341. *Alkoxy-, Thio-, and Amino-derivatives of Methylzinc*

By G. E. Coates and D. Ridley

Phenol and some aliphatic alcohols react with dimethylzinc forming tetramers $(MeZnOR)_4$. Some thiols yield insoluble products $(MeZnSR)_x$, but t-butylthiol gives pentamers $(MeZnSBu^t)_5$ and $(EtZnSBu^t)_5$ and isopropylthiol yields a hexamer $(MeZnSPr^i)_6$. Dimethylamine forms insoluble $[(Me_2N)_2Zn]_x$ and no methylzinc compound, but diphenylamine gives the dimer $(MeZnNPh_2)_2$. Methylzinc acetate and dimethylphosphinate are insoluble and involatile and are considered to be polymeric. All these products disproportionate when heated, evolving dimethylzinc, except $(MeZnOBu^t)_4$ which forms isobutene.

Reactions are described between many of these compounds and pyridine leading to the formation of monomeric and dimeric complexes containing four-co-ordinate zinc. Infrared data relating to methylzinc groups in 23 complexes are tabulated.

Reactions between zinc alkyls and various alcohols,[1] amines,[2] and other compounds containing reactive hydrogen have been described, but little was known about the constitution of the zinc-containing products. Compounds resulting from the displacement of only one alkyl group have generally been described as crystalline and soluble in inert solvents, though no molecular-weight data have been reported, and those arising from the loss of both alkyl groups appeared as insoluble, presumably polymeric, materials. The products from diethylzinc and acetoxime provide an example: [3]

$$\mathrm{Et_2Zn + Me_2C{:}NOH \longrightarrow EtZnON{:}CMe_2\ (soluble)}$$
$$\mathrm{Et_2Zn + 2Me_2C{:}NOH \longrightarrow Zn(ON{:}CMe_2)_2\ (insoluble)}$$

We now describe some reactions between dimethylzinc (and sometimes diethylzinc) and compounds containing reactive hydrogen, the object of the experiments having been to prepare compounds in which only one alkyl group is displaced, and to study their constitution. Several of these, in fact, disproportionate to the dialkyl and products containing no zinc–carbon bonds.

Reaction with alcohols. By slow addition of the alcohol to the zinc alkyl at about −70°, both diluted with an inert solvent, the alkylzinc alkoxides can be prepared with negligible displacement of the second alkyl group,

$$\mathrm{R_2Zn + R'OH \longrightarrow RZnOR'(I) + RH}$$

The product (I), if monomeric, would contain a co-ordinatively unsaturated zinc atom bound to an oxygen atom with pronounced donor character. Zinc alkyls form co-ordination complexes with ethers (relatively unstable with simple,[4] but much more stable with chelating,[5] ethers), and the acceptor character of the metal would be enhanced by the replacement of one of the carbon atoms by the more electronegative oxygen. Since, also, the donor character of oxygen is enhanced when one of the carbon atoms of an ether is replaced by a more electropositive atom (a metal), an effect[6] which, for example, results in $Et_2Al{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OEt$ having the structure (II) rather than (III), we may expect (I) to be associated by relatively strong co-ordination.

In the absence of complicating factors, the alkylzinc alkoxides would be expected to be dimers (IV), analogous to (II), the formation of dimers being favoured relative to that

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[1] A. Butlerow, *Jahresber.*, 1864, 467.

[2] E. Frankland, *Jahresber.*, 1867, 419.

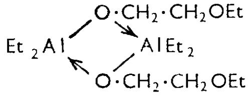
[3] J. G. Aston and D. F. Menard, *J. Amer. Chem. Soc.*, 1935, **57**, 1920.

[4] K. H. Thiele, *Z. anorg. Chem.*, 1962, **319**, 183.

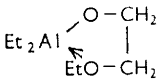
[5] K. H. Thiele, *Z. anorg. Chem.*, 1963, **322**, 71; J. G. Noltes and G. J. M. van der Kerk, *J. Organometallic Chem.*, 1964, **1**, 377.

