

591. *Trimethylgallium. Part V.¹ The Reactions of Trimethylaluminium, -gallium, and -indium with Some Primary and Secondary Phosphines and Arsines*

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The reactions of trimethyl-aluminium, -gallium, and -indium with dimethyl- and diethyl-phosphine and dimethylarsine have given compounds, exemplified by $(\text{Me}_2\text{Ga-PMe}_2)_x$, which are polymeric glasses in the condensed state at room temperature but cyclic trimers in benzene solution. Many of these products can be sublimed at low pressure without decomposition. Their n.m.r. spectra are consistent with a rapid inversion of a six-membered ring at 25°. This motion is considerably slower at -90° as shown by the broadened peaks. Phenylphosphine and methyl- and phenyl-arsine give only nonvolatile polymers, exemplified by $(\text{MeAl-AsMe})_x$.

IN Part III² of this series, the reactions of trimethylaluminium, trimethylgallium, and trimethylindium with diphenyl-phosphine and -arsine were described. Dimeric products of the type $(\text{Me}_2\text{Ga-PPh}_2)_2$ were obtained. The temperature at which the formation of

¹ Part IV, G. E. Coates and R. N. Mukherjee, *J.*, 1964, 1295.

² G. E. Coates and J. Graham, *J.*, 1963, 233.

(Me₂Ga-PPh₂)₂ takes place at a preparatively useful rate, 90—110°, is lower than the temperature of the corresponding reaction of trimethylaluminium, 140—160°. Therefore, since trimethylaluminium reacts with dimethylphosphine³ at 200—210° to yield methane and (Me₂Al-PMe₂)_x, trimethylgallium should react below 200°. The complex, Me₃Ga·PMe₂H, initially found to give a brown, tarry material⁴ at 240°, is now found to react at 150—155°, eliminating methane and quantitatively forming (Me₂Ga-PMe₂)_x after 19 hours' reaction time at higher pressures of reactants. The dimethyl- and diethylphosphino- and the dimethylarsino-derivatives of dimethyl-aluminium, -gallium, and -indium significantly extend the range of compounds of the type, (R₂M-DR'₂)_n, (M = Group III element, D = Group V donor). The factors affecting the degree of association, n, of these Group III-V organometallic compounds are not entirely clear, and are considered below in relation to the wider range of compounds on which data are now available.

The conditions of formation and some physical properties of the dialkyl compounds prepared in this investigation are listed in Table I. The order of reactivity is N < P < As

TABLE I

Reactions of dialkyl-phosphines and -arsines

Compound	Temp. of formation	Duration of pyrolysis (hr.)	Mole CH ₄ per mole Me ₃ M	Degree of association in solution	"Melting" point	Sublimation temp.
Me ₂ Al-PMe ₂	200—215°	12	0.933	3	238—244°	100—110°
Me ₂ Al-PEt ₂	200—215	35	0.723	3	—	120—130
		48	0.830			
Me ₂ Al-AsMe ₂	200—215	24	0.965	3	—	100—110
Me ₂ Ga-PMe ₂	150—155	19	1.01	3	265—267 ^a	100—110
Me ₂ Ga-PEt ₂	150—160	22	0.714	3	—	120—130
	165—175	28	0.764			
Me ₂ Ga-AsMe ₂ ...	30—50	5	1.01	3	199—201 ^a	100—110
Me ₂ In-PMe ₂	25—40	3	0.985	3	115—120 ^a	^c
Me ₂ In-PEt ₂	25—40	5	0.987	3	100—104 ^b	^c
Me ₂ In-AsMe ₂	15—25	1	0.957	3	84 ^a	^c

^a Decomposition occurred during melting. ^b Decomposition occurred at about 25° above the "melting point." ^c Sample could not be sublimed because of decomposition.

for trimethylgallium and trimethylindium but the reverse order was observed for trimethylaluminium, the order thus being identical for methyl and phenyl Group v derivatives, R₂DH. Diethylphosphine is less reactive than dimethylphosphine. All the products are glasses at room temperature as shown by Cu-K_α X-ray powder patterns and microscopic examination with polarized light. Cryoscopic molecular weight measurements in benzene show that only trimeric species, for example, (Me₂Ga-PMe₂)₃, are present in solution.

