Table V. Force Field of CF_3OSF[a]

CF^5	6.15	CF^5/CF^6	1.55	CF^6/F^5CF^7	−0.62
CF^6	5.49	CF^5/CF^7	1.36	CF^7/F^6CF^7	0.65
CF^7	5.75	CF^6/CF^7	1.15	CF^7/F^5CF^7	0.39
CO	5.36	CF^5/CO	0.69	CF^7/F^5CF^6	−0.44
OS	4.19	CF^6/CO	0.86	CO/COS	0.68
SF	4.48	CF^7/CO	0.75	CO/OS	0.60
F^5CF^6	2.30	CO/F^5CF^6	−0.81	OS/SF	0.50
F^5CF^7	2.20	CO/F^5CF^7	−0.56	OS/OSF	0.31
F^8CF^7	1.79	CO/F^6CF^7	−0.41	SF/OSF	0.24
F^5CO	1.77	CF^5/F^5CF^6	0.61	COS/OSF	0.72
F^6CO	1.09	CF^5/F^5CF^7	0.59	OS/COS	0.35
F^7CO	0.81	CF^5/F^6CF^7	−0.23		
COS	1.79	CF^6/F^5CF^6	0.47		
OSF	1.27	CF^6/F^6CF^7	0.14		
FCOS (torsion)	0.10				
FSCO (torsion)	0.21				

[a] Force constants in 10^2 N/m; bending force constants and bending–stretching constants normalized on 10^{-10} m.

Table III, vibrational frequencies and isotopic shifts from Table IV, and the program NCA[21] were used. The final result is shown in Table V, and the calculated frequencies and isotopic shifts are listed in Table IV. Because the vibrational couplings are very strong in this molecule, it was not possible to get a satisfying agreement between observed and calculated frequencies. Nevertheless, the results are reasonable for the proposed CF_3OSF structure.

2. UV Photolysis of $CF_3S(O)F$ in the Gas Phase and in CD_2Cl_2 Solution. Photolysis of $CF_3S(O)F$ in a quartz glass bulb at 10–100 mbar and 20 °C, or diluted in CD_2Cl_2 at −80 °C in an NMR tube, does not generate CF_3OSF. The molecules COF_2, SOF_2, CF_3SSCF_3, and C_2F_6 in various ratios could be detected by IR and ^{19}F NMR spectroscopy.

Conclusion

The compound CF_3OSF is formed by UV photolysis of matrix-isolated trifluoromethanesulfinyl fluoride, $CF_3S(O)F$. In contrast to the photoisomerization of S_2F_2[6] or Se_2F_2,[22] there is no stationary equilibrium between the isomers of $CF_3S(O)F$. By prolonged UV irradiation, it decomposed to COF_2 and SF_2.

CF_3OSF is the first known fluorosulfenyl ester. It was not possible to synthesize it on a preparative scale by gas-phase or solution photolysis. Likely primary photolysis products are CF_3 and OSF radicals, which may recombine in the matrix cage to CF_3OSF, but in the gas phase or in solution they can diffuse and form other more stable products.

For the fluorosulfenyl trifluoromethyl ester 13 of 15 possible fundamental vibrations were measured and assigned. Data were also obtained for the ^{13}C- and ^{18}O-enriched species, enabling us to deduce a reliable structure and force field for this unusual molecule.

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Registry No. $CF_3S(O)F$, 812-12-4; CF_3OSF, 115095-67-5; CF_3SF_3, 374-10-7; $^{13}CF_3S(O)F$, 115095-68-6; $CF_3S(^{18}O)F$, 115095-69-7; $CF_3{}^{34}S(O)F$, 115095-70-0; $^{13}CF_3OSF$, 115095-71-1; $CF_3{}^{18}OSF$, 115095-72-2; $CF_3O^{34}SF$, 115095-73-3.

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Anionic Perphosphido and Perarsenido Complexes of Gallium and Indium

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Reaction of 4 equiv of $LiEPh_2$ with MCl_3 in THF at −78 °C yields the anionic perphosphido and perarsenido complexes $[Li(THF)_4][M(EPh_2)_4]$ (**1**, M = Ga, E = P; **2**, M = In, E = P; **3**, M = Ga, E = As) in 70–80% yields. The air-sensitive complexes are yellow and crystalline and can be recrystallized from THF/toluene mixtures. The X-ray structures of **1**–**3** have been determined. The anionic moieties of **1**–**3** are very similar. The M–E bond lengths, EPh_2 geometries, and $M(EC_2)_4$ conformations are indicative of M–E single bonding in each case. Crystal data for **1**: $C_{64}H_{72}GaLiO_4P_4$, $M_r = 1105.84$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 13.945$ (7) Å, $b = 18.332$ (5) Å, $c = 23.671$ (4) Å, $V = 6051.7$ (3) Å^3, $D_{calcd} = 1.214$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 5.99 cm^{-1}. Refinement of 4127 reflections ($I > 3\sigma(I)$) out of 4155 unique observed reflections ($3° \le 2\theta \le 44°$) gave R and R_w values of 0.0688 and 0.0747, respectively. Crystal data for **2**: $C_{64}H_{72}InLiO_4P_4$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 14.017$ (4) Å, $b = 18.402$ (9) Å, $c = 23.696$ (5) Å, $V = 6112.6$ (9) Å^3, $D_{calcd} = 1.251$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 5.25 cm^{-1}. Refinement of 4163 reflections ($I > 3\sigma(I)$) out of 4189 unique observed reflections ($3° \le 2\theta \le 44°$) gave R and R_w values of 0.0558 and 0.0644, respectively. Crystal data for **3**: $C_{68}H_{80}As_4GaLiO_5$, triclinic, $P\bar{1}$ (No. 2), $a = 13.392$ (7) Å, $b = 13.521$ (5) Å, $c = 19.025$ (7) Å, $\alpha = 87.92$ (3)°, $\beta = 76.19$ (4)°, $\gamma = 83.16$ (3)°, $V = 3321.1$ (7) Å^3, $D_{calcd} = 1.354$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 24.30 cm^{-1}. Refinement of 8132 reflections ($3° \le 2\theta \le 44°$) gave R and R_w values of 0.0626 and 0.0707, respectively. There is a disordered THF molecule not bound to Li in the structure of **3**.

Over 20 years ago, Coates, Beachley, and co-workers pioneered the synthesis of compounds featuring bonding between the heavier group 13 and 15 elements.[1] Such compounds have attracted recent attention[2,3] because of their potential utility as percursors to compound semiconductor materials such as gallium arsenide and indium phosphide. Gallium–arsenic and indium–phosphorus compounds have now been characterized in which two or three phosphorus- or arsenic-containing groups are directly bonded to the group 13 element.[2,3] However, to the best of our knowledge, no compounds are known in which the gallium or indium to

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(1) See, for example: Coates, G. E.; Graham, J. *J. Chem. Soc.* **1963**, 233. Beachley, O. T.; Coates, G. E. *J. Chem. Soc.* **1965**, 3241.

