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Article

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

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The diphosphane *o*-$C_6H_4(PMe_2)_2$ reacts with GaX_3 (X = Cl, Br, or I) in a 1:1 molar ratio in dry toluene to give *trans*-$[GaX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaX_4]$, the cations of which contain the first examples of six-coordinate gallium in a phosphane complex. The use of a 1:2 ligand/$GaCl_3$ ratio produced $[GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][GaCl_4]$, containing a pseudotetrahedral cation, and similar pseudotetrahedral $[GaX_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaX_4]$ complexes are the only products isolated with the bulkier *o*-$C_6H_4(PPh_2)_2$. On the other hand, $Et_2P(CH_2)_2PEt_2$, which has a flexible aliphatic backbone, formed $[(X_3Ga)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$, in which the ligand bridges two pseudotetrahedral gallium centers. The diarsane, *o*-$C_6H_4(AsMe_2)_2$, formed $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$, 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 $[(I_3Ga)_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$ and $[GaX_3(AsMe_3)]$ are also described. The X-ray structures of *trans*-$[GaX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaX_4]$ (X = Cl, Br or I), $[GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaCl_4]$, $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$ (X = Cl or I), $[(I_3Ga)_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$, and $[GaX_3(AsMe_3)]$ (X = Cl, Br or I) are reported, and the structural trends are discussed. The solution behavior of the complexes has been explored using a combination of $^{31}P\{^1H\}$ and ^{71}Ga 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 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 GaX_3 in organic transformations.[7] The radioisotopes ^{67}Ga and ^{68}Ga 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 [$(I_3Ga)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}$][13] and the rare cationic [$GaX_2\{o\text{-}C_6H_4(PPh_2)_2\}$][$GaX_4$] (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 $^{31}P\{^1H\}$ and ^{71}Ga NMR spectroscopy.

Experimental Section

General Procedures. All the reactions and manipulations were performed in an inert atmosphere (N_2) 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 CaH_2. 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 $CDCl_3$ solution on a Bruker AV300; $^{31}P\{^1H\}$ (161.9 MHz) and ^{71}Ga (122.0 MHz) NMR spectra were recorded on a Bruker DPX400 and referenced to 85% H_3PO_4 and [$Ga(H_2O)_6$]$^{3+}$, respectively. $GaCl_3$ and GaI_3 were obtained from Aldrich and used as received. $GaBr_3$ (Aldrich) was sublimed in vacuo at 70 °C. The ligands $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(PPh_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $Ph_2P(CH_2)_2PPh_2$ and $Ph_2As(CH_2)_2AsPh_2$ 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. [$GaX_3(PPh_3)$] complexes were made as described.[11]

[$GaI_2\{o\text{-}C_6H_4(PMe_2)_2\}_2$][$GaI_4$]. GaI_3 (0.266 g, 0.590 mmol) was added to a solution of $o\text{-}C_6H_4(PMe_2)_2$ (0.117 g, 0.590 mmol) in toluene (15 cm^3) 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 cm^3. The resulting white precipitate was filtered off and dried in vacuo. Yield: 0.32 g, 85%. Anal. Calcd for $C_{20}H_{32}Ga_2I_6P_4$: C, 18.5; H, 2.5. Found: C, 18.7; H, 2.4. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.6−7.8 (m, [4H], C_6H_4), 1.74 (s, [12H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ −457 (br). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/5% CD_2Cl_2): δ −43.0 (s). IR (cm^{-1}, Nujol): ν 216 (s), 205 (m). Raman (cm^{-1}): 217 (s).

[$GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2$][$GaCl_4$]. This was prepared in a manner similar to that described above as a white solid. Yield: 82%. Anal. Calcd for $C_{20}H_{32}Cl_6Ga_2P_4$: C, 32.1; H, 4.3. Found: C, 32.2; H, 4.2. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.6−7.8 (m, [4H], C_6H_4) 1.75 (s, [12H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 251 (s). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/5% CD_2Cl_2): δ −40.8 (s). IR (cm^{-1}, Nujol): ν 372 (vs), 339 (m), 252 (m), 203 (m). Raman (cm^{-1}): 372 (w), 344 (s), 332 (m), 238 (s), 197 (m).

[$GaBr_2\{o\text{-}C_6H_4(PMe_2)_2\}_2$][$GaBr_4$]. This was prepared in a manner similar to that described above as a white solid. Yield: 90%. Anal. Calcd for $C_{20}H_{32}Br_6Ga_2P_4$: C, 23.7; H, 3.2. Found: C, 23.3; H, 3.1. ^1H NMR (300 MHz, CD_2Cl_2): δ 7.6−7.8 (m, [4H], C_6H_4), 1.73 (s, [12H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 63.5 (s). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/5% CD_2Cl_2): 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).

