765. *Metallo-organic Compounds containing Metal–Nitrogen bonds. Part I. Some Dialkylamino-derivatives of Titanium and Zirconium.*

By D. C. BRADLEY and I. M. THOMAS.

The compounds $M(NR_2)_4$, where M is either Ti or Zr, and R is Me, Et, Pr^n, or Bu^i, were prepared either by treating the metal chloride with the appropriate lithium dialkylamide or by aminolysis involving a tetrakisdialkylamino-metal compound and another dialkylamine. The latter method also gave mixed dialkylamino-derivatives of the type $M(NR_2)_x(NR'_2)_{4-x}$, where R′ was Et, Pr^n, Pr^i, Bu^i, or of the type $M(NR_2)_x(N\text{-organic})_{4-x}$, where N-organic was piperidino-, 2-methylpiperidino-, or 2,6-dimethylpiperidino-. These new compounds can all be distilled or sublimed *in vacuo*, and are soluble in common organic solvents, readily hydrolysed and converted by alcoholysis into metal alkoxides. The absence of appreciable metal–nitrogen intermolecular bonding is discussed.

ALTHOUGH the amino-derivatives of titanium and zirconium are well known and the reactions involving aliphatic amines and the tetrachlorides of these metals have been studied,[1] there were no authentic examples of metallo-organic compounds containing these metals exclusively bonded to alkylamino-groups. Such compounds occupy the position between the well-known metal alkoxides and the little known organometallic

---

[1] Trost, *Canad. J. Chem.*, 1952, **30**, 835, 842; Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.

compounds containing these metals bonded to aliphatic carbon atoms. Also, it was difficult to predict the physicochemical properties of tetrakisdialkylamino-derivatives from *a priori* considerations because of the lack of precise knowledge of the steric and electronic effects of four dialkylamino-groups centred round the metal. From similar principles to those deduced from the structural chemistry of metal alkoxides,[2] it seemed that the lower dialkylamines (*e.g.*, dimethylamine) might produce polymeric derivatives (especially with zirconium) owing to covalency expansion of the metal causing intermolecular metal–nitrogen bonding. With the higher dialkylamines it was expected that volatile monomeric derivatives would occur because of the pronounced steric factors involved. Moreover, the existence of a series of tetrakisdialkylamino-derivatives of the metals would facilitate the study of the nature of metal–nitrogen bonds in covalent neutral compounds. For these reasons we have made a detailed study of tetrakisdialkylamino-titanium and -zirconium compounds and have found them quite stable in the absence of water or other hydroxylic compounds.

Gilman *et al.*[3] recently prepared tetrakisdiethylaminouranium(IV) by treating uranium tetrachloride with lithium diethylamide and we have applied this method to the preparation of the tetrakisdialkylamino-derivatives of titanium and zirconium from the metal chlorides: *i.e.*,

$$MCl_4 + 4LiNR_2 \longrightarrow M(NR_2)_4 + 4LiCl$$

In addition, we have prepared other tetrakisdialkylamino-derivatives by aminolysis in which the metal derivative of a lower secondary amine was treated with a higher secondary amine:

$$M(NR_2)_4 + 4R'_2NH \longrightarrow M(NR'_2)_4 + 4R_2NH$$

A preliminary notification of this work appeared elsewhere.[4]

The thermal stability of the metal–nitrogen bond can be judged by the fact that these compounds survived distillation, in some cases at a fairly high temperature. However, they were extremely readily hydrolysed with liberation of the amine. Also, the amine was liberated and a metal alkoxide formed when the dialkylamino-compound was treated with an alcohol:

$$M(NR_2)_4 + 4ROH \longrightarrow M(OR)_4 + 4R_2NH$$

This reaction does not appear to be reversible since attempts to prepare dialkylamino-compounds by treatment of metal alkoxides with secondary amines under forcing conditions were unsuccessful. This could imply that the metal–oxygen bond is stronger than the metal–nitrogen bond but the situation is complicated by steric effects. The boiling points of the corresponding titanium and zirconium compounds are fairly close except for the dimethylamino-derivatives in which the zirconium compound has a considerably lower volatility. Molecular-weight determinations in boiling benzene show that this is due to a significant degree of polymerisation (1·22) in the zirconium compound, undoubtedly caused by intermolecular metal–nitrogen bonding. The titanium compound is practically monomeric. Similarly the diethylamino-derivatives of titanium and zirconium and the piperidino-derivative of titanium were all monomeric and it follows that the n-propylamino- and isobutylamino-derivatives of both metals must also be monomeric. This lack of polymerisation is extremely interesting because under favourable conditions it would be expected that nitrogen would form a stronger intermolecular co-ordinate bond than oxygen (in the alkoxides). It is reasonable to suggest that the shielding effect of a dialkylamino-group is much greater than that of the corresponding secondary alkoxide group. For example, zirconium tetraisopropoxide is trimeric under conditions where the tetrakisdimethylamino-zirconium has the degree of polymerisation of 1·22. Evidently branching

---

[2] Bradley, *Nature*, 1958, **182**, 1211.