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Table I. Crystal Structure Parameters for Complexes **1–3**

	1	**2**	**3**
	Description of Crystal		
color	yellow	yellow	yellow
habit	rhombohedral	rhombohedral	rhombohedral
max cryst dimens, mm	0.40 × 0.40 × 0.30	0.35 × 0.40 × 0.30	0.45 × 0.35 × 0.35
	Unit Cell		
cryst syst	orthorhombic	orthorhombic	triclinic
space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
unit cell params			
a, Å	13.945 (7)	14.017 (4)	13.392 (7)
b, Å	18.332 (5)	18.402 (9)	13.521 (5)
c, Å	23.671 (4)	23.696 (5)	19.025 (7)
α, deg	90	90	87.92 (3)
β, deg	90	90	76.19 (4)
γ, deg	90	90	83.16 (3)
V, Å^3	6051.7 (3)	6112.6 (9)	3321.1 (7)
molecules per unit cell	4	4	2
formula	$C_{64}H_{72}GaLiP_4O_4$	$C_{64}H_{72}InLiP_4O_4$	$C_{68}H_{80}As_4GaLiO_5$
mol wt	1105.84	1150.94	1353.74
calcd density, g cm^{-3}	1.214	1.251	1.354
μ(calcd), cm^{-1}	5.99	5.25	24.30
	Data Collection		
radiation (λ, Å)		Mo Kα (0.71073)	
scan technique		$\theta/2\theta$	
scan width, deg		0.80 + 0.35 (tan θ)	
range of indices *hkl*	+14, +19, +25	+14, +19, +25	+14, ±14, ±20
2θ range, deg		$3 \le 2\theta \le 44$	
no. of reflns measd	4155	4189	8565
std reflns			
intens	(305), $(30\bar{5})$	(305), $(30\bar{5})$	(030), (214)
orientation	$(\bar{7}61)$, $(\bar{7}45)$	(154), (136)	$(2\bar{6}\bar{5})$, $(17\bar{3})$
decay of stds, %	7.2	13.7	27.4
min transmission, %	94.35	90.56	65.65
max transmission, %	99.87	99.81	99.41
av transmission, %	97.65	95.94	82.38
agreement factor for averaged reflns			
F_o	not averaged	not averaged	0.028
intens	not averaged	not averaged	0.036
	Structure Determination		
no. of reflns used ($I > 3\sigma(I)$)	4127	4163	8132
no. of params varied	557	567	594
data/parameter ratio	7.41	7.34	13.69
shift/error ratio	1.551	1.334	1.232
esd of an observn of unit wt	4.270	4.510	4.272
R^a	0.0688	0.0558	0.0626
$R_w{}^a$	0.0747	0.0644	0.0707

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

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Li(THF)_4][Ga(PPh_2)_4]$ (**1**)[a]

Ga–P1	2.434 (6)	P3–C51	1.83 (2)
Ga–P2	2.399 (7)	P3–C61	1.85 (2)
Ga–P3	2.419 (7)	P4–C71	1.82 (2)
Ga–P4	2.386 (7)	P4–C81	1.84 (2)
P1–C11	1.90 (2)	O1–Li	2.01 (3)
P1–C21	1.84 (2)	O2–Li	1.89 (3)
P2–C31	1.86 (2)	O3–Li	1.97 (1)
P2–C41	1.87 (2)	O4–Li	1.87 (3)
P1–Ga–P2	100.5 (2)	Ga–P3–C51	105.5 (8)
P1–Ga–P3	99.7 (2)	Ga–P3–C61	105.0 (8)
P1–Ga–P4	112.3 (3)	C51–P3–C61	102 (1)
P2–Ga–P3	111.9 (2)	Ga–P4–C71	106.2 (7)
P2–Ga–P4	115.5 (2)	Ga–P4–C81	104.5 (8)
P3–Ga–P4	114.9 (2)	C71–P4–C81	105 (1)
Ga–P1–C11	106.2 (7)	O1–Li–O2	112 (2)
Ga–P1–C21	111.0 (7)	O1–Li–O3	106 (2)
C11–P1–C21	103 (1)	O1–Li–O4	109 (2)
Ga–P2–C31	103.2 (7)	O2–Li–O3	105 (2)
Ga–P2–C41	105.2 (7)	O2–Li–O4	117 (2)
C31–P2–C41	108 (1)	O3–Li–O4	107 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

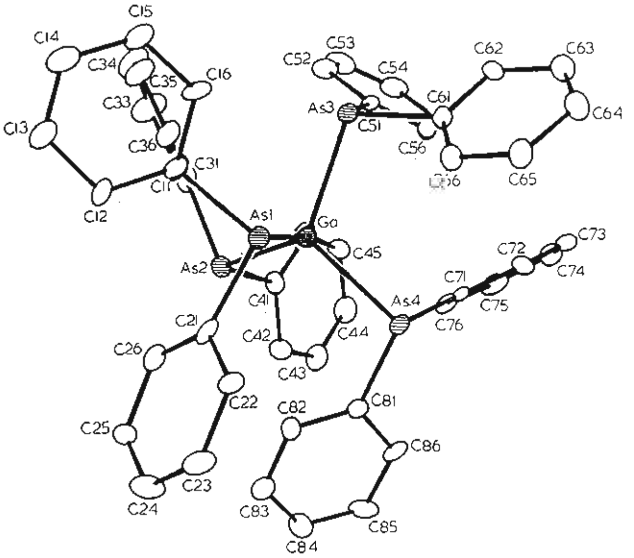

Figure 1. View (ORTEP) of the $[Ga(AsPh_2)_4]^-$ anion in **3** showing the atom-numbering scheme.