[$GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}$][$GaCl_4$]. This was prepared in a manner similar to that described above as a white solid by reaction of the ligand and $GaCl_3$ in a 1:2 molar ratio in hot toluene. Yield: 85%. Anal. Calcd for $C_{10}H_{16}Cl_6Ga_2P_2$: C, 21.8; H, 2.9. Found: C, 22.0; H, 2.9. ^1H NMR (300 MHz, CD_2Cl_2): insoluble. ^{71}Ga NMR (see text) (MeCN/5% CD_3CN): δ 251 (s). $^{31}P\{^1H\}$ NMR (MeCN/5% CD_3CN): δ −52.2 (br, [P]), −4.0 (br, [P]). $^{31}P-^1H$ coupled NMR (MeCN/5% CD_3CN): δ −52.2 (br, [P]), −4.0 (d, [P] $^1J_{PH}$ = 545 Hz). IR (cm^{-1}, Nujol): ν 410 (s), 380 (vs), 362 (s).

[$GaI_3\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}GaI_3$]. A solution of $Et_2P(CH_2)_2PEt_2$ (0.075 g, 0.364 mmol) in toluene (5 cm^3) was added dropwise to a stirred solution of GaI_3 (0.327 g, 0.726 mmol) in toluene (20 cm^3) 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 cm^3 in vacuo. The white precipitate was filtered off and dried in vacuo. Yield: 0.31 g, 77%. Anal. Calcd for $C_{10}H_{24}Ga_2I_6P_2$: C, 10.9; H, 2.2. Found: C, 11.6; H, 2.2. ^1H NMR (300 MHz, $CDCl_3$): δ 2.47 (d, [4H], CH_2), 2.22−2.00 (m, [8H], CH_2), 1.45−1.29 (m, [12H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ −132 (br). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/5% CD_2Cl_2): δ −27.6 (s). IR (cm^{-1}, Nujol): ν 240 (s), 229 (s). Raman (cm^{-1}): 230 (s).

[$GaCl_3\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}GaCl_3$]. This was prepared in a manner similar to that described above. Yield: 79%. Anal. Calcd for $C_{10}H_{24}Cl_6Ga_2P_2$: C, 21.5; H, 4.3. Found: C, 20.7; H, 4.6. ^1H NMR (300 MHz, $CDCl_3$): δ 2.26 (d, [4H], CH_2), 2.13−1.96 (m, [8H], CH_2), 1.44−1.23 (m, [12H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 274 (br). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/5% CD_2Cl_2): δ −2.0 (s). IR (cm^{-1}, Nujol): ν 376 (s), 350 (m). Raman (cm^{-1}): 381 (m), 353 (s).

[$GaBr_3\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}GaBr_3$]. This was prepared in a manner similar to that described above. Yield: 81%. Anal. Calcd for $C_{10}H_{24}Br_6Ga_2P_2$: C, 14.6; H, 3.0. Found: C, 14.3; H, 3.2. ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (d, [4H], CH_2), 2.17−1.95 (m, [8H], CH_2), 1.39−1.20 (m, [12H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 163 (br). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/5% CD_2Cl_2): δ −7.7 (s). IR (cm^{-1}, Nujol): ν 292 (s), 251 (w). Raman (cm^{-1}): 295 (m), 249 (s).

[$GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$][$GaCl_4$]. A solution of $o\text{-}C_6H_4(PPh_2)_2$ (0.29 g, 0.65 mmol) in toluene (25 cm^3) was added dropwise to a stirred solution of $GaCl_3$ (0.23 g, 1.31 mmol) in toluene (4 cm^3) 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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Table 1. Summary of Crystallographic Data[a]

	$[GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaCl_4]$	$[GaBr_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaBr_4]\cdot CH_2Cl_2$	$[GaI_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaI_4]\cdot nCH_2Cl_2$
formula	$C_{20}H_{32}Cl_6Ga_2P_4$	$C_{21}H_{34}Br_6Cl_2Ga_2P_4$	$C_{20.4}H_{32.8}Cl_{0.8}Ga_2I_6P_4$
fw	748.48	1100.16	1331.15
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	*C*2/*c* (No. 15)	*Pnma* (No. 62)	*Pnma* (No. 62)
a (Å)	13.2556(16)	14.688(3)	15.223(2)
b (Å)	14.536(2)	22.978(4)	23.406(4)
c (Å)	16.594(2)	10.4931(18)	11.0027(10)
α (deg)	90	90	90
β (deg)	104.131(8)	90	90
γ (deg)	90	90	90
V (Å^3)	3100.6(7)	3541.5(11)	3920.4(9)
Z	4	4	4
D_{calcd} (g cm^{-3})	1.603	2.063	2.255
μ(Mo Kα) (mm^{-1})	2.472	8.636	6.328
F(000)	1504	2104	2435.2
R1[b] $[I > 2\sigma(I)]$	0.026	0.041	0.050
wR2 [all data]	0.064	0.098	0.124

