g, 1.14 mmol) in toluene (3 cm³) at room temperature. The mixture was heated to 80 °C for 2 h and cooled, and the resulting white precipitate was

filtered off and dried in vacuo. Yield: 0.28 g, 79%. Anal. Calcd for C₁₀H₁₆As₂Cl₆Ga₂: C, 18.8; H, 2.5. Found: C, 18.8; H, 2.8. ¹H NMR (300 MHz, CDCl₃): δ 7.89–7.40 (m, [4H], C₆H₄), 2.12 (s, [6H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 256 (br) 250 (s). IR (cm⁻¹, Nujol): ν 421 (s), 378 (s) 356 (s), 265 (m). Raman (cm⁻¹): 422 (w), 381 (m), 361 (m), 344 (s), 265 (m).

[GaBr₂{*o*-C₆H₄(AsMe₂)₂}][GaBr₄]. This was prepared in a manner similar to that described above as a white solid. Yield: 72%. Anal. Calcd for C₁₀H₁₆As₂Br₆Ga₂: C, 13.3; H, 1.8. Found: C, 13.5; H, 1.7. ¹H NMR (300 MHz, CDCl₃): δ 7.90–7.40 (m, [4H], C₆H₄), 2.11 (s, [6H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 141 (br), 64 (s). IR (cm⁻¹, Nujol): ν 280 (s), 254 (m). Raman (cm⁻¹): 280 (w), 264 (w), 232 (m), 209 (s).

Table 2.	Selected E	Bond Length	ıs (Å) and	Angles ((deg) f	or
[GaX ₂ {o-	C ₆ H ₄ (PMe ₂	$)_{2}_{2}[GaX_{4}]$	(X = Cl,	Br or I)		

$[GaCl_2 \{o-C_6H_4(PMe_2)_2\}_2][GaCl_4]^a$				
Ga1-Cl1	2.3585(5)	Ga2-Cl2	2.1774(5)	
Ga1-P1	2.4806(5)	Ga2-Cl3	2.1695(5)	
Ga1-P2	2.4794(6)			
P2-Ga1-P1	81.751(15)	Cl1-Ga1-P1	87.321(19)	
Cl1-Ga1-P2	87.570(15)		0.1022(22)	
Cl2-Ga2-Cl2a	111.11(3)	Cl3-Ga2-Cl2	109.17(2)	
Cl3-Ga2-Cl2a	108.64(2)	Cl3-Ga2-Cl3a	110.10(3)	
[GaBr	$\{o-C_6H_4(PMe_2)\}$	$\left[GaBr_{4} \right] \cdot CH_{2}Cl_{2}^{b}$		
Ga1-Br1	2.5276(6)	Ga2-Br2	2.3440(10)	
Ga1-P1	2.4751(12)	Ga2-Br3	2.3311(7)	
Ga1-P2	2.4875(12)	Ga2-Br4	2.3370(10)	
P1-Ga1-P2	82.47(4)	P2-Ga1-Br1	92.88(3)	
P1-Ga1-Br1	94.39(3)			
Br3-Ga2-Br3a	109.33(4)	Br3-Ga2-Br4	110.82(3)	
Br2-Ga2-Br3	109.05(3)	Br2-Ga2-Br4	107.72(4)	
[GaI ₂]	$\{o-C_6H_4(PMe_2)_2\}$	$_{2}$ [GaI ₄]• <i>n</i> CH ₂ Cl ₂ ^c		
Ga1-I1	2.7481(6)	Ga2-I2	2.5509(14)	
Ga1-P1	2.487(2)	Ga2-I3	2.5559(14)	
Ga1-P2	2.499(2)	Ga2-I4	2.5401(10)	
P1-Ga1-P2	81.67(7)	P2-Ga1-I1	85.89(5)	
P1-Ga1-I1	86.49(5)			
I2-Ga2-I3	107.46(5)	I4-Ga2-I2	110.84(3)	
I4-Ga2-I4a	108.39(5)	I4-Ga2-I3	109.65(3)	

^{*a*} Symmetry operation: a 2 - x, y, 1/2 - z. ^{*b*} Symmetry operation: a x, 1/2 - y, *z*. ^{*c*} Symmetry operation: a x, 3/2 - y, *z*.

[GaI₂{*o***-C**₆**H**₄(**AsMe**₂)₂**}][GaI₄].** This was prepared in a manner similar to that described above as a white solid. Yield: 69%. Anal. Calcd for C₁₀H₁₆As₂Ga₂I₆: C, 10.1; H, 1.4. Found: C, 10.5; H, 1.1. ¹H NMR (CDCl₃): δ 7.90−7.40 (m, [4H], C₆H₄), 2.01 (s, [6H], CH₃). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ −166.0 (s), −450.7 (s). IR (cm⁻¹, Nujol): ν 266 (m), 223 (s), 216 (sh). Raman (cm⁻¹): 263 (m), 223 (s), 218 (m).