Table III. Positional Parameters and Their Estimated Standard Deviations for $[Li(THF)_4][Ga(PPh_2)_4]$ (**1**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Ga	0.0296 (2)	0.0527 (1)	0.0601 (1)	3.98 (4)	C31	−0.129 (2)	−0.012 (1)	−0.0344 (9)	4.4 (5)
P1	0.0331 (5)	0.1748 (3)	0.0197 (3)	4.6 (1)	C32	−0.168 (1)	0.055 (1)	−0.0317 (9)	5.3 (6)
P2	0.0034 (5)	−0.0187 (3)	−0.0234 (3)	4.6 (2)	C33	−0.265 (2)	0.064 (1)	−0.046 (1)	6.0 (7)
P3	−0.1140 (5)	0.0622 (4)	0.1170 (3)	5.0 (2)	C34	−0.321 (2)	0.009 (1)	−0.063 (1)	5.9 (6)
P4	0.1721 (5)	0.0249 (4)	0.1115 (3)	4.9 (2)	C35	−0.279 (2)	−0.058 (1)	−0.0678 (9)	5.7 (6)
O1	0.500 (2)	0.120 (1)	0.1625 (9)	10.7 (6)*	C36	−0.179 (2)	−0.072 (1)	−0.0526 (8)	4.5 (6)
O2	−0.071 (2)	−0.005 (1)	−0.2425 (9)	10.3 (6)*	C41	0.032 (2)	−0.115 (1)	−0.0024 (8)	5.1 (6)
O3	0.116 (2)	−0.090 (1)	−0.224 (1)	11.6 (7)*	C42	−0.046 (2)	−0.160 (1)	0.0250 (9)	4.6 (6)
O4	0.073 (2)	0.323 (1)	−0.281 (1)	14.0 (8)*	C43	−0.014 (2)	−0.232 (1)	0.036 (1)	6.5 (7)
C1′	0.149 (4)	−0.027 (3)	−0.186 (2)	18 (2)*	C44	0.077 (2)	−0.257 (1)	0.022 (1)	7.3 (8)
C1	0.082 (5)	0.392 (3)	−0.118 (3)	25 (3)*	C45	0.141 (2)	−0.208 (2)	−0.009 (1)	8.2 (8)
C2′	0.242 (3)	−0.048 (2)	−0.167 (2)	13 (1)*	C46	0.119 (2)	−0.138 (1)	−0.021 (1)	7.7 (7)
C2	0.524 (3)	0.115 (2)	0.068 (2)	14 (1)*	C51	−0.162 (2)	−0.031 (1)	0.1215 (9)	5.0 (6)
C3′	0.251 (3)	−0.127 (2)	−0.171 (2)	16 (2)*	C52	−0.249 (1)	−0.010 (1)	0.0895 (9)	5.4 (6)
C3	0.436 (3)	0.161 (2)	0.072 (2)	12 (1)*	C53	−0.298 (2)	−0.108 (1)	0.089 (1)	6.9 (7)
C4′	0.179 (4)	−0.149 (3)	−0.222 (2)	20 (2)*	C54	−0.259 (2)	−0.160 (2)	0.120 (1)	8.6 (8)
C4	0.418 (3)	0.162 (2)	0.136 (2)	15 (1)*	C55	−0.169 (2)	−0.157 (1)	0.1540 (8)	6.4 (7)
C5′	−0.161 (4)	−0.229 (3)	−0.240 (2)	18 (2)*	C56	−0.124 (2)	−0.089 (1)	0.1521 (9)	6.4 (7)
C5	−0.088 (3)	0.054 (2)	−0.278 (1)	12 (1)*	C61	−0.070 (2)	0.078 (1)	0.190 (1)	5.2 (7)
C6	−0.115 (4)	0.116 (3)	−0.238 (2)	18 (2)*	C62	−0.008 (2)	0.133 (1)	0.201 (1)	5.8 (7)
C6′	−0.129 (5)	−0.293 (3)	−0.196 (3)	24 (2)*	C63	0.019 (2)	0.153 (1)	0.257 (1)	7.7 (7)
C7	−0.101 (3)	0.093 (2)	−0.184 (2)	14 (1)*	C64	−0.025 (2)	0.118 (1)	0.305 (1)	8.8 (8)
C7′	−0.091 (5)	−0.251 (3)	−0.150 (3)	23 (2)*	C65	−0.099 (3)	0.062 (2)	0.291 (1)	11 (1)
C8	−0.124 (4)	0.018 (3)	−0.192 (2)	18 (2)*	C66	−0.123 (2)	0.048 (2)	0.2358 (9)	8.1 (8)
C8′	−0.153 (4)	−0.172 (3)	−0.167 (2)	23 (2)*	C71	0.143 (2)	−0.053 (1)	0.1560 (8)	4.2 (5)
C11	0.075 (2)	0.238 (1)	0.0785 (9)	5.3 (6)	C72	0.129 (2)	−0.042 (1)	0.2148 (9)	5.8 (7)
C12	0.155 (2)	0.224 (1)	0.113 (1)	6.9 (8)*	C73	0.103 (3)	−0.091 (1)	0.254 (1)	8.7 (9)
C13	0.172 (2)	0.277 (1)	0.156 (1)	6.8 (7)	C74	0.090 (2)	−0.159 (2)	0.234 (1)	8.5 (8)
C14	0.112 (2)	0.340 (1)	0.161 (1)	5.9 (7)	C75	0.100 (2)	−0.182 (1)	0.176 (1)	6.5 (7)
C15	0.030 (2)	0.350 (2)	0.128 (1)	9.0 (9)	C76	0.122 (2)	−0.128 (1)	0.135 (1)	6.3 (7)
C16	0.017 (2)	0.301 (1)	0.084 (1)	8.0 (8)	C81	0.256 (2)	−0.011 (1)	0.058 (1)	4.7 (6)
C21	0.129 (2)	0.183 (1)	−0.0332 (9)	4.2 (5)	C82	0.319 (2)	−0.067 (1)	0.071 (1)	7.6 (8)
C22	0.205 (1)	0.234 (1)	−0.026 (1)	5.5 (6)	C83	0.390 (2)	−0.090 (2)	0.034 (1)	10 (1)
C23	0.269 (2)	0.245 (1)	−0.070 (1)	6.7 (7)	C84	0.400 (2)	−0.058 (2)	−0.021 (1)	10.5 (9)
C24	0.255 (2)	0.205 (1)	−0.121 (1)	7.2 (8)	C85	0.341 (2)	0.000 (2)	−0.032 (1)	8.5 (9)
C25	0.192 (2)	0.153 (1)	−0.127 (1)	7.0 (8)	C86	0.268 (2)	0.027 (1)	0.007 (1)	5.9 (7)
C26	0.119 (2)	0.144 (1)	−0.080 (1)	7.1 (8)	Li	−0.015 (4)	−0.098 (3)	−0.255 (2)	9 (1)*

[a] Values marked with an asterisk denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Li(THF)_4][In(PPh_2)_4]$ (**2**)[a]