	$[GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaCl_4]$	$[(GaBr_3)_2\{Et_2P(CH_2)_2PEt_2\}]$	$[(GaI_3)_2\{Et_2P(CH_2)_2PEt_2\}]$
formula	$C_{30}H_{24}Cl_6Ga_2P_2$	$C_{10}H_{24}Br_6Ga_2P_2$	$C_{10}H_{24}Ga_2I_6P_2$
fw	798.57	825.13	1107.07
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	10.139(2)	7.4000(16)	7.7763(18)
b (Å)	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 (Å^3)	1642.6(7)	581.1(2)	653.1(3)
Z	2	1	1
D_{calcd} (g cm^{-3})	1.615	2.358	2.815
μ(Mo Kα) (mm^{-1})	2.246	12.760	9.268
F(000)	796	386	494
R1[b] $[I > 2\sigma(I)]$	0.048	0.037	0.038
wR2 [all data]	0.102	0.071	0.089

	$[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaCl_4]$	$[GaI_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaI_4]$	$[(GaI_3)_2\{Ph_2As(CH_2)_2AsPh_2\}]$
formula	$C_{10}H_{16}As_2Cl_6Ga_2$	$C_{10}H_{16}As_2Ga_2I_6$	$C_{26}H_{24}As_2Ga_2I_6$
fw	638.21	1186.91	1387.13
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/m$ (No. 11)	*Pnma* (No. 62)	$P2_1/n$ (No. 14)
a (Å)	9.941(2)	15.935(4)	10.1666(10)
b (Å)	10.111(3)	11.374(2)	15.4125(15)
c (Å)	10.206(2)	14.319(3)	23.181(2)
α (deg)	90	90	90
β (deg)	91.303(16)	90	99.036(5)
γ (deg)	90	90	90
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 Kα) (mm^{-1})	6.597	11.736	8.512
F(000)	612	2088	2504
R1[b] $[I > 2\sigma(I)]$	0.067	0.073	0.045
wR2 [all data]	0.146	0.150	0.091

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

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. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.01−7.31 (m, Ph). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 251 (br). ^{31}P{^{1}H} NMR (CH_2Cl_2/5%CD_2Cl_2): 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).

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

$[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaCl_4]$. A solution of o-$C_6H_4(AsMe_2)_2$ (0.163 g, 0.57 mmol) in toluene (5 cm^3) was added dropwise to a stirred solution of $GaCl_3$ (0.200 g, 1.14 mmol) in toluene (3 cm^3) 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 $C_{10}H_{16}As_2Cl_6Ga_2$: C, 18.8; H, 2.5. Found: C, 18.8; H, 2.8. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89−7.40 (m, [4H], C_6H_4), 2.12 (s, [6H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): 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).

$[GaBr_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaBr_4]$. This was prepared in a manner similar to that described above as a white solid. Yield: 72%. Anal. Calcd for $C_{10}H_{16}As_2Br_6Ga_2$: C, 13.3; H, 1.8. Found: C, 13.5; H, 1.7. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90−7.40 (m, [4H], C_6H_4), 2.11 (s, [6H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): 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 Bond Lengths (Å) and Angles (deg) for $[GaX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaX_4]$ (X = Cl, Br or I)

$[GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaCl_4]^a$			
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)		
Cl2−Ga2−Cl2a	111.11(3)	Cl3−Ga2−Cl2	109.17(2)
Cl3−Ga2−Cl2a	108.64(2)	Cl3−Ga2−Cl3a	110.10(3)
$[GaBr_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaBr_4]\cdot CH_2Cl_2^b$			
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)
$[GaI_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaI_4]\cdot nCH_2Cl_2^c$			
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*.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaCl_4]$

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)
Cl2−Ga1−P1	109.34(4)	Cl5−Ga2−Cl3	108.60(5)
Cl1−Ga1−P2	108.15(4)	Cl5−Ga2−Cl4	111.12(5)
Cl2−Ga1−P2	124.34(4)	Cl6−Ga2−Cl3	109.80(5)
Cl1−Ga1−Cl2	113.97(5)	Cl6−Ga2−Cl4	108.16(5)
P1−Ga1−P2	85.42(4)	Cl6−Ga2−Cl5	110.40(5)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[(GaX_3)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ (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 $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$ (X = Cl or I)

$[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaCl_4]^a$			
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)
$[GaI_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaI_4]^b$			
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*.

$[GaI_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaI_4]$. This was prepared in a manner similar to that described above as a white solid. Yield: 69%. Anal. Calcd for $C_{10}H_{16}As_2Ga_2I_6$: C, 10.1; H, 1.4. Found: C, 10.5; H, 1.1. ^1H NMR ($CDCl_3$): δ 7.90−7.40 (m, [4H], C_6H_4), 2.01 (s, [6H], CH_3). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): 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).

$[GaI_3\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}GaI_3]$. A solution of $Ph_2As(CH_2)_2AsPh_2$ (0.113 g, 0.23 mmol) in dichloromethane (3 cm^3) was added to stirred solution of GaI_3 (0.209 g, 0.465 mmol) in the same solvent (20 cm^3) at room temperature. After the mixture was stirred at room temperature overnight, the solvent was reduced to ∼3 cm^3 to give a white precipitate. The precipitate was filtered off, washed using CH_2Cl_2, and dried in vacuo. Yield: 0.19 g, 61%. Anal. Calcd for $C_{26}H_{24}As_2Ga_2I_6$: C, 22.5; H, 1.7. Found: C, 23.1; H, 1.6. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60−7.43 (m, [20H], Ph), 3.09 (s, [4H], CH_2). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ −206 (br). IR (cm^{-1}, Nujol): ν 244 (s), 233 (s). Raman (cm^{-1}): 247 (m), 233 (m).