[6] E. G. Hoffmann, *Annalen*, 1960, **629**, 104.

of trimers, tetramers, or more associated species on entropy grounds (greater number of independent molecules per unit mass). The objections to structure (IV) are first that it involves three-co-ordinate (and still co-ordinatively unsaturated) zinc, and secondly that both the oxygen and, more particularly, the metal atoms would be subject to some degree of angular strain. Neither objection to structure (IV) can be of great weight since nitrogen analogues to (IV) have been prepared from R_2Zn (R = Me or Et) and diphenylamine and are discussed below. However, all the alkoxides were found to be tetrameric (cryoscopically in benzene), and can reasonably be assumed to have eight-membered cyclic structures. There are several possible conformations of the latter, assuming the C–Zn–O angles are about 120° and the Zn–O–Zn angles about 105—110°. Since the existence of the dimer, $(MeZnNPh_2)_2$, shows that zinc atoms can tolerate substantial angular strain, the distorted cubic structure (V) should also be considered. This structure has the advantage of bringing positive and negative centres relatively close together, and if there is some degree of interaction between adjacent zinc and oxygen atoms, shown as non-bonded in (V), this would have the effect of increasing the co-ordination number both of zinc and oxygen. It is likely that the six possible forms of (V) would interconvert rapidly, in which case the time-average structure would be cubic. The infrared spectra of these compounds (as solids) are relatively simple, that of methylzinc methoxide, recorded as a Nujol mull from 200 to 2000 cm.$^{-1}$, consisting of only ten absorption bands, *viz.*, 287 and 397 (skeletal), 546 ν(Zn–Me), 678 (Zn–Me rock), 1022 ν(C–O), 1058sh (O–Me rock), 1160 δ_{sym}(Zn–Me), 1370 δ_{sym}(O–Me), and 1449 δ_{as}(O–Me). The proton magnetic resonance spectrum (60 Mc./s.) of the same compound in benzene solution consists of two double peaks, one due to Zn–Me at τ 10·366 and 10·407, and the other at τ 6·842 and 6·802. The components of the Zn–Me doublet are about equal in intensity and the splitting is very slightly less in toluene (0·036 p.p.m.) than in benzene (0·041 p.p.m.). The components of the methoxy-doublet are unequal and the splitting is a little greater in toluene than in benzene. When the solution in toluene is heated, the Zn–Me doublet collapses over a range of about ten degrees and becomes a sharp singlet at 45°. The methoxy-doublet, in contrast, remains as such even at 100°, and the splitting of the components increases slightly from 0·0686 p.p.m. at 23° to 0·0873 p.p.m. at 100°. The proton magnetic resonance spectrum of the tertiary butoxide $(MeZnOBu^t)_4$ consists of only two single sharp peaks, one due to Zn–Me at τ 10·179 and the other due to $\cdot OBu^t$ at τ 8·698. These results suggest that isomeric forms are accessible to the methoxy-compound, but denied to the t-butoxy-derivative on account of steric hindrance. Preliminary *X*-ray-crystallographic studies are in progress.



(II)



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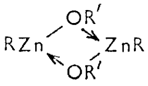
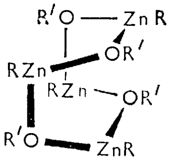
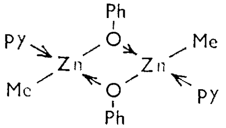


(IV)

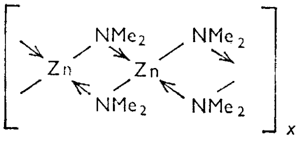
The methylzinc alkoxides do not behave as if they were co-ordinatively unsaturated, since they may be recovered unchanged from solutions to which pyridine has been added.



(V)



(VI)



(VII)

The phenoxide, in contrast, forms a pyridine adduct (VI). The oxygen of a phenoxy-group would be expected to have weaker donor character than that of an alkoxy-group. The phenoxide also differs from the alkoxides in that it disproportionates to dimethylzinc and zinc phenoxide (not investigated in detail) when heated at 120° at low pressure, whereas the alkoxides sublime unchanged under these conditions. The t-butoxide, which is much less sensitive to water than the other compounds examined, evolves isobutene when heated at about 270° under atmospheric pressure. The proton magnetic resonance spectrum of methylzinc phenoxide in fully deuterated toluene solution consists of a sharp singlet due to Zn–Me at τ 10·289 and a triplet due to phenyl groups at τ 2·981, 2·945, and 2·905.