In–P1	2.585 (2)	P3–C51	1.872 (9)
In–P2	2.576 (2)	P3–C61	1.870 (10)
In–P3	2.586 (3)	P4–C71	1.875 (10)
In–P4	2.556 (3)	P4–C81	1.796 (10)
P1–C11	1.832 (9)	O1–Li	1.97 (2)
P1–C21	1.852 (9)	O2–Li	1.86 (2)
P2–C31	1.838 (9)	O3–Li	1.89 (2)
P2–C41	1.845 (10)	O4–Li	1.93 (2)
P1–In–P2	101.46 (8)	In–P3–C51	104.1 (3)
P1–In–P3	100.78 (9)	In–P3–C61	104.9 (3)
P1–In–P4	111.29 (9)	C51–P3–C61	103.0 (4)
P2–In–P3	111.66 (8)	In–P4–C71	102.4 (3)
P2–In–P4	114.82 (8)	In–P4–C81	104.3 (4)
P3–In–P4	115.05 (8)	C71–P4–C81	104.1 (5)
In–P1–C11	104.2 (3)	O1–Li–O2	111 (1)
In–P1–C21	107.9 (3)	O1–Li–O3	108 (1)
C11–P1–C21	103.2 (5)	O1–Li–O4	107 (1)
In–P2–C31	100.9 (3)	O2–Li–O3	109 (1)
In–P2–C41	104.5 (3)	O2–Li–O4	113 (1)
C31–P2–C41	105.4 (5)	O3–Li–O4	108 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

phosphorus or arsenic ratio is 1:4. Compounds of this type are of interest because GaP, InP, GaAs, and InAs all feature tetrahedrally coordinated structures of the zinc blende type.[4]

We report here the synthesis of the first gallium and indium "ate" complexes of the type $[Li(THF)_4][M(EPh_2)_4]$ (**1**, M = Ga, E = P; **2**, M = In, E = P; **3**, M = Ga, E = As) and the first structural information for perphosphido and perarsenido "ate" complexes of the heavier group 13 elements.[5]

We find that the size of the phosphido or arsenido group is of critical importance. Thus, in the reaction of t-Bu_2ELi (E = P, As) with MCl_3, it is only possible to coordinate a maximum of three t-Bu_2E groups around Ga or In.[2b] On the other hand, the reaction of MCl_3 (M = Ga, In) with Ph_2ELi in 1:3 stoichiometry results in intractable, apparently oligomeric, materials. However, treatment of MCl_3 with Ph_2ELi in 1:4 stoichiometry affords the yellow crystalline "ate" complexes **1**–**3**. All three compounds proved to be suitable for X-ray crystallographic study. The structures of the anions in **1**–**3** are very similar, that of **3** being illustrated in Figure 1. Details of crystal structure parameters for the three compounds and other relevant information are given in Table I. Selected bond lengths and angles for **1** are given in Table II, and positional parameters appear in Table III. Selected bond lengths and angles and positional parameters for **2** are given in Tables IV and V, and those for **3** are presented in Tables VI and VII, respectively.

The solid-state structures of **1**–**3** comprise discrete ions of $[Li(THF)_4]^+$ and $[M(EPh_2)_4]^-$. Complexes **1** and **2** exist as one enantiomer in the space group $P2_12_12_1$ while **3** crystallizes in the centrosymmetric space group $P\bar{1}$ as a racemic mixture. Note also that **3** crystallizes with one disordered molecule of tetrahydrofuran per asymmetric unit. The ME_4 environment around gallium or

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(5) The synthetically useful perphosphido "ate" complexes of aluminum have been known for several years. However, to the best of our knowledge, no structural information is available. See: Finholt, A. E.; Helling, C.; Imhof, V.; Nielsen, L.; Jacobson, E. *Inorg. Chem.* **1963**, *2*, 504. See also: Wingleth, D. C.; Norman, A. D. *Chem. Commun.* **1967**, *1218*. Norman, A. D. *Chem Commun.* **1968**, 812.

Table V. Positional Parameters and Their Estimated Standard Deviations for $[Li(THF)_4][In(PPh_2)_4]$ (**2**)[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
In	0.02784 (9)	0.05475 (6)	0.05945 (5)	3.94 (2)	C31	−0.131 (1)	−0.015 (1)	−0.0367 (7)	4.9 (4)
P1	0.0335 (4)	0.1841 (2)	0.0171 (2)	4.8 (1)	C32	−0.171 (1)	0.055 (1)	−0.0335 (7)	5.5 (4)
P2	−0.007 (4)	−0.0229 (3)	−0.0294 (2)	5.1 (1)	C33	−0.269 (1)	0.066 (1)	−0.0452 (7)	6.0 (5)
P3	−0.1239 (3)	0.0636 (3)	0.1212 (2)	4.8 (1)	C34	−0.328 (1)	0.007 (1)	−0.0611 (9)	7.6 (5)
P4	0.1812 (4)	0.0253 (3)	0.1132 (2)	4.8 (1)	C35	−0.287 (2)	−0.062 (1)	−0.0647 (8)	7.8 (5)
O1	−0.496 (1)	0.1172 (9)	0.1636 (7)	10.6 (5)*	C36	−0.186 (1)	−0.075 (1)	−0.0541 (8)	7.3 (5)
O2	−0.072 (1)	−0.007 (1)	−0.2423 (7)	11.1 (5)*	C41	0.021 (2)	−0.1171 (9)	−0.0060 (7)	6.2 (5)
O3	0.109 (1)	−0.095 (1)	−0.2237 (7)	11.2 (5)*	C42	−0.047 (1)	−0.1576 (9)	0.0230 (7)	6.0 (5)
O4	−0.415 (2)	0.176 (1)	0.2779 (9)	15.6 (7)*	C47	−0.020 (2)	−0.233 (1)	0.0388 (8)	8.1 (6)
C1′	0.178 (3)	−0.150 (2)	−0.222 (2)	21 (2)*	C44	0.077 (2)	−0.255 (1)	0.0217 (9)	11.9 (7)
C1	0.418 (2)	0.160 (2)	0.141 (1)	14 (1)*	C45	0.134 (2)	−0.210 (1)	−0.009 (1)	10.9 (8)
C2	0.439 (2)	0.153 (2)	0.078 (1)	14 (1)*	C46	0.113 (2)	−0.141 (1)	−0.0227 (9)	8.7 (6)
C2′	0.232 (2)	−0.135 (2)	−0.167 (1)	13 (1)*	C51	−0.170 (1)	−0.0318 (9)	0.1239 (7)	5.1 (4)
C3	0.526 (3)	0.110 (2)	0.069 (1)	16 (1)*	C52	−0.252 (1)	−0.046 (1)	0.0922 (7)	5.8 (4)
C3′	0.239 (2)	−0.055 (2)	−0.170 (1)	12.9 (9)*	C53	−0.295 (2)	−0.113 (1)	0.0923 (9)	7.4 (6)
C4	0.586 (3)	0.110 (2)	0.124 (2)	21 (2)*	C54	−0.255 (2)	−0.165 (1)	0.1226 (8)	7.7 (6)
C4′	0.149 (3)	−0.038 (2)	−0.197 (2)	19 (1)*	C55	−0.170 (2)	−0.158 (1)	0.1565 (8)	6.9 (5)
C5′	−0.313 (4)	0.183 (3)	0.279 (2)	30 (3)*	C56	−0.127 (2)	−0.088 (1)	0.1557 (8)	6.8 (5)
C5	−0.116 (3)	0.024 (2)	−0.187 (2)	17 (1)*	C61	−0.079 (1)	0.0788 (9)	0.1945 (8)	5.4 (5)
C6′	−0.652 (4)	−0.227 (3)	0.225 (2)	24 (2)*	C62	−0.012 (1)	0.1350 (9)	0.2018 (7)	6.0 (5)
C6	−0.111 (3)	0.100 (2)	−0.183 (1)	15 (1)*	C63	0.016 (2)	0.155 (1)	0.2555 (8)	7.8 (6)
C7′	−0.634 (3)	−0.238 (2)	0.159 (2)	21 (2)*	C64	−0.021 (2)	0.121 (1)	0.3042 (9)	9.3 (7)
C7	−0.107 (3)	0.123 (2)	−0.243 (1)	16 (1)*	C65	−0.091 (2)	0.066 (1)	0.2953 (9)	11.1 (8)
C8′	0.572 (4)	0.181 (3)	0.339 (2)	24 (2)*	C66	−0.122 (2)	0.049 (1)	0.2400 (7)	8.3 (6)
C8	−0.088 (2)	0.058 (2)	−0.274 (1)	13.4 (9)*	C71	0.144 (1)	−0.054 (1)	0.1578 (6)	4.6 (4)
C11	0.078 (1)	0.2410 (9)	0.0749 (7)	5.6 (5)	C72	0.134 (1)	−0.040 (1)	0.2165 (7)	6.5 (5)
C12	0.154 (1)	0.229 (1)	0.1094 (9)	7.1 (5)	C73	0.101 (2)	−0.090 (1)	0.2536 (9)	7.9 (6)
C13	0.174 (2)	0.277 (1)	0.1543 (8)	8.1 (6)	C74	0.089 (2)	−0.160 (1)	0.2340 (9)	8.7 (6)
C14	0.117 (2)	0.338 (1)	0.1645 (9)	8.5 (6)	C75	0.097 (2)	−0.179 (1)	0.1771 (8)	7.1 (6)
C15	0.044 (2)	0.350 (1)	0.1319 (9)	7.9 (6)	C76	0.127 (1)	−0.124 (1)	0.1383 (8)	6.6 (5)
C16	0.020 (1)	0.306 (1)	0.0831 (8)	7.1 (5)	C81	0.258 (1)	−0.0138 (9)	0.0608 (9)	6.0 (4)
C21	0.132 (1)	0.1869 (8)	−0.0349 (8)	5.1 (4)	C82	0.319 (1)	−0.0749 (9)	0.0693 (8)	6.8 (5)
C22	0.210 (1)	0.237 (1)	−0.0282 (9)	6.5 (5)	C83	0.388 (2)	−0.095 (1)	0.029 (1)	9.9 (7)
C23	0.273 (1)	0.241 (1)	−0.0744 (9)	6.6 (5)	C84	0.391 (2)	−0.061 (1)	−0.026 (1)	9.6 (7)
C24	0.263 (2)	0.198 (1)	−0.1227 (8)	7.3 (6)	C85	0.336 (1)	0.003 (1)	−0.0352 (8)	7.9 (6)
C25	0.188 (2)	0.150 (1)	−0.1280 (9)	7.2 (6)	C86	0.268 (1)	0.026 (1)	0.0078 (9)	6.7 (5)
C26	0.117 (2)	0.144 (1)	−0.0825 (8)	6.7 (5)	Li	−0.485 (3)	0.096 (2)	0.245 (1)	8 (1)