$[GaCl_3(AsMe_3)]$. A solution of $AsMe_3$ (0.15 g, 1.24 mmol) in Et_2O (5 cm^3) was added dropwise to stirred solution of $GaCl_3$ (0.22 g, 1.24 mmol) in Et_2O (5 cm^3) 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 cm^3, and the resultant white precipitate was filtered off and dried in vacuo. Yield: 0.22 g, 76%. Anal. Calcd for $C_3H_9AsCl_3Ga$: C, 12.2; H, 3.1. Found: C, 11.7; H, 3.1. ^1H NMR (300 MHz, $CDCl_3$): δ 1.59 (s). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 264.5 (br). IR (cm^{-1}, Nujol): ν 390 (s), 344 (s).

[**$GaBr_3(AsMe_3)$]**. This was prepared in a manner similar to that for the chloride. Yield: 77%. Anal. Calcd for $C_3H_9AsBr_3Ga$: C, 8.4; H, 2.1. Found: C, 7.9; H, 2.3. ^1H NMR (300 MHz, $CDCl_3$): δ 1.53 (s). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): δ 147. IR (cm^{-1}, Nujol): ν 265 (s), 252 (sh).

$[GaI_3(AsMe_3)]$. This was prepared in a manner similar to that described above. Yield: 70%. Anal. Calcd for $C_3H_9AsGaI_3$: C, 6.3; H, 1.5. Found: C, 6.4; H, 1.5. ^1H NMR (300 MHz, $CDCl_3$): δ 1.49 (s). ^{71}Ga NMR (CH_2Cl_2/5% CD_2Cl_2): 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 CH_2Cl_2 solutions by vapor diffusion of hexane. Data collections used a Bruker-Nonius Kappa CCD diffractometer fitted with Mo K_α 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 straightforward,[20,21] with H atoms introduced into the models in calculated positions. Selected bond lengths and angles are given in Tables 2−6.

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(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 $[(GaI_3)_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$

Ga1−I1	2.5181(9)	Ga2−I4	2.5270(9)
Ga1−I2	2.5118(9)	Ga2−I5	2.4944(9)
Ga1−I3	2.5198(9)	Ga2−I6	2.5329(9)
Ga1−As1	2.4875(10)	Ga2−As2	2.4885(10)
As1−Ga1−I1	100.21(3)	As2−Ga2−I4	99.21(3)
As1−Ga1−I2	106.02(3)	As2−Ga2−I5	105.90(3)
As1−Ga1−I3	105.19(3)	As2−Ga2−I6	105.06(3)
I1−Ga1−I2	116.36(3)	I4−Ga2−I5	119.01(3)
I1−Ga1−I3	113.69(3)	I4−Ga2−I6	111.92(3)
I2−Ga1−I3	113.42(3)	I5−Ga2−I6	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 GaX_3 (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 CH_2Cl_2 solution and were revealed to be *trans*-$[GaX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaX_4]$, 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 → Br → I in the three complexes. The small chelate bite of the diphosphane results in quite acute ∠P−Ga−P of ~82°. Six-coordination is also present in the 2,2′-bipyridyl complexes $[GaX_2(2,2'\text{-}bipy)_2][GaX_4]$, but the cations are *cis* isomers.[24,25] The diphosphane complexes are poorly soluble in chlorocarbons but give single sharp $^{31}P\{^1H\}$ NMR resonances with small high-frequency coordination shifts, showing them to be exclusively the *trans* isomers in solution. Only the $[GaX_4]^-$ anions were observed in the ^{71}Ga 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 $[GaX_4]^-$,[27] and definite assignment of the a_{1g} (Raman) and a_{2u} (IR) GaX_2 vibrations of the cations was not possible. The Experimental Section lists the major vibrations below 400 cm^{-1}. The reaction of o-$C_6H_4(PMe_2)_2$ with two molar equivalents of $GaCl_3$ in hot toluene gave a white powder with the composition $2GaCl_3/o\text{-}C_6H_4(PMe_2)_2$, which was insoluble in chlorocarbons and decomposed by MeCN, $MeNO_2$, or DMSO with liberation of the diphosphane (and formation of $[o\text{-}C_6H_4(PMe_2)(PMe_2H)]^+$, identified by $^{31}P\{^1H\}$ NMR spectroscopy). The far-IR spectrum shows a strong band at 380 cm^{-1} assigned as ν_3 of $[GaCl_4]^-$, and two strong bands at 410 and 362 cm^{-1} are also assigned as Ga−Cl stretches. This complex is tentatively formulated as $[GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}][GaCl_4]$, 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.