The amorphous or glassy nature of these compounds at room temperature is probably due to the presence of polymers, or solutions of trimers, tetramers, etc., in polymers (which could be cyclic polymers) in the condensed state. Heating of these polymers results in their dissociation into trimers as shown by the vapour-density molecular weight³ of (Me₂Al-PMe₂)₃ at 210—218°. The observation that all the methyl compounds sublime at 100—110° and the ethyl compounds at 120—130° (both at *ca.* 0.01 mm.) might be consistent with the dissociation of the polymers at these temperatures into the volatile trimeric species. Condensation of these trimeric species above the hot zone results in polymerization and consequent formation of glassy material. In comparison, the vapour pressure⁵ of the crystalline compound, (H₂B-PMe₂)₃, is 6.8 mm. at 100°.

The dissolution of these glassy materials in benzene results in dissociation into trimeric

³ N. Davidson and H. C. Brown, *J. Amer. Chem. Soc.*, 1942, **64**, 316.

⁴ G. E. Coates and R. G. Hayter, *J.*, 1953, 2519.

⁵ A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

species, as shown by cryoscopic molecular weight measurements, and evidence for the cyclic nature of the trimeric species in solution was obtained by proton n.m.r. spectroscopy. As a typical example, the spectrum of $(\text{Me}_2\text{Ga}-\text{AsMe}_2)_3$ has only two very sharp peaks of equal intensity with a width at half height of one cycle sec^{-1} , corresponding to the gallium and arsenic methyl groups. Using tetramethylsilane as an internal standard one peak has a τ value of 9.177 p.p.m. and the other coincides with that of the tetramethylsilane. Cooling of the solution to -90° broadens the methyl resonances to a width at half height of 10 c./ sec^{-1} , whereas the tetramethylsilane resonance remains unchanged. These observations are consistent with the rapid inversion at room temperature between the two chair forms of the six-membered ring in which the axial and equatorial methyl groups are magnetically equivalent. At -90° , the low temperature limit of the apparatus, the ring inversion is considerably slower and a broadened resonance is observed. It was not possible to reduce the frequency of inversion to a stage at which it was possible to observe two magnetically non-equivalent axial and equatorial methyl groups. Very similar observations have been made about the n.m.r. spectra of methyl-substituted cyclohexanes ⁶ at -110° . The n.m.r. spectrum ⁷ of the trimer, $(\text{H}_2\text{Al}-\text{NMe}_2)_3$, also has only two resonances, corresponding to the aluminium hydrogen and the aminomethyl groups.

Since there can be no doubt concerning the glassy nature of these compounds, it was surprising to observe an effect which had very much the appearance of melting when the compounds were sealed in melting point tubes and subjected to the usual procedure for determining the melting point of an organic compound. For example the phosphino-aluminium compound, $(\text{Me}_2\text{Al}-\text{PMe}_2)_x$, had the appearance of a solid up to 238° and apparently melted without decomposition over the range $238-244^\circ$. In other words, over this temperature range the viscosity of the material appeared to decrease from the high values appropriate to a glass to the low values appropriate to a normal liquid. The phosphino-indium compound, $(\text{Me}_2\text{In}-\text{PEt}_2)_x$, similarly "melted" over the range $100-104^\circ$, and decomposition was observed in the range $125-130^\circ$. Several of the other compounds "melted" though with apparent decomposition over the temperature ranges

TABLE 2
Reactions of monosubstituted phosphines and arsines

Reactants	Reaction temp. ($^\circ\text{C}$)	Reaction time (hr.)	Mole CH_4 per g-atom of metal	g-Atom P(As) ^a per g-atom metal	Colour of product
$\text{Me}_3\text{Al}, \text{MeAsH}_2$	200—210	48	1.97	0.90	Yellow
$\text{Me}_3\text{Ga}, \text{PhPH}_2$	60—160	18	1.94	1.00	Colourless ^b
$\text{Me}_3\text{Ga}, \text{PhAsH}_2$	35—100	15	1.79	1.00	Yellow
$\text{Me}_3\text{Ga}, \text{MeAsH}_2$	95—100	13	1.43	0.933	Light yellow
"	0—200	19	1.41	0.925	Yellow-orange
"	0—25	960	1.43	1.00	Colourless
$\text{Me}_3\text{In}, \text{PhPH}_2$	0—140	18	1.91	0.993	Yellow-orange
$\text{Me}_3\text{In}, \text{PhAsH}_2$	0—100	12	2.02	0.986	Red-orange
$\text{Me}_3\text{In}, \text{MeAsH}_2$	0—130	339	1.86	0.968	Red-orange