[a] See footnote *a* of Table III.

Table VI. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Li(THF)_4][Ga(AsPh_2)_4]$ (**3**)[a]

As1–Ga	2.520 (4)	As3–C61	1.98 (2)
As1–C11	1.98 (2)	As4–Ga	2.490 (3)
As1–C21	1.92 (2)	As4–C71	1.93 (2)
As2–Ga	2.486 (3)	As4–C81	1.96 (2)
As2–C31	1.99 (2)	O1–Li	1.88 (5)
As2–C41	1.98 (2)	O2–Li	1.93 (54)
As3–Ga	2.493 (3)	O3–Li	1.92 (5)
As3–C51	1.93 (2)	O4–Li	1.95 (5)

Ga–As1–C11	106.7 (6)	As1–Ga–As2	113.4 (1)
Ga–As1–C21	105.4 (7)	As1–Ga–As3	97.3 (1)
C11–As1–C21	101.4 (8)	As1–Ga–As1	97.8 (1)
Ga–As2–C31	99.6 (6)	As2–Ga–As3	116.0 (1)
Ga–As2–C41	103.1 (6)	As2–Ga–As4	114.8 (1)
C31–As2–C41	102.6 (9)	As3–Ga–As4	114.6 (1)
Ga–As3–C51	104.8 (6)	O1–Li–O3	108 (2)
Ga–As3–C61	102.0 (5)	O1–Li–O4	111 (2)
C51–As3–C61	102.5 (9)	O3–Li–O4	104 (3)
Ga–As4–C71	102.4 (5)	O2–Li–O4	109 (2)
Ga–As4–C81	102.9 (6)	O2–Li–O3	112 (2)
C71–As4–C81	101.7 (9)	O1–Li–O2	113 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

indium is approximately tetrahedral; the E–M–E angles range from 99.7 (2) to 115.5 (2)° in **1**, from 100.78 (9) to 115.05 (8)° in **2**, and from 97.3 (1) to 116.0 (1)° in **3**. All the phosphido or arsenido groups of **1**–**3** possess pyramidal geometries. The average C–P–C angles of the phosphido groups are 105.4 (10) and 104.1 (5)° in **1** and **2**, respectively. As expected, the arsenido groups of **3** are slightly more pyramidal, the average C–As–C angle being 102.0 (9)°. No symmetry is apparent in the arrangement of EPh_2 moieties around Ga or In, although for each anion three of the four EPh_2 groups are related approximately by a C_3 axis. The structures of the $[M(EPh_2)_4]^-$ anions are thus quite different from those of neutral tetraphosphido[6] and tetraamido[7] transition-metal derivatives, which exhibit D_{2d} skeletal symmetry. The average M–P distances of 2.409 (7) and 2.576 (3) Å in **1** and **2**, respectively, are larger than those in gallium phosphide (2.360 Å) or indium phosphide (2.541 Å)[4] but shorter than those in the phosphido-bridged species $[t\text{-}Bu_2PMMe_2]_2$ (M = Ga, 2.474 (5) Å; M = In, 2.656 (4) Å).[2b,3] The average Ga–As bond length of 2.497 (4) Å in **3** is very similar to that in $[(mes)_2As]_3Ga$ (2.492 (1) Å,[2d] mes = mesityl) but somewhat longer than that in gallium arsenide (2.448 Å).[4] In summary, the M–E bond lengths, EPh_2 geometries, and $M(EC_2)_4$ conformations are indicative of M–E single bonding in each case.