[GaI₃{\mu-Ph₂As(CH₂)₂AsPh₂}GaI₃]. A solution of Ph₂As(CH₂)₂-AsPh₂ (0.113 g, 0.23 mmol) in dichloromethane (3 cm³) was added to stirred solution of GaI₃ (0.209 g, 0.465 mmol) in the same solvent (20 cm³) at room temperature. After the mixture was stirred at room temperature overnight, the solvent was reduced to \sim 3 cm³ to give a white precipitate. The precipitate was filtered off, washed using CH₂Cl₂, and dried in vacuo. Yield: 0.19 g, 61%. Anal. Calcd for C₂₆H₂₄As₂Ga₂I₆: C, 22.5; H, 1.7. Found: C, 23.1; H, 1.6. ¹H NMR (300 MHz, CDCl₃): δ 7.60–7.43 (m, [20H], Ph), 3.09 (s, [4H], CH₂). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ –206 (br). IR (cm⁻¹, Nujol): ν 244 (s), 233 (s). Raman (cm⁻¹): 247 (m), 233 (m).

[GaCl₃(AsMe₃)]. A solution of AsMe₃ (0.15 g, 1.24 mmol) in Et₂O (5 cm³) was added dropwise to stirred solution of GaCl₃ (0.22 g, 1.24 mmol) in Et₂O (5 cm³) at -78 °C. After it was stirred at -78 °C for 30 min, the mixture was allowed to warm to room temperature and was stirred for another 5 h. The solvent was reduced to ~2 cm³, and the resultant white precipitate was filtered off and dried in vacuo. Yield: 0.22 g, 76%. Anal. Calcd for C₃H₉-AsCl₃Ga: C, 12.2; H, 3.1. Found: C, 11.7; H, 3.1. ¹H NMR (300 MHz, CDCl₃): δ 1.59 (s). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 264.5 (br). IR (cm⁻¹, Nujol): ν 390 (s), 344 (s).

[GaBr₃(AsMe₃)]. This was prepared in a manner similar to that for the chloride. Yield: 77%. Anal. Calcd for C₃H₉AsBr₃Ga: C, 8.4; H, 2.1. Found: C, 7.9; H, 2.3. ¹H NMR (300 MHz, CDCl₃): δ 1.53 (s). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ 147. IR (cm⁻¹, Nujol): ν 265 (s), 252 (sh).

[GaI₃(AsMe₃)]. This was prepared in a manner similar to that described above. Yield: 70%. Anal. Calcd for C₃H₉AsGaI₃: C,

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [GaCl₂{*o*-C₆H₄(PPh₂)₂}][GaCl₄]

Ga1-Cl1	2.1457(11)	Ga2-Cl3	2.1757(13)
Ga1-Cl2	2.1575(12)	Ga2-Cl4	2.1806(13)
Ga1-P1	2.3787(12)	Ga2-Cl5	2.1748(12)
Ga1-P2	2.3865(11)	Ga2-Cl6	2.1647(12)
Cl1-Ga1-P1	112.11(4)	Cl3-Ga2-Cl4	$108.75(5) \\108.60(5) \\111.12(5) \\109.80(5) \\108.16(5) \\110.40(5)$
Cl2-Ga1-P1	109.34(4)	Cl5-Ga2-Cl3	
Cl1-Ga1-P2	108.15(4)	Cl5-Ga2-Cl4	
Cl2-Ga1-P2	124.34(4)	Cl6-Ga2-Cl3	
Cl1-Ga1-Cl2	113.97(5)	Cl6-Ga2-Cl4	
P1-Ga1-P2	85.42(4)	Cl6-Ga2-Cl4	

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(GaX_3)_2{\mu-Et_2P(CH_2)_2PEt_2}]$ (X = Br or I)

$[(GaBr_3)_2 \{Et_2P(CH_2)_2PEt_2\}]$		$[(GaI_3)_2 \{Et_2P(CH_2)_2PEt_2\}]$	
Ga1-Br1	2.3033(8)	Ga1-I1	2.5200(10)
Ga1-Br2	2.3226(8)	Ga1-I2	2.5405(10)
Ga1-Br3	2.3246(8)	Ga1-I3	2.5418(9)
Ga1-P1	2.3614(13)	Ga1-P1	2.3769(15)
Br1-Ga1-Br2	111.69(3)	I1-Ga1-I2	111.47(3)
Br1-Ga1-Br3	113.81(3)	I1-Ga1-I3	114.90(3)
Br2-Ga1-Br3	110.15(3)	I2-Ga1-I3	111.28(3)
Br1-Ga1-P1	110.36(4)	I1-Ga1-P1	108.99(5)
Br2-Ga1-P1	106.95(4)	I2-Ga1-P1	107.14(5)
Br3-Ga1-P1	103.37(4)	I3-Ga1-P1	102.38(4)

Table 5.	Selected Bond Lengths (Å) and Angles (deg) for	
[GaX ₂ { <i>o</i> -0	$_{6}H_{4}(AsMe_{2})_{2}][GaX_{4}] (X = Cl \text{ or } I)$	