^a In the reaction product. ^b The product was yellow between 200 and 280° , and became colourless when cooled below 200° .

indicated in Table 1. Similar relatively sharp "melting" points of glasses have also been observed for the dimethylamino-derivatives of dimethyl-aluminium, -gallium, and -indium.⁸

The reactions of Group V donor compounds containing two active hydrogens, phenylphosphine and phenyl- and methyl-arsine, are summarized in Table 2. Trimethyl-aluminium and trimethylindium react completely eliminating two moles of methane and

⁶ N. Muller and W. C. Tosch, *J. Chem. Phys.*, 1962, **37**, 1167.

⁷ J. K. Ruff and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1960, **82**, 2141.

⁸ O. T. Beachley and G. E. Coates, following Paper.

TABLE 3
Infrared spectra ^a

$\text{Me}_2\text{Al-PMe}_2$	$\text{Me}_2\text{Al-PEt}_2$	$\text{Me}_2\text{Al-AsMe}_2$	$\text{Me}_2\text{Ga-PMe}_2$	$\text{Me}_2\text{Ga-PEt}_2$	$\text{Me}_2\text{Ga-AsMe}_2$	$\text{Me}_2\text{In-PMe}_2$	$\text{Me}_2\text{In-PEt}_2$	$\text{Me}_2\text{In-AsMe}_2$	Assignment
1420m	—	1420m	1425m	—	1420m	1425m	—	1420m	D-CH ₃ , δ asym.
—	1418m	—	—	1421m	—	—	1418m	—	CH ₂ scissor *
1298w	—	1260w	1295w	—	1259w	1299w	—	1252w	D-CH ₃ , δ sym.
1282w	—	1247w	1281w	—	1248w	1278w	—	1245w	D-CH ₃ , δ sym.
—	1263vw	—	—	1262vw	—	—	1261w	—	CH ₂ wag *
—	1242w	—	—	1241w	—	—	1242w	—	M-CH ₃ , δ sym.
1179m	1179m	1182m	1181m	1181m	1181m	1150m	1149m	1146m	P-CH ₂ rock
—	1042m	—	—	1041m	—	—	1040m	—	P-CH ₂ rock
—	1028m	—	—	1029m	—	—	1028m	—	C-CH ₃ rock
—	1010w	—	—	1000w	—	—	995w	—	C-C stretch
—	974w	—	—	974w	—	—	972w	—	D-CH ₃ rock
946s	—	897m	941s	—	896s	946s	—	897s	D-CH ₃ rock
910s	—	864m	904s	—	860s	905s	—	862s	D-CH ₃ rock
723s	—	—	—	753m	—	720s	754m	—	P-C stretch
—	738m	—	—	—	—	—	738m	—	P-C stretch
666vs, br	667vs, br	668vs, br	740m	741m	743s	684vs	683vs	685vs	M-CH ₃ rock
—	—	—	716s	718s	721vs	—	—	—	M-CH ₃ rock
—	—	—	—	—	590m	—	—	584m	As-CH ₃ stretch
—	—	574m	—	—	574m	—	—	569m	As-CH ₃ stretch
—	—	—	553m	547m	557s	493s	484m	492s	M-CH ₃ stretch
557m	555m	554m	518m	516m	518s	467s	463m	462s	M-CH ₃ stretch

^a All spectra were observed as Nujol solutions, frequencies in cm^{-1} .
vw, very weak; w, weak; m, medium; s, strong; vs, very strong; br, broad. * Questionable assignments.

forming coloured involatile polymeric material. The reaction of trimethylgallium with methylarsine, however, gives only 1.43 moles of methane per mole of trimethylgallium. The remaining 0.57 mole of methane, expected on the basis of the reactions of trimethylaluminium and -indium, was not formed, even at 200°. Some permanent gas, such as hydrogen, and a small amount of benzene and trimethylgallium were also observed as pyrolysis products of the phenyl-phosphine and -arsine reactions. Infrared absorptions corresponding to P-H or As-H stretching vibration were observed in all the spectra of gallium-phosphorus and -arsenic polymers. No such absorptions were present in the spectra of the aluminium and indium polymers. It was not possible to isolate any compound corresponding to the intermediate $(Me_2M-DRH)_x$. The observations of more intense colours as more of the donor compound was eliminated during pyrolysis and the reversible, colourless-yellow, colour change at about 200° for the gallium-phosphorus polymer suggest the possibility of defect structures.