[3] Jones, Karmas, Martin, and Gilman, *J. Amer. Chem. Soc.*, 1956, **78**, 4285.

[4] Bradley and Thomas, *Proc. Chem. Soc.*, 1959, 225.

at the nitrogen atom in $M(NR_2)_4$ is more effective sterically than branching at the carbinol carbon atom in $M(O{\cdot}CHR_2)_4$. However, electronic effects must not be ignored and it is possible that the lower degree of polymerisation in $M(NR_2)_4$ is partly due to significant *intramolecular* co-ordination involving the π-bond $\overset{-}{M}=\overset{+}{N}R_2$ whereas in the alkoxides it is believed that the analogous π-bond structure $\overset{-}{M}=\overset{+}{O}-CHR_2$ contributes very little. Nevertheless, it is clear from the results of certain aminolyses that strong steric effects are operating in the alkylamino-compounds. Thus it was not possible to convert tetrakisdimethylaminotitanium into the diethylamino-derivative in spite of prolonged fractionation with excess of diethylamine. Instead, trisdiethylamino(mono)dimethylaminotitanium was isolated as a pale yellow liquid which could be distilled unchanged under reduced pressure. The results of a number of aminolyses which produced mixed dialkylamino-derivatives are included in Table 2. In reactions involving tetrakisdimethylaminotitanium and dialkylamines it is noteworthy that mixed dialkylamines of the general formula $Ti(NMe_2)B_3$ are obtained when $B = NEt_2$, NPr^n_2, or NBu^i_2, suggesting a similarity in steric effect of these groups in this type of molecule. Confirmation of the predominance of steric effects in these reactions is evident in the comparison of the behaviour of piperidine, 2-methylpiperidine, and 2,6-dimethylpiperidine. For example, piperidine, having a smaller steric effect than diethylamine, causes complete replacement of the dimethylamino-groups, whilst 2-methylpiperidine gives the same type of product as diethylamine or di-n-propylamine. Similarly, 2,6-dimethylpiperidine resembles di-isopropylamine in giving a product of the type $Ti(NMe_2)_3B$, where $B = NPr^i_2$, or NC_7H_{14}. Now if electronic effects were important we should expect the stronger base to be the more powerful substituting agent (assuming a nucleophilic reaction at the metal atom centre) and this is contrary to the behaviour of piperidine and its methyl derivatives. Another way in which electron effects might influence the degree of substitution is through partial double bonding $\overset{-}{M}=\overset{+}{N}R_2$ resulting in a higher electron density on the metal with consequent resistance to nucleophilic attack. If this phenomenon were operative it would lead to a decrease in degree of substitution with increase in base strength of the substituting amine and its effect would thus be similar to that of the steric effect. The behaviour of tetrakisdiethylaminotitanium in resisting replacement by di-n-propylamine but allowing replacement by piperidine also supports the view that steric effects are very pronounced in these systems. Further support is evident from the behaviour of the zirconium compounds. For example, with tetrakisdimethylaminozirconium the degree of replacement of dimethylamino-groups by the other amines is noticeably greater than for the titanium compound. Another interesting feature is that the slight difference in behaviour between di-isopropylamine and 2,6-dimethylpiperidine in their reactions with $Ti(NMe_2)_4$ is very much amplified in reactions with $Zr(NMe_2)_4$. Hence it appears that the steric effect of di-isopropylamine is greater than that of 2,6-dimethylpiperidine. The behaviour of tetrakisdiethylaminozirconium with these two amines also supports this view.

EXPERIMENTAL

Special precautions, *e.g.*, carefully dried all-glass apparatus, were adopted to avoid hydrolysis, and all experiments were conducted under an atmosphere of dry oxygen-free nitrogen. The amines and solvents were all dried over sodium and distilled immediately before use.

Analysis.—(a) *For the metals.* An accurately weighed sample of tetrakisdialkylamino-compound was hydrolysed in a platinum crucible and the hydrated oxide was then ignited to the dioxide. (b) *For the dialkylamino-group* (NR_2). The sample was hydrolysed, and the liberated dialkylamine was steam distilled and titrated with standard acid in a modified Kjeldahl apparatus.