Reaction with thiols. The thiols R′SH (R′ = Me, $\mathrm{Pr^n}$, and Ph) react with dimethylzinc forming products $(\mathrm{MeZnSR'})_x$ which are insoluble in hexane and in benzene, and which disproportionate with evolution of dimethylzinc when heated at 90° (R′ = Me), 70° ($\mathrm{Pr^n}$), and 60° (Ph). The product, $(\mathrm{MeZnSePh})_x$, from selenophenol evolved dimethylzinc even at 50°, and was also insoluble in benzene. From their lack of solubility we presume these compounds have polymeric structures. They all dissolve in benzene to which pyridine has been added, giving mobile solutions and a depolymerisation process must take place. Attempts to isolate pyridine adducts failed since only syrups were obtained, except in the case of the methylthio-derivative which dissolves in pyridine but this is lost at reduced pressure:

$$(\mathrm{MeZnSMe})_x \underset{\text{vacuum}}{\overset{\text{py}}{\rightleftharpoons}} (\mathrm{Me\ py\ ZnSMe})_n$$

The two branched-chain thiols investigated gave quite different methylzinc compounds: t-butylthiol yielded pentamers $(\mathrm{RZnSBu^t})_5$ (R = Me or Et), and isopropylthiol gave a hexamer $(\mathrm{MeZnSPr^i})_6$. Though no trend with concentration was apparent in the cryoscopic data (benzene solution), some additional evidence in support of these unusual and unexpected degrees of association was desirable. Dr. H. M. M. Shearer and Miss J. Willis of this department have made a preliminary *X*-ray diffraction study of $\mathrm{MeZnSBu^t}$ and report that the monoclinic crystals have the unit-cell dimensions: a = 12·02, b = 38·80, c = 9·61 Å, β = 117° 30′. From these data and the measured density (1·39 $\mathrm{g.c.c.^{-1}}$) the unit cell contains twenty monomer units. The space group is either $P2_1$, $P2_1/m$, or $P2_1/c$, the first requiring two decamers and the other two requiring four pentamers in the unit cell. We may conclude at this stage that the t-butylthio-compounds are pentameric both in solution and in the solid state. The branched-chain thio-derivatives differ also in withstanding higher temperatures before disproportionation becomes apparent, and in giving crystalline pyridine complexes, *e.g.*, $(\mathrm{Me\ py\ ZnSBu^t})_2$ analogous to (VI).

Reaction with amines. In its reaction with dimethylzinc, dimethylamine behaved quite differently from methanol or methanethiol in that no methylzinc derivative could be isolated, but only bisdimethylaminozinc, $[(\mathrm{Me_2N})_2\mathrm{Zn}]_x$, which is insoluble, involatile, and evidently polymeric, together with unreacted dimethylzinc. We do not know whether the bisamino-compound is formed by disproportionation of $[\mathrm{MeZnNMe_2}]_n$ or by further reaction of this with dimethylamine. Though bisdimethylaminozinc would be expected to be insoluble in hydrocarbon solvents if it is a co-ordination polymer (VII), it is remarkable that it is also insoluble in the donor solvents, dimethylformamide, pyridine, and solutions of 2,2′-bipyridyl in benzene. Evidently, the donor character of the dimethylamino-group when bound to zinc is so enhanced that even bipyridyl causes no displacement. An attempted preparation of $(\mathrm{Me_2N})_2\mathrm{Zn}$ bipy from the dimethylzinc complex $\mathrm{Me_2Zn}$ bipy [7] and dimethylamine at 80° yielded only black, involatile, and insoluble material in addition to methane. An alkylaminomethylzinc complex can be obtained from *NNN*′-trimethylethylenediamine. The stability of the product (VIII), analogous to a previously described methylberyllium complex,[7] to disproportionation may be attributed to the zinc being four-co-ordinate.

The liquid product, $(\mathrm{MeZn{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OMe})_4$, from dimethylzinc and 2-methoxyethanol, evidently resembles the other tetrameric alkoxides, the alkoxy-oxygen atoms being co-ordinated to metal in preference to the ether oxygens [cf. structures (II) and (III)].

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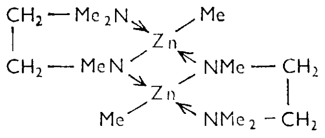
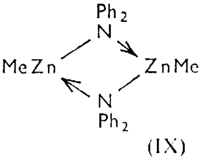
[7] G. E. Coates and S. I. E. Green, *J.*, 1962, 3340.

The formation of a tetramer in this instance, in preference to a dimer containing four-co-ordinate zinc, analogous to (VIII), provides further support for the suggestion that the metal is already effectively four-co-ordinate in this and the other tetrameric alkoxides. A structure similar to (V) would not be expected for the trimethylethylenediamine derivative, since Zn–N interactions having the effect of raising the co-ordination number of the metal to four would raise that of the nitrogen to five.