The principal infrared absorptions of the compounds prepared in this investigation are listed in Table 3. The bands characteristic of the dimethylaluminium, dimethylgallium, dimethylphosphino-, diethylphosphino- and dimethylarsino- groups are clearly evident in this closely related series of compounds. The symmetrical metal-methyl deformations were observed at the lower limit of the frequency range suggested from the spectra of dimethylaluminium and dimethylgallium derivatives of oxy- and thio-acids.¹ This medium to strong absorption occurs at 1179–1200 and 1181–1203 cm^{-1} for the dimethylaluminium and dimethylgallium compounds. The corresponding vibration for dimethylindium compounds is in the range 1146–1151 cm^{-1} . The symmetrical methyl deformations for $P^{III}-CH_3$ and $As^{III}-CH_3$ were observed as sharp doublets in the range 1278–1299 and 1245–1260 cm^{-1} , respectively. A sharp doublet in the range 1280–1320 cm^{-1} is also characteristic of a P^V-Me_2 group (δ sym. $P-CH_3$).⁹

There has been some confusion over the assignment of the very strong and rather broad absorption observed with maxima in the range 666–668 cm^{-1} in the spectra of dimethylaluminium compounds. The only other absorption due to an Me_2-Al vibration occurred in the range 554–557 cm^{-1} . Absorptions corresponding to the symmetrical and antisymmetrical stretching of the Me_2-Al group have been identified at 585 and 720 cm^{-1} and 616 and 772 cm^{-1} for $Me_4Al_2Cl_2$ and Me_6Al_2 , respectively, and confirmed by isotopic substitution.¹⁰ The methyl rocking vibrations occur at 700 cm^{-1} . Therefore, these intense and rather broad bands with maxima in the range 666–668 cm^{-1} probably contain both the rocking and antisymmetrical stretching vibrations of the Me_2Al group, unresolved, rather than being entirely the antisymmetrical stretching mode as previously suggested.¹ The bands in the range 554–557 cm^{-1} can only be the symmetrical Me_2Al stretching vibration.

The spectra of the dimethylindium compounds have three absorptions characteristic of the Me_2In group. The intense, broad bands with maxima in the range 683–685 cm^{-1} are due to the methyl rocking vibrations. The broad appearance might be due to the presence of two unresolved rocking modes. The symmetrical and antisymmetrical stretching modes are in the range 462–467 and 484–493 cm^{-1} , respectively. These and the two rocking and the two stretching vibrations of the Me_2Ga group are assigned on the basis of previous spectra.¹ The absorptions due to the methyl rocking and stretching vibrations of the PMe_2 , PEt_2 , and $AsMe_2$ groups are also assigned on the basis of the spectra of related compounds.^{1,9}

Organometallic compounds of a Group III acceptor bound to a Group V donor atom have been observed as monomers, dimers, trimers, tetramers, and polymers. The existence of monomeric compounds appears to be due to electronic and steric effects within the molecule and in this group is almost confined to boron-nitrogen compounds. When association

⁹ M. Halmann, *Spectrochim. Acta*, 1960, **16**, 407.

¹⁰ A. P. Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

occurs, there are four factors which affect the degree of association—steric interference, valency angle strain, entropy, and the nature of the intermediates involved in their formation. These factors apparently divide the compounds into two classes—those which form dimers and those which form trimers, tetramers, and polymers.