The ^{71}Ga NMR chemical shifts for **1** and **3** are similar (δ 226 and 206, respectively). The peak widths at half-height for both anions are quite large (~3500 Hz); hence, it is not possible to discern phosphorus coupling in the case of **1**. The broadness of the ^{71}Ga signals is presumably a consequence of the overall C_1 symmetry at gallium. The ^{31}P NMR chemical shifts of **1** (−33.4 ppm) and **2** (−30.2 ppm) are in the region anticipated for terminal phosphido groups behaving as one-electron donors[6] and are similar to that of Ph_2PLi (−38.5 ppm, 0.5 M, THF).

Experimental Section

All operations were performed under oxygen-free argon or under vacuum. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen. Toluene was distilled

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Table VII. Positional Parameters and Their Estimated Standard Deviations for $[Li(THF)_4][Ga(AsPh_2)_4]$ (**3**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
As1	0.2994 (2)	0.1228 (2)	0.1506 (1)	5.06 (6)	C34	0.007 (2)	0.486 (2)	0.370 (2)	13 (1)
As2	0.3258 (2)	0.4163 (2)	0.2001 (1)	5.47 (6)	C35	0.024 (2)	0.395 (2)	0.329 (2)	11 (1)
As3	0.2903 (2)	0.1725 (2)	0.3455 (1)	5.37 (6)	C36	0.120 (2)	0.374 (2)	0.281 (1)	7.9 (7)
As4	0.5583 (2)	0.1750 (2)	0.1780 (1)	5.16 (6)	C41	0.422 (2)	0.482 (2)	0.243 (1)	5.7 (6)
Ga	0.3717 (2)	0.2364 (2)	0.2232 (1)	4.46 (6)	C42	0.507 (2)	0.521 (2)	0.191 (1)	7.4 (7)
O1	0.097 (1)	0.193 (1)	0.709 (1)	11.3 (6)*	C43	0.575 (2)	0.567 (2)	0.223 (1)	7.3 (7)
O2	0.114 (1)	0.806 (1)	0.171 (1)	10.8 (6)*	C44	0.567 (2)	0.573 (2)	0.297 (1)	8.8 (8)
O3	0.107 (2)	0.128 (2)	0.863 (1)	11.6 (6)*	C45	0.481 (2)	0.533 (2)	0.344 (1)	7.6 (7)
O4	0.043 (2)	0.348 (2)	0.836 (1)	12.4 (6)*	C46	0.412 (2)	0.482 (2)	0.316 (1)	7.0 (7)
O91	0.180 (3)	0.837 (3)	0.433 (2)	23 (1)*	C51	0.320 (1)	0.263 (2)	0.412 (1)	5.3 (6)
C1	0.060 (3)	0.146 (3)	0.655 (2)	17 (1)*	C52	0.237 (2)	0.333 (2)	0.445 (1)	8.3 (8)
C1′	0.132 (3)	0.144 (3)	0.930 (2)	15 (1)*	C53	0.258 (2)	0.404 (2)	0.495 (1)	10.1 (9)
C2′	0.161 (3)	0.045 (3)	0.960 (2)	19 (2)*	C54	0.355 (2)	0.399 (2)	0.511 (1)	8.9 (8)
C2	0.151 (3)	0.127 (3)	0.592 (2)	16 (1)*	C55	0.435 (2)	0.328 (2)	0.479 (1)	7.7 (8)
C3	0.234 (3)	0.162 (3)	0.609 (2)	16 (1)*	C56	0.416 (2)	0.259 (2)	0.429 (1)	5.4 (6)
C3′	0.171 (3)	−0.027 (3)	0.908 (2)	15 (1)*	C61	0.385 (1)	0.051 (1)	0.354 (1)	4.9 (5)
C4′	0.138 (4)	0.029 (4)	0.848 (3)	21 (2)*	C62	0.398 (2)	0.025 (2)	0.424 (1)	6.4 (6)
C4	0.203 (3)	0.224 (3)	0.675 (2)	19 (2)*	C63	0.459 (2)	−0.068 (2)	0.431 (1)	7.6 (7)
C5	−0.166 (3)	0.143 (3)	0.897 (2)	18 (2)*	C64	0.494 (2)	−0.131 (2)	0.372 (1)	7.6 (7)
C5′	−0.046 (4)	0.419 (4)	0.866 (3)	21 (2)*	C65	0.476 (2)	−0.104 (2)	0.303 (1)	7.7 (7)
C6′	−0.011 (4)	0.502 (4)	0.891 (3)	20 (2)*	C66	0.420 (2)	−0.011 (2)	0.295 (1)	6.1 (6)
C6	−0.272 (3)	0.166 (3)	0.890 (2)	13 (1)*	C71	0.615 (1)	0.200 (2)	0.259 (1)	5.4 (6)
C7	−0.287 (3)	0.212 (3)	0.827 (2)	15 (1)*	C72	0.645 (2)	0.119 (2)	0.298 (1)	7.2 (7)
C7′	0.092 (4)	0.500 (4)	0.847 (2)	21 (2)*	C73	0.685 (2)	0.130 (2)	0.359 (1)	7.9 (7)
C8	−0.186 (4)	0.218 (4)	0.782 (3)	21 (2)*	C74	0.706 (2)	0.223 (2)	0.377 (1)	10.1 (9)
C8′	0.120 (4)	0.411 (4)	0.802 (3)	22 (2)*	C75	0.682 (2)	0.307 (2)	0.337 (1)	8.7 (8)
C11	0.148 (1)	0.158 (1)	0.175 (1)	4.8 (5)	C76	0.632 (1)	0.297 (2)	0.277 (1)	5.7 (6)
C12	0.096 (1)	0.201 (2)	0.124 (1)	6.0 (6)	C81	0.609 (1)	0.280 (2)	0.109 (1)	5.1 (6)
C13	−0.017 (2)	0.220 (2)	0.146 (1)	7.6 (7)	C82	0.552 (2)	0.315 (2)	0.060 (1)	5.9 (6)
C14	−0.068 (2)	0.193 (2)	0.214 (1)	8.8 (8)	C83	0.592 (2)	0.385 (2)	0.006 (1)	7.0 (7)
C15	−0.014 (2)	0.147 (2)	0.263 (1)	7.5 (7)	C84	0.687 (2)	0.416 (2)	0.001 (1)	7.0 (7)
C16	0.097 (2)	0.125 (2)	0.243 (1)	7.3 (7)	C85	0.745 (2)	0.382 (2)	0.047 (1)	8.5 (8)
C21	0.336 (1)	0.171 (2)	0.052 (1)	5.6 (6)	C86	0.709 (2)	0.312 (2)	0.103 (1)	7.3 (7)
C22	0.395 (2)	0.103 (2)	0.003 (1)	6.6 (7)	C91	0.101 (3)	0.762 (3)	0.502 (2)	14 (1)*
C23	0.433 (2)	0.131 (2)	−0.071 (1)	8.7 (8)	C93	0.026 (4)	0.820 (4)	0.535 (3)	9 (2)*
C24	0.417 (2)	0.230 (2)	−0.094 (1)	8.0 (7)	C94	0.028 (6)	0.915 (6)	0.514 (4)	17 (3)*
C25	0.356 (2)	0.298 (2)	−0.044 (1)	6.0 (6)	C95	0.107 (5)	0.939 (5)	0.451 (4)	13 (2)*
C26	0.316 (1)	0.270 (2)	0.029 (1)	5.9 (6)	C96	0.162 (5)	0.694 (5)	0.489 (4)	12 (2)*
C31	0.193 (2)	0.440 (1)	0.274 (1)	6.8 (6)	C97	0.254 (4)	0.700 (4)	0.444 (3)	12 (2)*
C32	0.176 (2)	0.531 (2)	0.312 (1)	9.1 (8)	C98	0.253 (4)	0.746 (4)	0.410 (3)	9 (2)*
C33	0.077 (2)	0.554 (2)	0.361 (2)	14 (1)	Li	0.031 (3)	0.214 (3)	0.807 (2)	8 (1)*