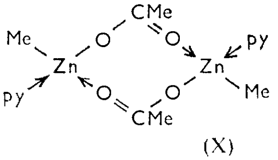
Diphenylamine, in contrast, yields the only products obtained in the course of this work which have to be formulated with three-co-ordinate zinc as a part of a four-membered ring, (IX) and its ethyl analogue. The significance of the ability of zinc to tolerate such an angular valency strain has been discussed earlier in connection with the alkoxides. The dimer (IX) reacts with pyridine in an unexpected way, since addition of pyridine in the proportion of 1 mol. of pyridine to 1 g. atom of zinc does not yield the diphenylamino-analogue of (VI), but disproportionation takes place immediately giving dimethylzinc and the pale yellow complex $py_2Zn(NPh_2)_2$. Pyridine in excess yields the bright yellow $Me\,py_2ZnNPh_2$.



(VIII)



(IX)



(X)

Acetates and dimethylphosphinates. The trimethyl derivatives of some Group III metals react with acetic and with phosphinic acids, eliminating methane (1 mol.) and giving volatile dimeric products such as $(Me_2Ga\cdot OAc)_2$ and $(Me_2GaO_2PMe_2)_2$, formulated with eight-membered rings on the basis of infrared evidence [8] and of *X*-ray structure analysis as well in the case of the second compound.[9] Both these compounds contain four-co-ordinate metal, but the analogous products from dimethylzinc would contain three-co-ordinate zinc. Both methylzinc acetate and methylzinc dimethylphosphinate are, however, insoluble in benzene and involatile at temperatures at which their gallium analogues sublime; they disproportionate above 75 and 140°, respectively, evolving dimethylzinc. Since the infrared absorptions due to $\nu(CO_2)$ and $\nu(PO_2)$ are very similar for all these compounds, we believe the zinc compounds also contain bridging acetate and phosphinate groups and that their insolubility is due to cross-linking between the zinc atoms of one dimer unit (thereby raising their co-ordination number to four) and oxygen atoms of another.

Both acetate and phosphinate dissolve in benzene on addition of pyridine, and dimeric adducts, (X) and the phosphinate analogue, can be isolated. The very strong infrared absorptions due to $\nu(CO_2)$ in (X), at 1449 and 1550 cm.$^{-1}$, do not differ greatly from those at 1408 and 1600 cm.$^{-1}$ in the insoluble methylzinc acetate (both as Nujol mulls). Even a solution of (X) in pyridine has no absorption in the region characteristic of a free carbonyl group, hence the acetate bridge is not broken even by an excess of pyridine. The intense absorptions (1026 and 1156 cm.$^{-1}$) due to $\nu(PO_2)$ in methylzinc dimethylphosphinate are again similar to those of its pyridine adduct (1053 and 1163 cm.$^{-1}$); compare the similar PO_2 absorptions in NaO_2PMe_2 (1068 and 1168 cm.$^{-1}$) [10] and the more widely spaced $\nu(PO)$ absorptions, 1042 and 1230 cm.$^{-1}$ of the methyl ester $Me_2P(:O)OMe$.[8] The pyridine adduct $(Me\,py\,ZnO_2PMe_2)_2$ is appreciably dissociated in dilute solution in benzene, since the apparent molecular weight decreases as the solution is diluted.

Infrared characteristics of the Zn–Me *group.* The infrared and Raman spectra of dimethylzinc have been analysed [11] in some detail, and some data are also available for

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[8] G. E. Coates and R. N. Mukherjee, *J.*, 1964, 1295.
[9] H. M. M. Shearer and J. Willis, personal communication.
[10] D. E. C. Corbridge and E. J. Lowe, *J.*, 1954, 4555.
[11] H. S. Gutowsky, *J. Chem. Phys.*, 1949, **17**, 128.

diethylzinc.[12] Since no spectroscopic data are recorded for zinc alkyl co-ordination complexes, absorptions due to Zn–Me and in a few instances Zn–Et groups are collected in the Table. No assignments are included in cases where there may be confusion with absorptions due to the remainder of the compound in question. There is a tendency for ν(Zn–Me) to fall as the co-ordination number of the metal increases, from 615 cm.$^{-1}$ in dimethylzinc to 506—514 cm.$^{-1}$ in those compounds in which the metal is undoubtedly four-co-ordinate. The absorptions at 510 and 453 cm.$^{-1}$ of the tetramethylethylenediamine complex of dimethylzinc would be due to the asymmetric and symmetric C–Zn–C stretching modes, respectively. The relatively high Zn–Me stretching frequencies of the alkoxides and thio-derivatives suggest that the metal is three- rather than four-co-ordinate in these compounds, but the frequencies of these vibrations should not be used as a guide to co-ordination number until reliable structural information becomes available for some of the compounds concerned. The symmetrical Zn–Me deformation frequencies of the methylzinc complexes cover a wider range (1145—1178 cm.$^{-1}$) than that of the corresponding mode of vibration of dimethyl-aluminium and -gallium complexes[8] (both about 1180—1200 cm.$^{-1}$).