It can be shown by molecular models that there is more steric interference between bulky substituents in a trimer than in the corresponding dimer. Therefore, dimers would be favoured for compounds of the small metal and donor atoms and compounds containing large substituent groups. In a similar manner, the entropy effect favours the dimer over the trimer or polymer within a given phase. There must necessarily be valency angle strain in dimers, but this is tolerated more readily by heavier elements than those of the first period.¹¹ These three factors alone cannot account for all the observed degrees of association. For example compare the compound,¹² $\text{Me}_2\text{In-NMe}_2$, which exists as a dimer and $\text{Me}_2\text{B-PMe}_2$, which is observed as a trimer.⁵ Both compounds contain relatively small substituents and a first period element. The indium–nitrogen and boron–phosphorus bond lengths, based on covalent radii, are 2.24 and 1.90 Å, respectively. Therefore an indium–nitrogen six-membered ring would be larger than a boron–phosphorus ring. The consideration of only steric effects, as the entropy and valency angle strain would be similar in the two cases, would favour $\text{Me}_2\text{In-NMe}_2$ as a trimer and $\text{Me}_2\text{B-PMe}_2$ as a dimer, but the observations are the other way round.

The remaining factor, the nature of the reaction intermediates, might be the most significant. All the dialkylphosphino- and dialkylarsino-compounds of dimethyl-boron,⁵ -aluminium,³ -gallium, and -indium are observed as trimers, tetramers, and polymers whereas most of the organometallic-amino-compounds are monomers, dimers, or polymers. Phosphines and arsines, which undergo similar reactions, do not always react the same way nor by the same mechanism as amines. Polymeric intermediates in the phosphine- or arsine-organometallic reactions, formed by an intermolecular condensation, would favour the observed polymer, tetramer, and trimer as the isolated species. Similarly, a monomeric intermediate, formed by an intramolecular condensation, would favour the dimer as the associated species. It is doubtful that three monomeric intermediates would associate to the trimer. In the case of the diphenylphosphino- and diphenylarsino-derivatives, which are observed only as dimers,² for example, $(\text{Me}_2\text{Ga-PPh}_2)_2$, the bulky phenyl group would hinder formation of a polymeric intermediate. The electronic effects of the phenyl groups could then stabilize a monomeric intermediate. A compound having the properties of a monomer,² $\text{Me}_2\text{Ga-PPh}_2$, was observed.

Further examples of the effect of the mechanism and the nature of the intermediates are the preparation of $\text{H}_2\text{B-NMe}_2$ and $(\text{H}_2\text{Al-NMe}_2)_3$. If $\text{H}_2\text{B-NMe}_2$ is prepared from the adduct,^{13,14} $\text{H}_3\text{B-NMe}_2\text{H}$, or from sodium borohydride and dimethylammonium chloride,¹⁵ $\text{H}_2\text{B-NMe}_2$ exists only as an equilibrium mixture of monomer and dimer. However, the reaction of B_5H_9 with NMe_2H gives both the trimer,¹⁶ which can be separated and remains as trimer, and the equilibrium mixture of monomer and dimer. If B_5H_9 reacts with the equilibrium mixture, trimer is produced. However, no trimer is formed when $(\text{H}_2\text{B-NMe}_2)_{1-2}$ is heated alone.¹⁶ The preparation of the trimer,⁷ $(\text{H}_2\text{Al-NMe}_2)_3$, from lithium aluminium hydride and dimethylammonium chloride might go through five-co-ordinate aluminium for the formation of a polymeric intermediate. A similar mechanism involving five-co-ordinate boron must be excluded, and this difference might explain the difference in the degree of association of the borane and alane. If this is true, then as the compound,¹⁷

¹¹ R. J. Gillespie, *J. Amer. Chem. Soc.*, 1960, **82**, 5978.

¹² G. E. Coates and R. A. Whitcombe, *J.*, 1956, 3351.

¹³ E. Wiberg, A. Bolz, and P. Buchheit, *Z. anorg. Chem.*, 1948, **256**, 285.

¹⁴ A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, 1951, **73**, 953.

¹⁵ G. W. Schaeffer and E. R. Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 2143.

¹⁶ L. M. Trefonas and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1959, **81**, 4435; A. B. Burg, *ibid.*, 1957, **79**, 2129.

¹⁷ N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Inorg. Chem.*, 1963, **2**, 1036.

$\text{H}_3\text{Ga}(\text{NMe}_2)_2$, is unstable above -63° , $\text{H}_2\text{Ga}-\text{NMe}_2$ would be predicted to be dimeric on the basis of its reaction intermediate.