	[GaCl ₂ {o-C ₆ H ₄ (As	$Me_2)_2$][GaCl ₄] ^a	
Ga1-Cl1	2.123(3)	Ga1-Cl2	2.164(3)
Ga1-As1	2.442(1)	Ga2-Cl3	2.159(2)
Ga2-Cl4	2.174(4)	Ga2-Cl5	2.198(4)
Cl1-Ga1-Cl2	118.65(12)	Cl1-Ga1-As1	113.96(7)
Cl2-Ga1-As1	107.84(7)	As1-Ga1-As1a	91.05(6)
Cl3-Ga2-Cl3b	108.87(13)	Cl3-Ga2-Cl4	111.00(9)
Cl3-Ga2-Cl5	111.46(9)	Cl4-Ga2-Cl5	102.99(15)
	[GaI ₂ { <i>o</i> -C ₆ H ₄ (As	$Me_2)_2$ [GaI ₄] ^b	
Ga1-I1	2.491(3)	Ga1-I2	2.496(3)
Ga1-As1	2.450(2)	Ga2-I3	2.563(3)
Ga2-I4	2.547(3)	Ga2-I5	2.537(2)
I1-Ga1-I2	127.78(10)	As1-Ga1-I1	105.90(8)
As1-Ga1-I2	110.57(8)	As1-Ga1-As1a	89.26(10)
I5-Ga2-I5a	110.83(10)	I3-Ga2-I4	106.71(9)
I3-Ga2-I5	109.54(6)	I4-Ga2-I5	110.07(6)

^{*a*} Symmetry operation: a x, 1/2 - y, z; b x, 3/2 - y, z. ^{*b*} Symmetry operation: a x, 1/2 - y, z.

6.3; H, 1.5. Found: C, 6.4; H, 1.5. ¹H NMR (300 MHz, CDCl₃): δ 1.49 (s). ⁷¹Ga NMR (CH₂Cl₂/5% CD₂Cl₂): δ –169.5. IR (cm⁻¹, Nujol): ν 227 (m).

X-ray Crystallography. Brief details of the crystallographic data and refinement parameters are given in Table 1. Crystals were grown from CH₂Cl₂ solutions by vapor diffusion of hexane. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo K_{α} radiation ($\lambda = 0.71073$ 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 straightforward,^{20,21} with H atoms introduced into the models in calculated positions. Selected bond lengths and angles are given in Tables 2–6.

⁽²⁰⁾ Sheldrick, G. M. SHELXS-97, Program for crystal structure solution; University of Göttingen: Göttingen, Germany, 1997.

⁽²¹⁾ Sheldrick, G. M. SHELXL-97, Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $[(GaI_3)_2\{\mu-Ph_2As(CH_2)_2AsPh_2\}]$

Ga1-I1 Ga1-I2 Ga1-I3 Ga1-As1	2.5181(9) 2.5118(9) 2.5198(9) 2.4875(10)	Ga2-I4 Ga2-I5 Ga2-I6 Ga2-As2	2.5270(9) 2.4944(9) 2.5329(9) 2.4885(10)
$\begin{array}{c} As1-Ga1-I1\\ As1-Ga1-I2\\ As1-Ga1-I3\\ I1-Ga1-I2\\ I1-Ga1-I3\\ I2-Ga1-I3\\ I2-Ga1-I3 \end{array}$	100.21(3) 106.02(3) 105.19(3) 116.36(3) 113.69(3) 113.42(3)	$\begin{array}{l} As2-Ga2-I4\\ As2-Ga2-I5\\ As2-Ga2-I6\\ I4-Ga2-I5\\ I4-Ga2-I6\\ I5-Ga2-I6\\ I5-Ga2-I6 \end{array}$	99.21(3) 105.90(3) 105.06(3) 119.01(3) 111.92(3) 113.46(3)

Results

Diphosphanes. The diphosphane $o-C_6H_4(PMe_2)_2$, which is an exceptionally strong σ -donor with small steric demands and is preorganized for chelation,²² reacted with GaX₃ (X = Cl, Br or I) in a 1:1 molar ratio in hot toluene to form white powders with microanalyses consistent with 1:1 complexes. Crystals of all three complexes were obtained from CH₂Cl₂ solution and were revealed to be trans-[GaX₂- $\{o-C_6H_4(PMe_2)_2\}_2$ [GaX₄], which are the first examples of gallium(III) phosphanes with six-coordinate gallium centers. All show tetrahedral anions and trans pseudo-octahedral cations (Table 2, Figures 1 and 2). The cations are centrosymmetric and show the "stepped" arrangement found in many o-phenylene diphosphane or diarsane transition metal complexes.²³ The Ga-X and Ga-P distances in the cations are longer than in the pseudotetrahedral $[GaX_3(PR_3)]$ complexes,⁹⁻¹³ attributable to the increased coordination number of the metal, but the Ga-P distances increase only slightly as the halogen coligands change $Cl \rightarrow Br \rightarrow I$ in the three complexes. The small chelate bite of the diphosphane results in quite acute $\angle P$ -Ga-P of $\sim 82^{\circ}$. Six-coordination is also present in the 2,2'-bipyridyl complexes [GaX₂(2,2'bipy)₂][GaX₄], but the cations are *cis* isomers.^{24,25} The diphosphane complexes are poorly soluble in chlorocarbons but give single sharp ³¹P{¹H} NMR resonances with small high-frequency coordination shifts, showing them to be exclusively the *trans* isomers in solution. Only the [GaX₄]⁻ anions were observed in the ⁷¹Ga NMR spectra;²⁶ fast relaxation in the lower-symmetry cations accounts for the absence of the resonances (see below). The far-IR and Raman spectra are dominated by strong features assigned to [GaX₄]^{-,27} and definite assignment of the a1g (Raman) and a2u (IR) GaX2 vibrations of the cations was not possible. The Experimental

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(23) (a) Higgins, S. J.; Jewiss, H. C.; Levason, W.; Webster, M. Acta. Crystallogr., Sect. C 1985, 41, 695–697. (b) Champness, N. R.; Levason, W.; Pletcher, D.; Webster, M. J. Chem. Soc., Dalton Trans. 1992, 3243–3247.