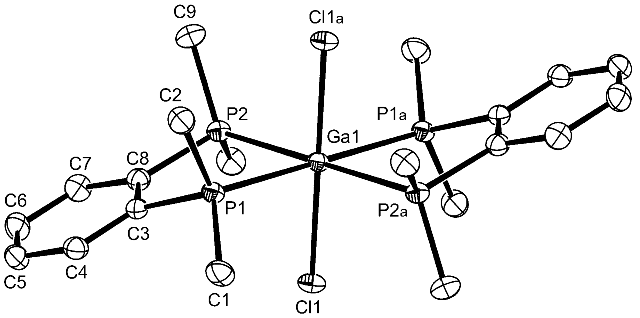

Figure 1. Crystal structure of the cation in $[GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaCl_4]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a 1 − *x*, −*y*, 1 − *z*.

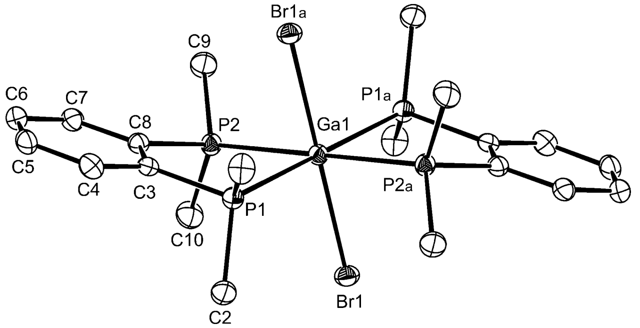

Figure 2. Crystal structure of the cation in $[GaBr_2\{o\text{-}C_6H_4(PMe_2)_2\}_2][GaBr_4]\cdot CH_2Cl_2$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a −*x*, 1 − *y*, 1 − *z*. The iodo analogue is isomorphous.

The phenyl-substituted diphosphane, o-$C_6H_4(PPh_2)_2$, 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 GaX_3 only $[GaX_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaX_4]$ complexes are isolated even with excess diphosphane. The structure of the chloro complex (Table 3, Figure 3) shows a very distorted tetrahedral cation with ∠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 $[GaI_2\{o\text{-}C_6H_4(PPh_2)_2\}]^+$, Ga−P = 2.398(1) and 2.409(1) Å,[14] indicating weaker Lewis acidity in the di-iodogallium cation and

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[22] Levason, W. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: New York, 1990; Vol. 1, pp 568−641.

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[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 ^{71}Ga NMR chemical shifts for $[GaX_4]^-$ are X = Cl , δ 251; X = Br, δ 64; X = I , δ −455 (all in CH_2Cl_2 solution).

[27] Tetrahedral $[GaX_4]^-$ 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 $\nu_1 = 346$, $\nu_3 = 386$; X = Br $\nu_1 = 210$, $\nu_3 = 278$; X = I $\nu_1 = 145$, $\nu_3 = 222$. Data from Nakamoto, K. *IR Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970.

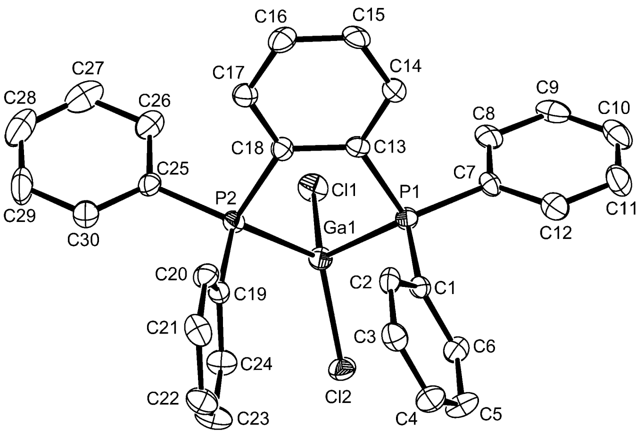

Figure 3. Crystal structure of the cation in $[GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaCl_4]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

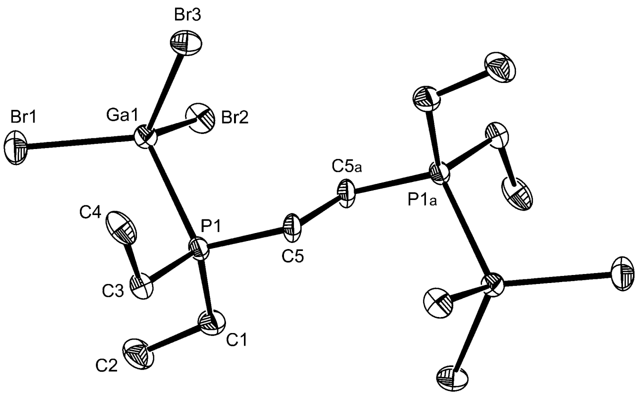

Figure 4. Crystal structure of $[(GaBr_3)_2\{Et_2P(CH_2)_2PEt_2\}]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a $1 - x, -y, -z$.