[a] See footnote *a* of Table III.

from sodium under nitrogen. Instruments: IR, Perkin Elmer 1330, Digilab FTS-40; NMR, GE QE 300 (^{1}H, 300 MHz). IR spectra were recorded as KBr pellets. NMR spectra were recorded in THF at ambient temperature and are in ppm referenced to Me_4Si (δ 0.0; ^{1}H, ^{13}C), 85% H_3PO_4(aq) (δ 0.0; ^{31}P), and 1.3 M $Ga(NO_3)_3$ in D_2O (δ 0.0; ^{71}Ga). Melting points were measured in sealed capillaries under argon (1 atm) and are uncorrected. $LiPPh_2$ and $LiAsPh_2$ were prepared from PPh_3 and $AsPh_3$, respectively, by the literature methods.[8] PPh_3 and $AsPh_3$ were purchased from Alfa and were used as received. $GaCl_3$ and $InCl_3$ were purchased from Johnson Matthey, Inc., and were used as received.

Synthesis of Compounds 1–3. A similar procedure was used for the preparation of all three compounds. A typical procedure for the preparation of **2** is described below.

$[Li(THF)_4][In(PPh_2)_4]$ (2). A solution of $LiPPh_2$ (51.5 mL of a 0.37 M solution in THF, 18.5 mmol) was added dropwise to a solution of $InCl_3$ (1.03 g, 4.6 mmol) in THF (50 mL) at −78 °C. The resulting vivid orange solution was warmed slowly to room temperature and stirred magnetically for 12 h. Volatile materials were removed under vacuum until the total volume of the solution was ca. 30 mL. Toluene (60 mL) was added, the solution filtered, and the filtrate cooled (−20 °C) to give yellow-orange crystals of **2**. The supernatant liquid was decanted from the crystals, which were dried under a stream of argon.

1: yield 75%; mp 159–165 °C dec; IR 3044 w, 1576 m, 1473 m, 1430 m, 1378 m, 1044 m, 1027 m, 890 m, 734 m, 695 m cm^{-1}; ^{1}H NMR (300 MHz) δ 7.00 m, 6.84 m, 6.76 m (P*Ph*); ^{13}C{^{1}H} NMR (75.466 MHz) δ 144.73 br s, 135.20 s, 127.33 s, 124.40 s (P*Ph*); ^{31}P{^{1}H} NMR (121.482 MHz) δ −33.4. ^{71}Ga NMR (91.519 MHz) δ 226.

2: yield 82%; mp 110–115 °C dec; IR 3044 w, 1577 m, 1473 m, 1430 m, 1379 m, 1043 m, 1028 m, 890 m, 735 m, 694 m cm^{-1}; ^{1}H NMR δ 144.46 br s, 134.97 s, 127.31 s, 124.10 s; ^{31}P{^{1}H} NMR δ −30.2.

3: yield 70%; mp 167–170 °C dec; IR 3043 w, 1578 m, 1478 m, 1429 m, 1378 m, 1045 m, 1022 m, 891 s, 732 m, 995 m cm^{-1}; ^{1}H NMR δ 7.05 m, 6.85 m, 6.76 m (P*Ph*); ^{13}C{^{1}H} NMR δ 144.36 br s, 1366.2 s, 127.24 s, 124.70 s; ^{71}Ga NMR δ 206.

Satisfactory elemental analyses (C,H) were obtained for all three compounds.

X-ray Crystallography. Data were collected on an Enraf-Nonius CAD-4 diffractometer at 23 ± 2 °C using graphite-monochromated Mo Kα radiation. All calculations were performed on a PDP 11/44 computer using the Enraf-Nonius software package SDP-PLUS.[9] For each structure the data were corrected for Lorentz, polarization, and decay effects. Empirical absorption corrections (program EAC) were also applied. The structures were solved by the use of Patterson maps, which revealed the location of the Ga or In and P or As atoms. Successive cycles of difference Fourier maps and full-matrix least-squares refinements gave the final R and R_W values shown in Table I. Suitable crystals of all three compounds were grown from THF/toluene solutions at −20 °C and mounted in thin-walled glass capillaries under an argon atmosphere saturated with solvent.

The unit cell parameters for **1** were obtained by centering 25 reflections having 2θ values between 28 and 30°. The orthorhombic space group $P2_12_12_1$ (No. 19) was uniquely determined by the following systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$. Data were collected in the hkl octant between 2θ values of 3.0 and 44.0°. The Ga and P atoms were refined anisotropically as were the carbon atoms of the phenyl rings. The Li atom and atoms of the THF molecules were refinred isotropically, except for C(11). Hydrogen atoms were not located, but their contributions were included in the refinements.[10] Data with intensities less than $3\sigma(I)$ and $((\sin\theta)/\lambda)$ less than 0.10 were ex-

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(8) See, for example: Levason, W.; Smith, K. G.; McAuliffe, C. A.; McCullough, F. P.; Sedgwick, R. D.; Murray, S. G. *J. Chem. Soc., Dalton Trans.* **1979**, 1718 and references therein.

(9) *SDP-PLUS*, 4th ed.; B. A. Frenz and Associates: College Station, TX, 1981.

cluded, and a non-Poisson-contribution weighting scheme with an instability factor of $P = 0.08$ was used in the final stages of refinement. The maximum peak in the final difference Fourier had a height of 0.397 e Å^{-3}.