- (24) Carty, A. J. Can. J. Chem. 1968, 46, 3779-3784.
- (25) Restivo, R.; Palenik, G. J. J. Chem. Soc., Dalton Trans. 1972, 341-344.
- (26) Mason, J. *Multinuclear NMR*; Plenum: New York, 1987. The ⁷¹Ga NMR chemical shifts for $[GaX_4]^-$ are X = Cl , δ 251; X = Br, δ 64; X = I , δ -455 (all in CH₂Cl₂ solution).
- (27) Tetrahedral [GaX₄]⁻ show one IR active stretch (ν_3 , t_2) and two Raman active stretches (ν_1 , a_1 and ν_3 , t_2). Literature values (cm⁻¹) are X = Cl ν_1 = 346, ν_3 = 386; X = Br ν_1 = 210, ν_3 = 278; X = I ν_1 = 145, ν_3 = 222. Data from Nakamoto, K. *IR Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970.



Figure 1. Crystal structure of the cation in $[GaCl_2\{o-C_6H_4(PMe_2)_2\}_2]$ -[GaCl₄] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a 1 - x, -y, 1 - z.



Figure 2. Crystal structure of the cation in $[GaBr_2\{o-C_6H_4(PMe_2)_2\}_2]$ - $[GaBr_4]\cdotCH_2Cl_2$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a -x, 1 - y, 1 - z. The iodo analogue is isomorphous.

Section lists the major vibrations below 400 cm⁻¹. The reaction of o-C₆H₄(PMe₂)₂ with two molar equivalents of GaCl₃ in hot toluene gave a white powder with the composition 2GaCl₃/o-C₆H₄(PMe₂)₂, which was insoluble in chlorocarbons and decomposed by MeCN, MeNO₂, or DMSO with liberation of the diphosphane (and formation of [o-C₆H₄-(PMe₂)(PMe₂H)]⁺, identified by ³¹P{¹H} NMR spectroscopy). The far-IR spectrum shows a strong band at 380 cm⁻¹ assigned as ν_3 of [GaCl₄]⁻, and two strong bands at 410 and 362 cm⁻¹ are also assigned as Ga–Cl stretches. This complex is tentatively formulated as [GaCl₂{o-C₆H₄(PMe₂)₂}][GaCl₄], containing a pseudotetrahedral cation (cf., the diarsane complexes described below), but its insolubility has prevented us from obtaining crystals to confirm this by an X-ray structural study.

The phenyl-substituted diphosphane, o-C₆H₄(PPh₂)₂, is also preorganized for chelation but is considerably bulkier, and although it forms six-coordinate complexes with some transition metals,²² we find in agreement with Sigl et al.¹⁴ that with GaX₃ only [GaX₂{o-C₆H₄(PPh₂)₂}][GaX₄] complexes are isolated even with excess diphosphane. The structure of the chloro complex (Table 3, Figure 3) shows a very distorted tetrahedral cation with \angle P-Ga-P = 85.4° and with Ga-Cl = 2.157(1), 2.146(1) Å and Ga-P = 2.379-(1), 2.386(1) Å, ~0.2 and 0.1 Å shorter, respectively, than in the six-coordinate complex above. In [GaI₂{o-C₆H₄-(PPh₂)₂]⁺, Ga-P = 2.398(1) and 2.409(1) Å,¹⁴ indicating weaker Lewis acidity in the di-iodogallium cation and



Figure 3. Crystal structure of the cation in $[GaCl_2{o-C_6H_4(PPh_2)_2}][GaCl_4]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

perhaps steric crowding, although the P–Ga–P angle (84.5°) is little different. The complexes are characterized by singlet ³¹P{¹H} NMR resonances to low frequency of the ligand chemical shift, which are invariant over the temperature range of 295–183 K. The ⁷¹Ga NMR spectra show only the sharp resonances of the [GaX₄]⁻ anions, the resonances of the cations were not observed. Solutions of [GaX₂{*o*-C₆H₄- $(PPh_2)_2$ [GaX₄] containing excess (~3-fold) o-C₆H₄(PPh₂)₂ show evidence for the formation of other species, although only the $[GaX_2\{o-C_6H_4(PPh_2)_2\}][GaX_4]$ have been isolated as solids. Thus, a dichloromethane solution of $[GaI_2 \{o-C_6H_4 (PPh_2)_2$ [GaI₄] containing excess $o-C_6H_4(PPh_2)_2$ shows a new ⁷¹Ga resonance at $\delta = -162$, and the ³¹P{¹H} NMR spectrum shows ligand ($\delta = -13$) and resonances at $\delta =$ -24 and -19, which we tentatively attribute to $[GaI_3{\kappa^1}$ $o-C_6H_4(PPh_2)_2$]. It is notable that even with a large excess (~10-fold) of added o-C₆H₄(PPh₂)₂, significant amounts of $[GaI_2{o-C_6H_4(PPh_2)_2}][GaI_4]$ are still present. Similar but more complex behavior was evident in mixtures of [GaCl₂- $\{o-C_6H_4(PPh_2)_2\}$][GaCl₄]/ $o-C_6H_4(PPh_2)_2$ in CH₂Cl₂ solution, which seems to contain several species including the hydrolysis product $[o-C_6H_4(PPh_2)(PPh_2H)]^+$.²⁸