Methyl- and ethyl-zinc infrared absorptions [a] (cm.$^{-1}$)

Compound	δ(Zn–Me)$_{\text{sym}}$	Zn–Me rock	ν(Zn–Me)
Me_2Zn	1185m	707vs	615vs
Et_2Zn		619 [b]	562 [c]
$Me_2Zn(Me_2N{\cdot}CH_2{\cdot})_2$	1178m	645, 610vs	510s, 453m
$(MeZnNMeC_2H_4NMe_2)_2$ (VIII)	1175m	627s	506s
(Me py $ZnOPh)_2$ (VI)		653s	508s
(Me py $ZnSBu^t)_2$		639s	506s
(Me py $ZnOAc)_2$ (X)	1150m	654s	506s
(Me py $ZnO_2PMe_2)_2$	1145m	638s	514s
$(MeZnOMe)_4$	1160m	678vs	546vs
$(MeZnOBu^t)_4$	1174s	675vs	544vs
$(MeZnOPh)_4$	1161m	685vs	552vs
$(EtZnOPr^i)_4$		613vs [b]	541vs [c]
$(EtZnOBu^t)_4$		611s [b]	540vs [c]
$(MeZnSMe)_x$	1161m	655s	525s
$(MeZnSPr^n)_x$	1163m	654vs	521s
$(MeZnSPh)_x$	1158mw	675vs	526s
$(MeZnSePh)_x$	1152mw	667vs	526s
$(MeZnSBu^t)_5$		669vs	531s
$(MeZnSPr^i)_6$	1156s	669vs	531s
$(EtZnSBu^t)_5$		610vs [b]	505s [c]
$(MeZnOAc)_x$	1169w	680vs	540s
$(MeZnO_2PMe_2)_x$		662vs	535vs
$(MeZnNPh_2)_2$		667s	548s
$(EtZnNPh_2)_2$		620s [b]	518s [c]
Me py_2 $ZnNPh_2$	1163m	621vs	505s

s, strong; m, medium; w, weak; v, very.

As Nujol mulls except Me_2Zn (gas) and Et_2Zn (liquid film). [b] CH_2 rock. ν($Zn{-}CH_2$).

EXPERIMENTAL

Infrared spectra were recorded using Grubb–Parsons double-beam prism-grating spectrometers, samples having been prepared, generally as Nujol mulls, in a nitrogen-filled glove-box.

Methylzinc Methoxide.—Methanol (0·64 g.) in hexane (10 c.c.) was slowly added to dimethylzinc (1·92 g., 1 mol.) in hexane (40 c.c.) at about −70° with stirring. Methane was evolved when the resulting clear solution warmed to about −30°, with deposition of colourless solid. When gas evolution had ceased the mixture was heated to 50° to dissolve the solid, and the *methoxide* crystallised as short broad needles on cooling the filtrate to room temperature. The product became white and opaque at 150—170° then melted at 190—191° with simultaneous evolution of dimethylzinc (identified by infrared spectrum) leaving a white residue insoluble in benzene. Methylzinc methoxide sublimed without decomposition at 60°/10^{-4} mm. [Found: Zn, 58·8; hydrolysable methyl, 13·6%; *M* (cryoscopically in 1·12, 1·69 wt.-% benzene), 461, 458. $C_8H_{24}O_4Zn_4$ requires Zn, 58·7; hydrolysable methyl, 13·5%; *M*, 446]. The methoxide

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[12] H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta*, 1959, **15**, 360.

dissolved in pyridine but no adduct could be isolated; removal of volatile material yielded unchanged methoxide (identical i.r. spectrum).