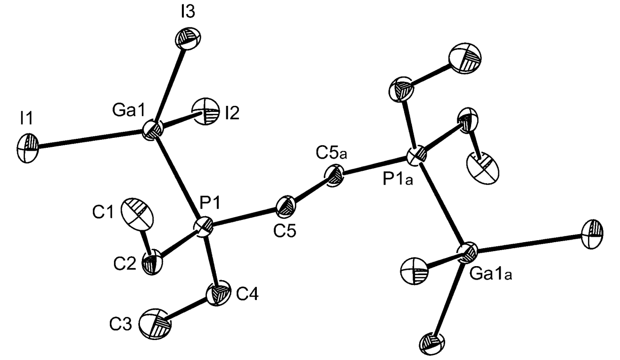

Figure 5. Crystal structure of $[(GaI_3)_2\{Et_2P(CH_2)_2PEt_2\}]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The molecule has a center of symmetry. Symmetry operation: a $2 - x, 2 - y, -z$.

perhaps steric crowding, although the P−Ga−P angle (84.5°) is little different. The complexes are characterized by singlet $^{31}P\{^1H\}$ NMR resonances to low frequency of the ligand chemical shift, which are invariant over the temperature range of 295−183 K. The ^{71}Ga NMR spectra show only the sharp resonances of the $[GaX_4]^-$ anions, the resonances of the cations were not observed. Solutions of $[GaX_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaX_4]$ containing excess (~3-fold) $o\text{-}C_6H_4(PPh_2)_2$ show evidence for the formation of other species, although only the $[GaX_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaX_4]$ have been isolated as solids. Thus, a dichloromethane solution of $[GaI_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaI_4]$ containing excess $o\text{-}C_6H_4(PPh_2)_2$ shows a new ^{71}Ga resonance at $\delta = -162$, and the $^{31}P\{^1H\}$ NMR spectrum shows ligand ($\delta = -13$) and resonances at $\delta = -24$ and -19, which we tentatively attribute to $[GaI_3\{\kappa^1\text{-}o\text{-}C_6H_4(PPh_2)_2\}]$. It is notable that even with a large excess (~10-fold) of added $o\text{-}C_6H_4(PPh_2)_2$, significant amounts of $[GaI_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaI_4]$ are still present. Similar but more complex behavior was evident in mixtures of $[GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}][GaCl_4]/o\text{-}C_6H_4(PPh_2)_2$ in CH_2Cl_2 solution, which seems to contain several species including the hydrolysis product $[o\text{-}C_6H_4(PPh_2)(PPh_2H)]^+$.[28]

The diphosphane $Et_2P(CH_2)_2PEt_2$,which usually behaves as a strongly bound chelate to transition metals,[22] gives $[(X_3Ga)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ with bridging diphosphane ligands coordinated to pseudotetrahedral GaX_3 units as the only complex type in the gallium(III) systems. The $^{31}P\{^1H\}$ and ^{71}Ga NMR spectra show these are the only significant species present in CH_2Cl_2 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 $[(X_3Ga)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ (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 $[(I_3Ga)_2\{\mu\text{-}Et_2P(CH_2)_2PEt_2\}]$ (2.377(1) Å) than in $[(I_3Ga)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}]$ (2.40(1), 2.41(1) Å)[13] which suggests that the alkyldiphosphane is more strongly bound. The conformation of the two GaX_3 residues is determined by the inversion center in the molecule.

Diarsanes. The reaction of $GaCl_3$ with $o\text{-}C_6H_4(AsMe_2)_2$ in hot toluene produced a white complex with the composition 2:1 $GaCl_3$/diarsane, regardless of the ratio of reagents used. This was identified as $[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaCl_4]$ by a crystal structure determination (see below) and is the correct formulation for the substance formulated as $[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2][Ga_3Cl_{10}]$ (based on microanalytical and conductivity data only) in an early report.[29] The reaction of GaX_3 (X = Br or I) with $o\text{-}C_6H_4(AsMe_2)_2$ in a 2:1 mole ratio similarly affords $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$, 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) $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$, 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 $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]X$ and $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$, 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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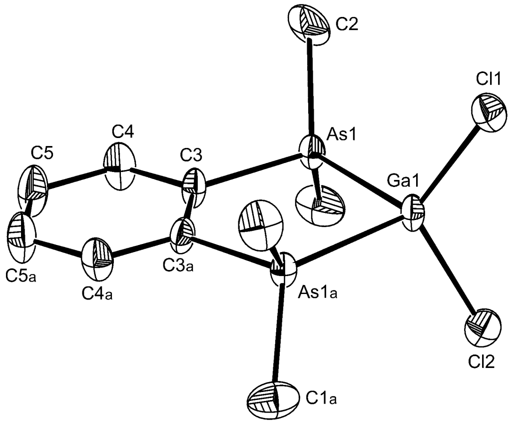

Figure 6. Crystal structure of the cation in $[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$-$[GaCl_4]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The cation has mirror plane symmetry. Symmetry operation: a x, $1/2 - y$, z.