Preparation of Tetrakisdialkylamino-compounds from the Metal Chlorides.—Since the technique used was essentially the same in each experiment the details are given for the preparation of tetrakisdiethylaminotitanium alone, and the other results are summarised in

Table 1. Butyl-lithium solution (300 c.c., 1·37N) was prepared in the usual manner [5] from n-butyl bromide (72 g.) and lithium (8·2 g.) in ether cooled to −20°. To this solution diethylamine (30 g.) was added slowly with stirring at −10°, stirring was continued for a further 30 min., and the products were allowed to attain room temperature. Titanium tetrachloride (16·2 g.) in benzene (100 c.c.) was next added during 30 min. with vigorous stirring and cooling to keep the temperature below about 10°. A brown intermediate product is precipitated in the initial stages of the reaction and the system, following completion of the addition of the tetrachloride, was refluxed (approx. 2 hr.) until the intermediate product disappeared and a pale yellow solution remained over a white precipitate of lithium salts. After removal of the ether by evaporation and its replacement by an equal volume of benzene, the solution was filtered, and the filtrate evaporated to dryness under reduced pressure. Distillation of the residue gave *tetrakisdiethylaminotitanium* as an orange liquid, b. p. 112°/0·1 mm. (19·2 g., 67%) [Found: Ti, 14·2; NEt_2, 85·3; Cl, 0·0. $Ti(NEt_2)_4$ requires Ti, 14·2; NEt_2, 85·8%].

In each of the preparations listed in Table 1, the yield is based on the distilled product. Each product was tested for the presence of chloride but it was invariably absent. In the preparation of the zirconium compounds, the zirconium tetrachloride was added to the lithium dialkylamide through a transfer tube under nitrogen.

TABLE 1.

Compound	Wt. of MCl_4 * (g.)	Product g.	Product yield (%)	B. p./mm.	Colour	Found (%) M *	Found (%) NR_2	Calc. (%) M *	Calc. (%) NR_2
$Ti(NMe_2)_4$ ...	15·0	15·1	85	50°/0·05	Yellow	21·0	77·4	21·4	78·6
$Ti(NPr^n_2)_4$ ...	6·7	12·0	76	150/0·1	Red	10·8	89·5	10·7	89·3
$Ti(NBu^i_2)_4$ ...	8·5	12·1	48	170/0·1	Red	8·6	91·1	8·5	91·5
$Ti(NC_5H_{10})_4$...	13·5	12·2	45	180/0·1	Red [a]	12·4	86·3	12·5	87·5
$Zr(NMe_2)_4$ ...	34·0	23·1	59	80/0·05	White [b]	33·7	66·5	34·1	65·9
$Zr(NEt_2)_4$ ...	23·0	25·3	79	120/0·1	Green	24·1	76·0	24·0	76·0

* M = Ti or Zr. [a] M. p. 100°. [b] M. p. 70°.

Aminolysis of Tetrakisdialkylamino-derivatives of Titanium and Zirconium.—The following experiment is typical of all the others. Diethylamine (180 c.c.) was added to tetrakisdimethylaminotitanium (10·4 g.), and the solution refluxed under a fractionating column. Dimethylamine was immediately detected in the distillate and was fractionated off as it formed. The reaction was continued (about 5 days) until gas–liquid chromatography of the distillate proved that dimethylamine was absent. Removal of the diethylamine under reduced pressure followed by distillation of the residue afforded the pale yellow *trisdiethylamino(mono)dimethylaminotitanium* (13·45 g., 94%), b. p. 95°/0·05 mm. [Found: Ti, 15·8; Total base, 85·2.

TABLE 2.