The other alkoxides were similarly prepared but were more soluble and were crystallised from hexane at low temperature. *Methylzinc t-butoxide* was sublimed at 95°/10^{-4} mm.; it dissolved only slowly in a boiling mixture of acetone and dilute sulphuric acid and this, with the ethyl analogue were the only alkylzinc compound sufficiently stable to air to permit combustion analysis by conventional methods [Found: C, 38·9; H, 7·6; Zn, 42·8%; *M* (cryoscopically in 1·71, 2·43 wt.-% benzene), 595, 603. $C_{20}H_{48}O_4Zn_4$ requires C, 39·1; H, 7·8; Zn, 42·6%; *M*, 612]. *Ethylzinc t-butoxide* sublimed at 105°/10^{-4} mm. [Found: C, 42·7; H, 8·2; Zn, 38·8%; *M* (cryoscopically in 1·43, 2·86 wt.-% benzene), 691, 680. $C_{24}H_{56}O_4Zn_4$ requires C, 43·0; H, 8·4; Zn, 39·1%; *M*, 668]. Ethylzinc isopropoxide has been described elsewhere.[13] though its molecular weight was not reported, m. p. 258—260° (decomp.) (Found: Zn, 43·0; hydrolysable ethyl, 19·1%; *M* (cryoscopically in 1·51, 2·26 wt.-% benzene), 599, 632. Calc. for $C_{20}H_{48}O_4Zn_4$: Zn, 42·6; hydrolysable ethyl, 18·9%; *M*, 614]. *Methylzinc phenoxide* melted at 219—221° (decomp.) when heated quickly, but began to evolve dimethylzinc at 120° when heated *in vacuo* [Found: Zn, 37·6; hydrolysable methyl, 8·7%, *M* (cryoscopically in 1·77, 3·05 wt.-% benzene), 684, 720. $C_{28}H_{32}O_4Zn_4$ requires Zn, 37·7; hydrolysable methyl, 8·65%; *M*, 694]. *Methyl(pyridine)zinc phenoxide*, $(\text{Me py ZnOPh})_2$, (VI), crystallised as colourless prisms when an excess of pyridine was added to methylzinc phenoxide in benzene and the solution set aside at room temperature, m. p. 193—200° (decomp.) [Found: Zn, 25·8; hydrolysable methyl, 6·1%; *M*(cryoscopically in 1·10, 1·11, 1·34 wt.-% benzene), 513, 515, 520. $C_{21}H_{26}N_2O_2Zn_2$ requires Zn, 25·9; hydrolysable methyl, 5·9%; *M*, 505]. It is sparingly soluble in benzene (about 2·5 wt.-% at room temperature). *Methylzinc 2-methoxyethoxide* distilled at 70°/*ca.* 10^{-2} mm. [Found: Zn, 41·8; hydrolysable methyl, 9·5%; *M*(cryoscopically in 1·83, 2·29 wt.-% benzene), 624, 631. $C_{16}H_{40}O_8Zn_4$ requires Zn, 42·1; hydrolysable methyl, 9·65%; *M*, 622].

Methyl Methylzinc Sulphide, $(\text{MeZnSMe})_x$.—This was precipitated with some gas evolution, when methanethiol (1 mol.) was slowly condensed into dimethylzinc in hexane. When all the thiol had been added, the mixture was allowed to warm to room temperature and more gas was evolved. The colourless product was insoluble in boiling hexane and in boiling benzene (Found: Zn, 51·0; hydrolysable methyl, 11·5. C_2H_6SZn requires Zn, 51·3; hydrolysable methyl, 11·8%). The infrared spectrum included absorptions at 225 and 299 cm.$^{-1}$ attributable to skeletal Zn–S vibrations. *Methylzinc n-propyl sulphide*, $(\text{MeZnSPr}^n)_x$, was precipitated when n-propylthiol (1 mol. in hexane) was added to dimethylzinc (also in hexane) at −80° and the mixture allowed to warm to room temperature (Found: Zn, 41·7; hydrolysable methyl, 9·4. $C_4H_{10}SZn$ requires Zn, 42·0; hydrolysable methyl, 9·65%). *Methylzinc phenyl sulphide* (Found: Zn, 34·3; hydrolysable methyl, 7·75. C_7H_8SZn requires Zn, 34·5; hydrolysable methyl, 7·9%) and *methylzinc phenyl selenide* (Found: Zn, 27·4; hydrolysable methyl, 6·1. C_7H_8SeZn requires Zn, 27·7; hydrolysable methyl, 6·35%) were similarly prepared but the whole of the methane appeared to be liberated at *ca.* −80°. *Isopropyl methylzinc sulphide*, $(\text{MeZnSPr}^i)_6$, was not precipitated but crystallised when the solution was cooled after evaporation of some of the hexane [Found: Zn, 41·5; hydrolysable methyl, 9·4%; *M* (cryoscopically in 1·66, 1·97, 2·03, 2·49 wt.-% benzene), 942, 942, 966, 919. $C_{24}H_{60}S_6Zn_6$ requires Zn, 42·0; hydrolysable methyl, 9·65%; *M*, 934]. It melted over the range 90—105° with previous shrinking at 75°, and under reduced pressure evolved dimethylzinc at 95°. *Methylzinc t-butyl sulphide*, $(\text{MeZnSBu}^t)_5$, crystallised from hexane as colourless needles [Found: Zn, 38·4; hydrolysable methyl, 8·9%; *M* (cryoscopically in 2·49, 3·05, 3·47 wt.-% benzene), 875, 846, 861. $C_{25}H_{60}S_5Zn_5$ requires Zn, 38·6; hydrolysable methyl, 8·9%; *M*, 847]. The *pyridine adduct*, $(\text{Me py ZnSBu}^t)_2$, was prepared by addition of excess of pyridine to a solution of the t-butyl sulphide (1 g.) in benzene (10 c.c.) followed by removal of all volatile matter and recrystallisation from benzene–hexane (1 : 10), m. p. 147—155° (decomp.) [Found: Zn, 26·4; hydrolysable methyl, 6·1%; *M* (cryoscopically in 0·87, 1·75 wt.-% benzene), 470, 481. $C_{20}H_{34}N_2S_2Zn_2$ requires Zn, 26·3; hydrolysable methyl, 6·0%; *M*, 497]. *Ethylzinc t-butyl sulphide*, $(\text{EtZnSBu}^t)_5$, was more soluble than its methyl analogue and was crystallised from hexane at −70° [Found: Zn, 35·9; hydrolysable ethyl, 15·9%; *M* (cryoscopically in 2·67, 3·64 wt.-% benzene), 940, 954. $C_{30}H_{70}S_5Zn_5$ requires Zn, 35·7; hydrolysable ethyl, 15·8%; *M*, 917].