type *trans*-$[GaX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]^+$ described above, the diarsane affords only pseudotetrahedral $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^+$. We note that $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2][GaX_4]$ 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 $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]X$. The different stoichiometries obtained with gallium halides for these two *o*-phenylene 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 $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaX_4]$ 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)° (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 $[GaCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaCl_4]$ contains strong bands at 421 and 356 cm^{-1}, which we assign as the $a_1 + b_1$ $GaCl_2$ vibrations of the cation; the bands appear at similar frequencies but with reversed relative intensities in the Raman spectrum. The ^{71}Ga NMR spectrum shows only a sharp feature at δ 250 assigned to $[GaCl_4]^-$ superimposed on a broader feature δ ~256. The far-IR spectrum of $[GaBr_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaBr_4]$ contains features at 264 and 233 cm^{-1} assigned as the $a_1 + b_1$ $GaBr_2$ vibrations, and corresponding features in the spectrum of

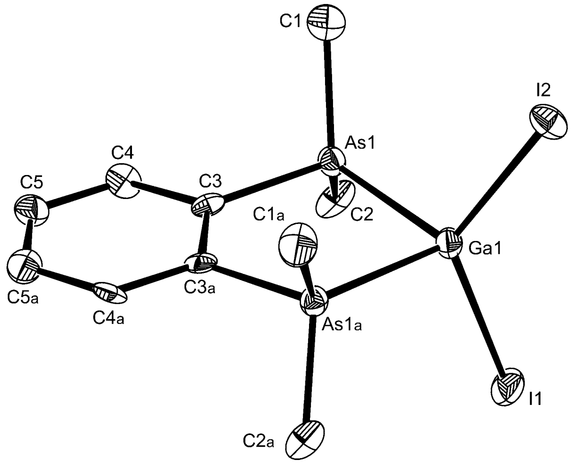

Figure 7. Crystal structure of the cation in $[GaI_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaI_4]$ showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. The cation has mirror symmetry. Symmetry operation: a x, $1/2 - y$, z.

$[GaI_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaI_4]$ are found at 226 and 216 cm^{-1}. The ^{71}Ga NMR spectrum of $[GaBr_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$-$[GaBr_4]$ shows resonances at δ 64 ($[GaBr_4]^-$)[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 $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^+$, 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 As_2X_2 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 GaX_3As environment produced by rearrangement in solution. The δ values in each case are close to those observed in C_{3v} GaX_3As species (see Table 7), but since we have no values for GaX_2As_2 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 $[GaCl_3(PR_3)]$, PR_3, and $SbCl_5$ in dry CH_2Cl_2 failed; the products identified by a combination of ^{71}Ga, ^{31}P and ^{1}H NMR spectroscopy were unchanged $[GaCl_3(PR_3)]$ and $[PR_3Cl]^+$, the latter resulting from chlorination of the PR_3 by $SbCl_5$.[32]

Since no other gallium diarsane complexes have been reported, we prepared $[(I_3Ga)_2\{\mu\text{-}Ph_2As(CH_2)_2AsPh_2\}]$ which is an exact analogue of $[(I_3Ga)_2\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}]$.[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 ^{71}Ga NMR exhibits a single resonance at δ −206, which may be compared with the δ −220 value in $[GaI_3(AsPh_3)]$[11] and δ −169.5 in $[GaI_3(AsMe_3)]$. The three $[GaX_3(AsMe_3)]$ (X = Cl, Br or I) were also prepared for comparison purposes; details of their structures are given in the Supporting Information.

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

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(30) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126−3140.

(31) The X-ray data for $[GaBr_2\{o\text{-}C_6H_4(AsMe_2)_2\}][GaBr_4]$ gave a largish R_{int} (0.11) with the systematic absences suggesting space groups *Pmmn* (No. 59) or *Pmn*2$_1$ (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 ≈ 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.

(32) Corcoran, S. M.; Levason, W.; Patel, R.; Reid, G. *Inorg. Chim. Acta* **2005**, *358*, 1263−1268.

Table 7. Selected ^{71}Ga and ^{31}P{^{1}H} NMR Data

	$\delta(^{31}P)^a$	Δ^b	$\delta(^{71}Ga)^c$
[$GaCl_3(PPh_3)$]	−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)
[$GaCl_2\{o\text{-}C_6H_4(PPh_2)_2\}$][$GaCl_4$]	−18.9 (s)	−5.9	251^d
[$GaBr_2\{o\text{-}C_6H_4(PPh_2)_2\}$][$GaBr_4$]	−21.8 (s)	−8.8	64^d
[$GaI_2\{o\text{-}C_6H_4(PPh_2)_2\}$][$GaI_4$]	−30.7 (s)	−17.7	−456^d
[$GaCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2$][$GaCl_4$]	−40.8 (s)	+14.2	251^d
[$GaBr_2\{o\text{-}C_6H_4(PMe_2)_2\}_2$][$GaBr_4$]	−41.2 (s)	+13.8	66^d
[$GaI_2\{o\text{-}C_6H_4(PMe_2)_2\}_2$][$GaI_4$]	−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 CH_2Cl_2 solution unless indicated otherwise, relative to 85% H_3PO_4. ^{b} Coordination shift δ(complex) − δ(ligand). Ligand chemical shifts are PPh_3 (−6), $Et_2P(CH_2)_2PEt_2$ (−18), $o\text{-}C_6H_4(PPh_2)_2$ (−13), $o\text{-}C_6H_4(PMe_2)_2$ (−55). ^{c} At 295 K relative to $[Ga(H_2O)_6]^{3+}$ in water at pH 1. ^{d} Resonance of $[GaX_4]^-$ anion only, see text.