The diphosphane Et₂P(CH₂)₂PEt₂, which usually behaves as a strongly bound chelate to transition metals,²² gives $[(X_3 Ga_{2}\{\mu-Et_{2}P(CH_{2}),PEt_{2}\}$ with bridging diphosphane ligands coordinated to pseudotetrahedral GaX₃ units as the only complex type in the gallium(III) systems. The ${}^{31}P{}^{1}H{}$ and ⁷¹Ga NMR spectra show these are the only significant species present in CH₂Cl₂ solution over the temperature range of 295-183 K, and apart from small temperature drifts, the spectra are little affected by varying the temperature; no spin-spin couplings were resolved. Structures of $[(X_3Ga)_2 \{\mu$ -Et₂P(CH₂)₂PEt₂ $\}$] (X = Br or I) were determined, and the results are presented in Figures 4 and 5 and Table 4. The Ga-P bond length is slightly shorter in $[(I_3Ga)_2 \{\mu$ - $Et_2P(CH_2)_2PEt_2$] (2.377(1) Å) than in $[(I_3Ga)_2\{\mu-Ph_2P(CH_2)_2 PPh_{2}$ (2.40(1), 2.41(1) Å)¹³ which suggests that the alkyldiphosphane is more strongly bound. The conformation



Figure 4. Crystal structure of $[(GaBr_3)_2{Et_2P(CH_2)_2PEt_2}]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a 1 - x, -y, -z.



Figure 5. Crystal structure of $[(GaI_3)_2{Et_2P(CH_2)_2PEt_2}]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a 2 - x, 2 - y, -z.

of the two GaX_3 residues is determined by the inversion center in the molecule.

Diarsanes. The reaction of GaCl₃ with o-C₆H₄(AsMe₂)₂ in hot toluene produced a white complex with the composition 2:1 GaCl₃/diarsane, regardless of the ratio of reagents used. This was identified as $[GaCl_2\{o-C_6H_4(AsMe_2)_2\}]$ -[GaCl₄] by a crystal structure determination (see below) and is the correct formulation for the substance formulated as $[GaCl_2{o-C_6H_4(AsMe_2)_2}][Ga_3Cl_{10}]$ (based on microanalytical and conductivity data only) in an early report.²⁹ The reaction of GaX₃ (X = Br or I) with o-C₆H₄(AsMe₂)₂ in a 2:1 mole ratio similarly affords $[GaX_2\{o-C_6H_4(AsMe_2)_2\}]$ -[GaX₄], but with a 1:1 metal/ligand ratio, substances with higher and variable C and H content were obtained. However, the IR and Raman spectra of these materials are very similar to those of (crystallographically authenticated) [GaX₂{o- $C_{6}H_{4}(AsMe_{2})_{2}$ [GaX₄], differing only in the relative intensities of the bands assigned to the $[GaX_4]^-$ anions, which are very weak in some samples, while the bands associated with the cations appear unchanged. We conclude that these substances with a higher C, H content are almost certainly mixtures of $[GaX_2\{o-C_6H_4(AsMe_2)_2\}]X$ and $[GaX_2\{o-C_6H_4 (AsMe_2)_2$ [GaX₄], although we have been unable to obtain samples free of the tetrahalogallate(III) anions. In contrast to the pseudooctahedral cations with the diphosphane of the

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Figure 6. Crystal structure of the cation in $[GaCl_2\{o-C_6H_4(AsMe_2)_2\}]$ [GaCl₄] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The cation has mirror plane symmetry. Symmetry operation: a *x*, 1/2 - y, *z*.

type *trans*- $[GaX_2{o-C_6H_4(PMe_2)_2}_2]^+$ described above, the diarsane affords only pseudotetrahedral [GaX₂{*o*-C₆H₄- $(AsMe_{2})_{2}$]⁺. We note that $[GaX_{2}\{o-C_{6}H_{4}(AsMe_{2})_{2}\}_{2}][GaX_{4}]$ compounds proposed to contain six-coordinate cations were reported in the early study (based only on microanalytical and molecular weight data),²⁹ but it seems clear that these were $[GaX_2\{o-C_6H_4(AsMe_2)_2\}]X$. The different stoichiometries obtained with gallium halides for these two ophenylene ligands contrasts starkly with their very extensive transition metal chemistry, where they form analogous complexes in almost all cases, which differ only slightly in stability or spectroscopic properties.^{22,30} The crystal structures of [GaX₂{*o*-C₆H₄(AsMe₂)₂}][GaX₄] show distorted pseudotetrahedral cations and close to tetrahedral anions (Table 5, Figures 6 and 7).³¹ The cations (X = Cl or I) have As-Ga-As angles close to 90° as a result of the rigid ligand's bite, and correspondingly, the X-Ga-X angles are 118.6- $(1)^{\circ}$ (Cl) and 127.8(1)° (I). The Ga–As distances are very similar, 2.442(1) (Cl) and 2.450(2) Å (I); the Ga–X distances in the anions are somewhat longer than in the cations.