EXPERIMENTAL

All the compounds are sensitive to air or moisture and were handled in vacuum or under an atmosphere of purified nitrogen. The metals were determined by an e.d.t.a. titration which has been previously described.² Aluminium compounds were analysed for the metal and hydrolysable methyl content. The gallium and indium compounds were analysed only for the metal on account of the difficulty in achieving quantitative hydrolysis on a vacuum apparatus. The molecular weights were measured cryoscopically in benzene as 1–3.5 wt.-% solutions. Analytical data are given in Table 4.

The infrared spectra were recorded with either a Grubb-Parsons G.S.2A or Spectromaster prism-grating spectrometer between 5 and 25 μ . The compounds were examined as contact films of solutions in Nujol. The proton n.m.r. spectra were observed (toluene solutions) at 60 Mc./sec. using an A.E.I. R.S.2 spectrometer.

Trimethylindium was prepared by the reaction of an indium-magnesium alloy with methyl chloride in diethyl ether.¹⁸ The ether was removed by a fractional distillation with benzene. No difficulty was encountered in the preparation and a yield of 80% was obtained.

TABLE 4

Analytical data

Compound	Empirical formula	Metal analysis		Hydrolysable methyl analysis		Formula weight	M	n
		Found	Required	Found	Required			
$\text{Me}_2\text{Al}-\text{PMe}_2$	$\text{C}_4\text{H}_{12}\text{AlP}$	22.5	22.8	25.3	25.4	118	371	3.14
$\text{Me}_2\text{Al}-\text{PEt}_2$	$\text{C}_6\text{H}_{16}\text{AlP}$	18.3	18.5	20.5	20.5	146	442, 446	3.02, 3.05
$\text{Me}_2\text{Al}-\text{AsMe}_2$	$\text{C}_4\text{H}_{12}\text{AlAs}$	16.4	16.7	18.4	18.5	162	476, 453	2.94, 2.78
$\text{Me}_2\text{Ga}-\text{PMe}_2$	$\text{C}_4\text{H}_{12}\text{GaP}$	42.6	43.4	—	—	160	477, 468	2.96, 2.90
$\text{Me}_2\text{Ga}-\text{PEt}_2$	$\text{C}_6\text{H}_{16}\text{GaP}$	36.5	36.8	—	—	189	563, 558	2.98, 2.95
$\text{Me}_2\text{Ga}-\text{AsMe}_2$	$\text{C}_4\text{H}_{12}\text{AsGa}$	33.7	33.8	—	—	204	610, 579	2.99, 2.84
$\text{Me}_2\text{In}-\text{PMe}_2$	$\text{C}_4\text{H}_{12}\text{InP}$	55.6	55.8	—	—	206	617, 628	2.99, 3.05
$\text{Me}_2\text{In}-\text{PEt}_2$	$\text{C}_6\text{H}_{16}\text{InP}$	49.0	49.2	—	—	234	722, 705	3.08, 3.01
$\text{Me}_2\text{In}-\text{AsMe}_2$	$\text{C}_4\text{H}_{12}\text{AsIn}$	45.8	46.0	—	—	250	755, 744	3.02, 2.98

To illustrate the experimental method, the preparation of $(\text{Me}_2\text{Ga}-\text{PMe}_2)_x$ is described as a typical example. Trimethylgallium (2.28 mmole) and dimethylphosphine (2.28 mmole) were condensed into a heavy-walled pyrolysis tube. After the tube had been sealed, the sample was heated at $150-155^\circ$ in a horizontal tube furnace for 19 hr. The pyrolysis tube was then attached to the vacuum system through a piece of heavy-walled rubber tubing. The sample was cooled to -196° ; the tube was broken open and the methane was measured by means of a Töpler pump and gas burette assembly. The compound, $(\text{Me}_2\text{Ga}-\text{PMe}_2)_x$, was then purified by vacuum sublimation at $100-110^\circ$ at 0.01 mm. All further manipulations of the compound were carried out under purified nitrogen. All the other compounds were prepared in a very similar manner.

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¹⁸ E. Todt and R. Dötzer, *Z. anorg. Chem.*, 1963, **321**, 120.