The space group of **2** was determined as for **1**. Data were collected in the *hkl* octant between 2θ values of 3.0 and 44.0°. The In, Li, and P atoms were refined anisotropically as were the carbon atoms of the phenyl rings. The atoms of the THF molecules were refined isotropically. Hydrogen atoms were not located, but their contributions were included in the refinements.[10] Data with intensities less than $3\sigma(I)$ and $(\sin\theta)/\lambda$ less than 0.10 were excluded, and a non-Poisson-contribution weighting scheme with $P = 0.08$ was used. The maximum peak in the final difference Fourier had a height of 0.462 e Å^{-3}.

The unit cell parameters for **3** were determined from 25 reflections with 2θ values between 28 and 30°. The triclinic space group $P\bar{1}$ (No. 2) was chosen on the basis of successful refinement of the structure. A hemisphere of data was collected between 2θ values of 3.0 and 44.0°. There was a severe decay in the crystal during the course of data collection. However, this does not appear to have adversely affected the structure. The Ga, As, and C atoms of the phenyl rings were refined anisotropically. The atoms of the THF molecules and Li were refined isotropically. There was a disordered THF molecule also found in the structure that was not bound to Li. The atoms of this unit (O(91) and C(91)–C(98)) were refined isotropically. Hydrogen atoms were not located, but their contributions were included in the refinement.[10] A non-Poisson contribution to the weighting scheme was employed ($P = 0.06$). The maximum peak in the final difference Fourier had a height of 0.505 e Å^{-3}.

Supplementary material for **1–3** is available.[11] Scattering factors were taken from ref 12.

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Registry No. 1, 114860-65-0; **2**, 114860-67-2; **3**·THF, 114860-70-7.

Supplementary Material Available: Tables of bond lengths, bond angles, positional parameters, and thermal parameters for **1–3** (23 pages); tables of observed and calculated structure factors for **1–3** (38 pages). Ordering information is given on any current masthead page.

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(10) *P* is used in the calculation of $\sigma(I)$ to downweight intense reflections in the leasth-squares refinement. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 4(|F_o|)^2/[\sum(|F_o|)^2]^2$, $[\sum(|F_o|)^2]^2 = [S^2(C + R^2B) + (P(|F_o|)^2)^2]/Lp^2$, S^2 is the scan rate squared, *C* is the total background count, R^2 is the ratio of scan time to background count squared, and L_p is the Lorentz–polarization factor.

(11) See paragraph at the end of the paper regarding supplementary material.

(12) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Contribution from Rocketdyne, A Division of Rockwell
International, Canoga Park, California 91303

Synthesis and Properties of $XeO_2F^+AsF_6^-$ and $[FO_2XeFXeO_2F]^+AsF_6^-$

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The new compound $XeO_2F^+AsF_6^-$ was prepared from XeO_2F_2 and an excess of AsF_5 with anhydrous HF as a solvent. The compound is a white solid having a dissociation pressure of 7 Torr at 23 °C. On pumping or exposure to a laser beam, it loses AsF_5 and is converted into $[FO_2XeFXeO_2F]^+AsF_6^-$, which was also obtained by the direct combination of XeO_2F_2 with AsF_5 in a 2:1 mole ratio in HF. Both XeO_2F_2 adducts were characterized by Raman spectroscopy. By analogy with the closely related $XeF^+MF_6^-$ and $[FXeFXeF]^+MF_6^-$ salts, $XeO_2F^+AsF_6^-$ exhibits $FO_2Xe\cdots FAsF_5$ bridging and distortion of the AsF_6^- anion, whereas the anion–cation interaction in $[FO_2XeFXeO_2F]^+AsF_6^-$ appears to be minimal.

Introduction

Relatively little is known about the fluoride ion donor properties of XeO_2F_2. To our knowledge, the only previous publications in this area are those by Schrobilgen and co-workers. In 1972, they reported the synthesis of a yellow solid having the composition $XeO_2F_2 \cdot 1.8SbF_5$ by adding SbF_5 to an HF solution of XeO_2F_2. The solid dissolved in SbF_5 to give a yellow-green solution that slowly evolved oxygen. Cooling to 5 °C caused the gas evolution to cease and caused the color of the solution to intensify to a dark green.[1]

In a subsequent paper on the ^{19}F NMR spectrum of XeO_2F^+, it was stated that pure $XeO_2F^+Sb_2F_{11}^-$ is white and that the yellow color was due to its decomposition product $XeF^+Sb_2F_{11}^-$.[2] The Raman spectrum of solid $XeO_2F^+Sb_2F_{11}^-$ was also published;[3] however, of the six fundamental vibrations expected for an XeO_2F^+ cation of symmetry C_s, only four were observed. Furthermore, the complexity of the $Sb_2F_{11}^-$ part of the spectrum did not allow any conclusions about the extent of fluorine bridging and anion distortion frequently encountered with ionic xenon fluoride adducts. Finally, the synthesis of $XeO_2F^+SbF_6^-$ from SbF_5 and a 2-fold excess of XeO_2F_2 in HF solution was briefly mentioned in a paper on ^{129}Xe NMR spectroscopy, but no properties of the salt were given except for its NMR data.[4] In view of the paucity of data available for XeO_2F^+, the convenient XeO_2F_2 synthesis recently discovered by us,[5] and the reluctance of AsF_5 to form stable polyanions, a study of the adduct formation between XeO_2F_2 and AsF_5 was undertaken, the results of which are reported in this paper.

Experimental Section

Materials. Commercial AsF_5 (Ozark Mahoning) was of good quality and was used without further purification after removal of any material noncondensable at −196 °C. Hydrogen fluoride (Matheson) was dried by storage over BiF_5.[6] The synthesis of XeO_2F_2 is described elsewhere.[5]

Caution! The hydrolysis of XeO_2F_2 produces highly explosive XeO_3.

Apparatus. Volatile materials used in this work were handled in a well-passivated (with ClF_3) stainless-steel Teflon–FEP vacuum line.[7] Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox. Reactions were carried out in either 0.5 in. o.d. sapphire (Tyco) or Teflon–FEP tubes closed by either stainless-steel or Teflon–PFA (Fluoroware Inc.) valves. Raman spectra were recorded on either a Spex Model 1403 or a Cary Model 83 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser or the 488-nm exciting line of an Ar ion laser, respectively. Sealed melting point capillaries or the sapphire reactors were used as sample containers in the transverse-view-

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(1) Gillespie, R. J.; Landa, B.; Schrobilgen, G. J. *J. Chem. Soc., Chem. Commun.* **1972**, 607.

(2) Gillespie, R. J.; Schrobilgen, G. J. *Inorg. Chem.* **1974**, *13*, 2370.

(3) Gillespie, R. J.; Landa, B.; Schrobilgen, G. J. *Inorg. Chem.* **1976**, *15*, 1256.

(4) Schrobilgen, G. J.; Holloway, J. H.; Granger, P.; Brevard, C. *Inorg. Chem.* **1978**, *17*, 980.

(5) Christe, K. O.; Wilson, W. W., to be submitted for publication.

(6) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(7) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

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