The far-IR spectrum of $[GaCl_2\{o-C_6H_4(AsMe_2)_2\}][GaCl_4]$ contains strong bands at 421 and 356 cm⁻¹, which we assign as the $a_1 + b_1$ GaCl₂ vibrations of the cation; the bands appear at similar frequencies but with reversed relative intensities in the Raman spectrum. The ⁷¹Ga NMR spectrum shows only a sharp feature at δ 250 assigned to $[GaCl_4]^$ superimposed on a broader feature $\delta \sim 256$. The far-IR spectrum of $[GaBr_2\{o-C_6H_4(AsMe_2)_2\}][GaBr_4]$ contains features at 264 and 233 cm⁻¹ assigned as the $a_1 + b_1$ GaBr₂ vibrations, and corresponding features in the spectrum of



Figure 7. Crystal structure of the cation in $[GaI_2\{o-C_6H_4(AsMe_2)_2\}][GaI_4]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The cation has mirror symmetry. Symmetry operation: a x, 1/2 - y, z.

 $[GaI_2{o-C_6H_4(AsMe_2)_2}][GaI_4]$ are found at 226 and 216 cm⁻¹. The ⁷¹Ga NMR spectrum of $[GaBr_2\{o-C_6H_4(AsMe_2)_2\}]$ -[GaBr₄] shows resonances at δ 64 ([GaBr₄]⁻)²⁶ and 141, while the iodo complex has 71 Ga resonances at δ -451 $([GaI_4]^{-})^{26}$ and -166. The second resonance in each complex could be from $[GaX_2\{o-C_6H_4(AsMe_2)_2\}]^+$, which would indicate that the electric field gradients around the gallium center in these two cations are small, despite the distortions from cubic symmetry produced by the chelate ligand and the As₂X₂ donor set, and hence quadrupolar relaxation is slowed sufficiently for the resonance to be observed. However, the two gallium resonances in each complex deviate markedly from 1:1 relative intensities, and it seems more likely that the second resonance in each complex is the result of a GaX₃As environment produced by rearrangement in solution. The δ values in each case are close to those observed in $C_{3\nu}$ GaX₃As species (see Table 7), but since we have no values for GaX₂As₂ from other systems, it is not possible to rule out the alternative assignment. It should be noted that all our attempts to prepare $[GaCl_2(PR_3)_2]^+$ cations from [GaCl₃(PR₃)], PR₃, and SbCl₅ in dry CH₂Cl₂ failed; the products identified by a combination of ⁷¹Ga, ³¹P and ¹H NMR spectroscopy were unchanged [GaCl₃(PR₃)] and [PR₃Cl]⁺, the latter resulting from chlorination of the PR₃ by SbCl₅³²

Since no other gallium diarsane complexes have been reported, we prepared [(I₃Ga)₂{ μ -Ph₂As(CH₂)₂AsPh₂}] which is an exact analogue of [(I₃Ga)₂{ μ -Ph₂P(CH₂)₂PPh₂}].¹³ The crystals (Table 6, Figure 8) are isomorphous, and the structure reveals the expected ligand bridged dimer geometry; the Ga–I distances in the two complexes are very similar. The ⁷¹Ga NMR exhibits a single resonance at δ –206, which may be compared with the δ –220 value in [GaI₃(AsPh₃)]¹¹ and δ –169.5 in [GaI₃(AsMe₃)]. The three [GaX₃(AsMe₃)] (X = Cl, Br or I) were also prepared for comparison purposes; details of their structures are given in the Supporting Information.

⁷¹Ga NMR Studies and Some Comparisons. Gallium has two naturally occurring isotopes, ⁶⁹Ga (60.1%) and

⁽³⁰⁾ Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126–3140. (31) The X-ray data for [GaBr₂{o-C₆H₄(AsMe₂)₂}][GaBr₄] gave a largish R_{int} (0.11) with the systematic absences suggesting space groups *Pmmn* (No. 59) or *Pmn*2₁ (No. 31) (both in the standard setting). A solution in the centrosymmetric *Pmmn* readily emerged with the cation having mirror symmetry, but two of the aromatic carbon atoms showed very elongated displacement ellipsoids perpendicular to the plane of the ring (R1 \approx 0.10). This suggested the lower symmetry solution, but attempts here gave unsatisfactory refinement and no improvement to the model. Although the chemical identity is not in doubt, the structure is not presented here.