Methylzinc acetate, $(\text{MeZnOAc})_x$, was precipitated when acetic acid (1 mol.) in hexane was

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[13] R. J. Herold, S. L. Aggarwal, and V. Neff, *Canad. J. Chem.*, 1963, **41**, 1368.

added to a stirred solution of dimethylzinc in hexane at −80°. Gas evolution was rapid at this temperature. The product was washed several times with benzene, in which it was insoluble (Found: Zn, 46·7; hydrolysable methyl, 10·6. $C_3H_6O_2Zn$ requires Zn, 46·9; hydrolysable methyl, 10·8%). It dissolved when pyridine in excess was added to a suspension in benzene, and addition of hexane precipitated the *pyridine adduct*, $(\mathrm{Me\,py\,ZnOAc})_2$, (X), which was recrystallised from benzene–hexane (1 : 1) as feathery needles, m. p. 106—108° [Found: Zn, 29·9; hydrolysable methyl, 6·9%; *M* (cryoscopically in 0·81, 1·62 wt.-% benzene), 420, 427. $C_{16}H_{22}N_2O_4Zn_2$ requires Zn, 29·9; hydrolysable methyl, 6·9%; *M*, 436].

Methylzinc dimethylphosphinate, $[\mathrm{MeZnOP(:O)Me_2}]_x$, was prepared by stirring overnight a suspension of dimethylphosphinic acid in hexane at 40° containing dimethylzinc. Gas evolution was very slow on account of the insolubility of both the phosphinic acid and the product. The phosphinate was also insoluble in benzene (Found: Zn, 37·6; hydrolysable methyl, 8·6. $C_3H_9O_2PZn$ requires Zn, 37·7; hydrolysable methyl, 8·65%). It dissolved when an excess of pyridine was added to a warm suspension in benzene–hexane (1 : 1). Addition of hexane following by cooling caused the *pyridine adduct* $[\mathrm{Me\,py\,ZnOP(:O)Me_2}]_2$ to crystallise, m. p. 85—92° (decomp.) with shrinking at 70° [Found: Zn, 25·8; hydrolysable methyl, 5·9%, *M* (cryoscopically in 0·98, 1·96, 2·75 wt.-% benzene), 350, 406, 440. $C_{16}H_{28}N_2O_4P_2Zn_2$ requires Zn, 25·9; hydrolysable methyl, 5·9%; *M*, 504].

Bisdimethylaminozinc, $[(\mathrm{Me_2N})_2\mathrm{Zn}]_x$, (VII).—Dimethylamine (1 mol.) and dimethylzinc were heated in the gas phase fo 2 hr. at 70°. When the reaction vessel was opened, methane (1 mol.) and dimethylzinc (0·5 mol.) were separated from the colourless involatile *product*, m. p. 270—290° (decomp.) [Found: Zn, 42·9; Me_2N (by hydrolysis), 57·3. $C_2H_6N_2Zn$ requires Zn, 42·6; Me_2N, 57·4%].