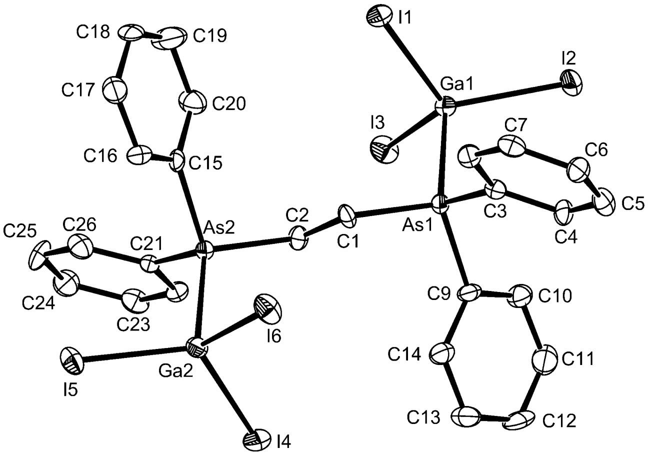

Figure 8. Crystal structure of [$(GaI_3)_2\{Ph_2As(CH_2)_2AsPh_2\}$] showing the atom numbering scheme adopted. Ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

^{71}Ga (39.9%), both with $I = 3/2$, the less abundant ^{71}Ga being preferred for NMR studies because of its lower quadrupole moment (Q), which results in narrower lines and a higher receptivity (R_c) (^{69}Ga, $Q = 0.178 \times 10^{-28}$ m^2, $R_c = 237$; ^{71}Ga, $Q = 0.112 \times 10^{-28}$ m^2, $R_c = 319$).[26] The key factor governing whether a ^{71}Ga resonance can be observed or gallium coupling resolved on ^{31}P NMR resonances will be the electric field gradient surrounding the gallium center. Given the relatively favorable nuclear parameters, ^{71}Ga 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 ^{71}Ga resonances are easily observed for the tetrahedral $[GaX_4]^-$ anions and for the X_3P environments in the C_{3v} [$GaX_3(PR_3)$] and [$(X_3Ga)_2$(μ-diphosphane)] complexes (Table 7). Typically, in these complexes, the ^{71}Ga 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 ^{31}P resolved (although it is observed for [$GaX_3(PPh_3)$] (X = Cl, Br, or I), with $^1J(^{71}Ga-^{31}P)$ falling with X, Cl → Br → I).[11] The $\delta(^{71}Ga)$ are characteristic, with Cl_3P donor sets lying in the range from ~260 to 280, Br_3P from ~150 to 160, and I_3P from ~−130 to −150 ppm. The incorporation of arsenic in place of phosphorus has little effect on the ^{71}Ga resonance frequency as shown by the data on [$GaX_3(AsMe_3)$] (Table 7). The $\delta(^{71}Ga)$ 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 ^{71}Ga resonances from either the pseudotetrahedral cations $[GaX_2\{o\text{-}C_6H_4(PPh_2)_2\}]^+$ or the pseudooctahedral $[GaX_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]^+$, in both cases the lower symmetry producing unfavorable electric field gradients and fast relaxation. The cases of $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^+$ (X = Br or I) have been discussed above.

The ^{31}P{^{1}H} NMR spectra are singlets, sharp for the cations (showing that fast quadrupolar relaxation effectively decouples the gallium nuclei) and rather broader for the C_{3v} X_3P coordination environments. For a fixed ligand, the ^{31}P chemical shifts move to low frequency as the halide changes Cl → Br → 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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(33) (a) Davis, M. F.; Clarke, M.; Levason, W.; Reid, G.; Webster, M. *Eur. J. Inorg. Chem.* **2006**, 2773−2782. (b) Genge, A. R. J.; Levason, W.; Reid, G. *Inorg. Chim. Acta* **1999**, *288*, 142−149.

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 $[GaX_2\{o\text{-}C_6H_4(AsMe_2)_2\}]^+$ 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-coordination[34] $r^+ = 62$ 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) = ∼2.17 Å, d(Ga−P) = ∼2.35 Å, and d(Ga−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) < d(Sn−Br) ≈ d(Sn−P),[33] and the disparity between M−X and M−P is even greater in complexes of Group 15 halides ($M'X_3$, 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 $GaEX_3$ with cationic $GaE_2X_2^+$ (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.

Acknowledgment. We thank RCUK (EP/C006731/1) and the Royal Society (University Research Fellowship to ALH) for support.

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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