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	$\delta(^{31}\mathrm{P})^a$	Δ^b	$\delta(^{71}{ m Ga})^c$
$[GaCl_3(PPh_3)]$	-5.4 (m) (273 K)	+0.6	264 (br d, $J = 721$)
[GaBr ₃ (PPh ₃)]	-10.7 (m)	-4.7	152 (d, J = 693)
[GaI ₃ (PPh ₃)]	-29.7 (m)	-23.7	-151 (d, J = 466)
$[(GaCl_3)_2 \{Et_2P(CH_2)_2PEt_2\}]$	-2.0 (s)	+16.0	274 (s)
$[(GaBr_3)_2 \{Et_2P(CH_2)_2PEt_2\}]$	-7.7 (s)	+10.3	160 (s)
$[(GaI_3)_2 \{Et_2P(CH_2)_2PEt_2\}]$	-27.6 (s)	-9.6	-132 (s)
$[GaCl_2\{o-C_6H_4(PPh_2)_2\}][GaCl_4]$	-18.9 (s)	-5.9	251^{d}
$[GaBr_2\{o-C_6H_4(PPh_2)_2\}][GaBr_4]$	-21.8 (s)	-8.8	64^d
$[GaI_2\{o-C_6H_4(PPh_2)_2\}][GaI_4]$	-30.7 (s)	-17.7	-456^{d}
$[GaCl_2\{o-C_6H_4(PMe_2)_2\}_2][GaCl_4]$	-40.8 (s)	+14.2	251^{d}
$[GaBr_2{o-C_6H_4(PMe_2)_2}_2][GaBr_4]$	-41.2 (s)	+13.8	66^{d}
$[GaI_2{o-C_6H_4(PMe_2)_2}_2][GaI_4]$	-43.0 (s)	+12.0	-457^{d}
$[(GaI_3)_2\{Ph_2As(CH_2)_2AsPh_2\}]$			-206 (s)
[GaCl ₃ (AsMe ₃)]			264.5 (s)
[GaBr ₃ (AsMe ₃)]			147 (s)
[GaI ₃ (AsMe ₃)]			-169.5 (s)

^{*a*} At 295 K in CH₂Cl₂ solution unless indicated otherwise, relative to 85% H₃PO₄. ^{*b*} Coordination shift δ (complex) – δ (ligand). Ligand chemical shifts are PPh₃ (-6), Et₂P(CH₂)₂PEt₂ (-18), *o*-C₆H₄(PPh₂)₂ (-13), *o*-C₆H₄(PMe₂)₂ (-55). ^{*c*} At 295 K relative to [Ga(H₂O)₆]³⁺ in water at pH 1. ^{*d*} Resonance of [GaX₄]⁻ anion only, see text.



Figure 8. Crystal structure of [(GaI₃)₂{Ph₂As(CH₂)₂AsPh₂}] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

⁷¹Ga (39.9%), both with I = 3/2, the less abundant ⁷¹Ga being preferred for NMR studies because of its lower quadrupole moment (Q), which results in narrower lines and a higher receptivity (R_c) (⁶⁹Ga, $Q = 0.178 \times 10^{-28} \text{ m}^2$, $R_c = 237$; ⁷¹Ga, $Q = 0.112 \times 10^{-28} \text{ m}^2$, $R_c = 319$).²⁶ The key factor governing whether a ⁷¹Ga resonance can be observed or gallium coupling resolved on ³¹P NMR resonances will be the electric field gradient surrounding the gallium center. Given the relatively favorable nuclear parameters, ⁷¹Ga resonances should be easily observed in cubic symmetry, but decreasing symmetry (and increasing field gradients) will broaden and then lead to loss of the gallium resonance. The ⁷¹Ga resonances are easily observed for the tetrahedral $[GaX_4]^-$ anions and for the X₃P environments in the $C_{3\nu}$ $[GaX_3(PR_3)]$ and $[(X_3Ga)_2(\mu$ -diphosphane)] complexes (Table 7). Typically, in these complexes, the ⁷¹Ga resonances had line widths of a few hundred Hertz at ambient temperatures, although lines often broadened upon cooling of the solutions, but with only small temperature drifts in the chemical shifts. In none of the complexes in this work was the doublet coupling to ³¹P resolved (although it is observed for [GaX₃-(PPh₃)] (X = Cl, Br, or I), with ${}^{1}J({}^{71}Ga - {}^{31}P)$ falling with X, Cl \rightarrow Br \rightarrow I).¹¹ The δ (⁷¹Ga) are characteristic, with Cl₃P

donor sets lying in the range from ~ 260 to 280, Br₃P from \sim 150 to 160, and I₃P from \sim -130 to -150 ppm. The incorporation of arsenic in place of phosphorus has little effect on the ⁷¹Ga resonance frequency as shown by the data on $[GaX_3(AsMe_3)]$ (Table 7). The δ ⁽⁷¹Ga) in the chloro complexes are only slightly to high frequency of that in $[GaCl_4]^-$ ($\delta = 251$),²⁶ but replacement of the single phosphane by bromide or iodide results in marked low-frequency shifts (cf. $[GaBr_4]^- \delta = 64$ and $[GaI_4]^- \delta = -455$). In contrast to the C_{3v} complexes, we were unable to observe ⁷¹Ga resonances from either the pseudotetrahedral cations $[GaX_2\{o-C_6H_4(PPh_2)_2\}]^+$ or the pseudooctahedral $[GaX_2\{o-C_6H_4(PPh_2)_2\}]^+$ $C_6H_4(PMe_2)_2_2_1^+$, in both cases the lower symmetry producing unfavorable electric field gradients and fast relaxation. The cases of $[GaX_2\{o-C_6H_4(AsMe_2)_2\}]^+$ (X = Br or I) have been discussed above.