Reaction between Dimethylzinc and NNN′-*Trimethylethylenediamine*.—Dimethylzinc (1 mol.) was condensed on the amine and the mixture allowed to warm to room temperature. The colourless crystalline adduct rapidly lost methane (1 mol.) when heated at 40—45°. The product was purified by sublimation at 75°/0·01 mm. forming colourless prisms of $[\mathrm{MeZn{\cdot}N(Me){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2}]_2$, VII), m. p. 110—111° with shrinking at 99° [Found: Zn, 36·25; hydrolysable methyl, 8·3%, *M* (cryoscopically in 1·22, 2·43 wt.-% benzene), 358, 365. $C_{12}H_{32}N_4Zn_2$ requires Zn, 36·05; hydrolysable methyl, 8·3%; *M*, 363].

Methyl(diphenylamino)zinc $(\mathrm{MeZnPh_2})_2$, (IX).—Freshly sublimed diphenylamine (1 mol.) and dimethylzinc were heated at 70° in a sealed tube. The *product* was crystallised from benzene [Found: Zn, 26·2; hydrolysable methyl, 6·0%; *M* (cryoscopically in 0·74, 1·48 wt.-% benzene), 465, 475. $C_{26}H_{26}N_2Zn_2$ requires Zn, 26·3; hydrolysable methyl, 6·0%; *M*, 497].

Ethyl(diphenylamino)zinc $(\mathrm{EtZnNPh_2})_2$.—In a similar preparation, the reactants were heated at 50—60° overnight. Ethane (1 mol.) and a white solid product, very soluble in benzene, were obtained. The solid was crystallised from hexane at low temperature as small colourless plates, m. p. 99—100° with shrinking at 89° [Found: Zn, 24·8; hydrolysable ethyl, 11·02%; *M* (cryoscopically in 1·5, 1·79 wt.-% benzene), 514, 540. $C_{28}H_{30}N_2Zn_2$ requires Zn, 24·9; hydrolysable ethyl, 11·05%; *M*, 525].

Reactions between Methyl(diphenylamino)zinc (IX) *and Pyridine*.—(*a*) *With an excess*. When dry pyridine (2 c.c.) was added to compound (IX) (1 g.) in benzene (15 c.c.) the solution immediately became bright yellow. Addition of hexane caused the crystallisation of *diphenylamino(methyl)bispyridinezinc*, $\mathrm{Me\,py_2\,ZnNPh_2}$, which was recrystallised from benzene–hexane as yellow small feathery needles [Found: Zn, 16·2; hydrolysable methyl, 3·74%; *M* (cryoscopically in 1·26, 1·58, 1·66 wt.-% benzene), 370, 385, 390. $C_{23}H_{23}N_3Zn$ requires Zn, 16·1: hydrolysable methyl, 3·69%; *M*, 406]. When heated slowly it melted over the range 185—195°, but this is the melting range of partly decomposed material. By placing a specimen in a melting point apparatus previously heated to various temperatures, a sharp melting point of 110° was observed. The complex decomposed rapidly when exposed to the air.

(*b*) *With* 1 *mol. pyridine*. Addition of pyridine (0·64 g., 1 mol.) to compound (IX) (2·0 g.) in hot benzene (20 c.c.) caused the development of a pale yellow colour. After addition of hexane (10 c.c.) and benzene (10 c.c.) the mixture was heated to about 80° and allowed to cool. Large, very pale yellow crystals of *bisdiphenylaminobispyridinezinc*, $\mathrm{py_2\,Zn(NPh_2)_2}$, m. p. 210—211°, separated overnight [Found: Zn, 11·5; Ph_2N, 60·6%; *M* (cryoscopically in 1·02, 1·14 wt.-% (benzene), 553, 571. $C_{34}H_{30}N_4Zn$ requires Zn, 11·7; Ph_2N, 60·1%; *M*, 559]. The complex was less air-sensitive than $\mathrm{Me\,py_2\,ZnNPh_2}$. The presence of dimethylzinc in the filtrate was evident from the effect of admitting a trace of air.

Dimethyl-(NNN′N′*-tetramethylethylenediamine*)*zinc.*—Dimethylzinc was condensed on the freshly distilled diamine (1 mol.), and the product purified by sublimation at 35°/0·01 mm., m. p. 57—58° [Found: Zn, 30·7; hydrolysable methyl, 14·1%; *M* (cryoscopically in 0·75, 0·85 wt.-% benzene), 219, 225. $C_8H_{22}N_2Zn$ requires Zn, 30·9; hydrolysable methyl, 14·2%; *M*, 211].

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