The ³¹P{¹H} NMR spectra are singlets, sharp for the cations (showing that fast quadrupolar relaxation effectively decouples the gallium nuclei) and rather broader for the $C_{3\nu}$ X_{3} P coordination environments. For a fixed ligand, the ³¹P chemical shifts move to low frequency as the halide changes $Cl \rightarrow Br \rightarrow I$, but the coordination shifts, Δ , are irregular (Table 7), giving both positive and negative values. This phenomenon has been observed before in p-block chemistry,^{14,33} although the reasons remain unclear. In contrast, the majority of coordination shifts in transition metal phosphane complexes are to high frequency (positive). Examination of the data in Table 7 shows that the stronger σ -donor phosphanes tend to produce higher frequency coordination shifts than the weaker donor arylphosphanes.

Conclusions

This systematic study of the complexes of GaX_3 with diphosphanes and diarsanes with flexible and rigid linking groups and differing steric requirements has revealed the first examples of six-coordinate (distorted octahedral) Ga(III) cations, based on the sterically small and very strong σ -donor

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Complexes of Gallium(III) Halides

 $o-C_6H_4(PMe_2)_2$, and a rare, but distinct, difference in the ligand properties of this diphosphane compared to the analogous diarsane, $o-C_6H_4(AsMe_2)_2$ (which gives only the pseudotetrahedral [GaX₂{ $o-C_6H_4(AsMe_2)_2$ }]⁺ cations).

The study has also confirmed a clear preference for the Ga(III) center in phosphane complexes to be four-coordinate with a X_3P donor set. Even for the strong σ -donating (but flexible) $Et_2P(CH_2)_2PEt_2$, bridging bidentate coordination is observed. The reluctance to form six-coordinate Ga(III) compounds must reflect electronic preference, since gallium-(III) (ionic radius in six-coordination³⁴ $r^+ = 62$ pm) is of similar size to later 3d metals such as Fe^{3+} (r = 64.5 pm) or Co^{3+} (r = 61 pm) which readily form octahedral complexes. A second striking difference between the present complexes and phosphane or arsane complexes of the 3d metals is in the relative affinity for the halide versus the P(As) ligand. In the neutral four-coordinate gallium complexes, typically $d(Ga-Cl) = \sim 2.17$ Å, $d(Ga-P) = \sim 2.35$ Å, and $d(Ga-P) = \sim 2.35$ Å = 2.35 Å, and $d(Ga-P) = \sim 2.35$ Å = 2.35 As) = ~ 2.48 Å, with d(Ga-Br) in the corresponding bromides being ~ 2.32 Å, that is, Ga–Cl is much shorter than Ga-P which is similar or slightly longer than Ga-Br, with d(Ga-As) being longest (see Tables 2, 4, and 5). In contrast, for low-spin six-coordinate phosphane or arsane complexes of Fe(III) or Co(III), the d(M-P) values are usually slightly shorter than the d(M-Cl) distances, with d(M-Br) being much longer. Correspondingly, d(M-As)is usually shorter than d(M-Br).^{22,23,30} Thus, in the gallium compounds, one may conclude that the primary interaction is Ga-X, with weaker binding of the neutral ligand completing the distorted tetrahedron. Similar behavior is observed in the six-coordinate $[SnX_4(diphosphane)]$, where d(Sn-Cl)

(34) Shannon, R. D.; Prewitt, C. T. Acta Crystallogr., Sect. B 1970, 26, 1046–1048. $< d(Sn-Br) \approx d(Sn-P)$,³³ and the disparity between M–X and M–P is even greater in complexes of Group 15 halides (M'X₃, M = As, Sb, or Bi), although here the varying degree of stereochemical activity of the M-based lone pair further complicates structural comparisons.^{35,36} Although the number of examples is relatively small, the comparison of neutral GaEX₃ with cationic GaE₂X₂⁺ (for fixed E) shows Ga–X is shorter in the cationic species, whereas Ga–P(As) is little changed, again evidence that the Ga–X is the dominant interaction (see Tables 3–6 and refs 11–15). We discount any explanation involving π -acceptance as contributing to the shorter M–P bonds in the transition metal systems; for oxidation state III of Co or Fe, any π component of the bonding will be small, rather the explanation must lie in the different σ bonding effects in the d- and p-block systems.

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Supporting Information Available: X-ray crystallographic data in CIF format for the compounds in Table 1 and for the isomorphous $[GaX_3(AsMe_3)]$, (X = Cl, Br or I) together with an ORTEP picture of the Br compound. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available from the Cambridge Crystallographic Data Centre with CCDC deposition numbers 645884–645895 at www.ccdc.cam.ac. uk/data_request/cif.

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