Reactants *	Product	Yield (%)	Duration of reaction	B.p./mm.	Colour	Found (%) M	Found (%) Total NR_2	Calc. (%) M	Calc. (%) Total NR_2
$Ti(NMe_2)_4 + Pr^n_2NH$	$Ti(NMe_2)(NPr^n_2)_3$	89	3 days	95°/0·05	Yellow	12·1	86·7	12·2	87·8
$Ti(NMe_2)_4 + Pr^i_2NH$	$Ti(NMe_2)_3(NPr^i_2)$ †	—	6 days	80/0·05	Orange [a]	19·3	—	17·1	82·9
$Ti(NMe_2)_4 + Bu^i_2NH$	$Ti(NMe_2)(NBu^i_2)_3$	80	3 days	170/0·1	Red	10·3	89·0	10·0	90·0
,, $+ C_5H_{10}NH$	$Ti(NC_5H_{10})_4$	85	24 hr.	108/0·1 [e]	Red	12·4	87·4	12·5	87·5
,, $+ C_6H_{12}NH$	$Ti(NMe_2)(NC_6H_{12})_3$	78	5 days	160/0·1	Red	12·7	85·8	12·4	87·6
,, $+ C_7H_{14}NH$	$Ti(NMe_2)_3(NC_7H_{14})$	52	3 days	120/0·05	Red	16·0	81·5	16·4	83·6
$Ti(NEt_2)_4 + C_5H_{10}NH$	$Ti(NC_5H_{10})_4$	89	36 hr.	See above		12·5	87·0	12·5	87·5
,, $+ Pr^n_2NH$	No reaction		several days						
$Zr(NMe_2)_4 + Et_2NH$	$Zr(NEt_2)_4$	87	16 hr.	120/0·1	Green	24·4	76·0	24·0	76·0
,, $+ Pr^n_2NH$	$Zr(NPr^n_2)_4$	80	3 days	165/0·1	Green	18·8	80·6	18·5	81·5
,, $+ Pr^i_2NH$	$Zr(NMe_2)_2(NPr^i_2)_2$	80	7 days	subl. 100/0·05	Green	24·1	76·2	24·0	76·0
,, $+ C_6H_{12}NH$	$Zr(NC_6H_{12})_4$	56	2 days	190/0·1	Blue	19·1	—	18·9	81·1
,, $+ C_7H_{14}NH$	$Zr(NC_7H_{14})_4$	26	6 days	200/0·05	Red	17·3	—	16·9	83·1
$Zr(NEt_2)_4 + Pr^i_2NH$	$Zr(NEt_2)_3(NPr^i_2)$	84	2 days	112/0·05	Green [b]	22·6	77·3	22·4	77·6
,, $+ Bu^i_2NH$	$Zr(NBu^i_2)_4$	77	4 days	180/0·1 [c]	Green	15·3	84·5	15·1	84·9
,, $+ C_5H_{10}NH$	$Zr(NC_5H_{10})_4$	62	6 hr.	190/0·2 [d]	Brown	21·3	78·0	21·3	78·7

* NC_5H_{10} = piperidino; NC_6H_{12} = 2-methylpiperidino; and NC_7H_{14} = 2,6-dimethylpiperidino. † This product was a mixture with $Ti(NMe_2)_4$. [a] M. p. 40°. [b] M. p. 40°. [c] Sublimes. [d] M. p. 80°. [e] M. p. 100°

---

[5] Gilman, Beel, Brannen, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499.

$Ti(NMe_2)(NEt_2)_3$ requires Ti, 15·5; Total base, 84·5%]. The presence of both dimethylamino- and diethylamino-groups in the product was proved by gas–liquid chromatography of the volatile products of alcoholysis of a sample. This technique of checking the presence of different dialkylamino-groups and the general method outlined above were adopted for all other reactions, the results of which are summarised in Table 2.

Molecular-weight Determinations.—Some measurements were carried out in benzene by using the previously described [6] all-glass ebulliometer and the method of internal calibration [7] using fluorene. The results are given in Table 3.

TABLE 3.

Compound	Range in wt. of cpd. (g.)	$\Delta T/m$	Fluorene: range in wt. (g.)	$\Delta T/m$	*M* Found	Calc.
$Ti(NMe_2)_4$	0·0575—0·2094	131°	0·0092—0·0813	194·4°	247	224·2
$Ti(NEt_2)_4$	0·0880—0·2391	50·0	0·0341—0·0896	98·2	327	336·4
$Ti(NC_5H_{10})_4$	0·0152—0·1720	78·5	0·0118—0·0897	172·0	362	384·5
$Zr(NMe_2)_4$	0·0720—0·2485	88·9	0·0116—0·0710	173·9	325	267·5
$Zr(NEt_2)_4$	0·0730—0·2707	88·4	0·0185—0·0904	190·0	358	379·7

The high value found for tetrakisdimethylaminotitanium suggested a small degree of polymerisation in this compound. However, subsequent work has shown that this compound is appreciably volatile in benzene and hence the molecular-weight determination is suspect. The volatility of this compound suggests that it is monomeric.

Alcoholysis of Dialkylamino-metal Compounds.—Qualitative experiments showed that alcohols reacted vigorously with these titanium and zirconium compounds to release the amine and form the metal alkoxide. The quantitative aspect of this reaction was demonstrated by the following reaction. n-Butanol (60 c.c.) was added to tetrakisdi-n-propylaminotitanium (5·30 g.) dissolved in benzene (10 c.c.) and caused an exothermic reaction. Di-n-propylamine was separated by fractional distillation and the excess of butanol was evaporated off under reduced pressure. Distillation of the residue gave titanium tetra-n-butoxide (3·85 g., 95%) [Found: Ti, 13·9; NPr^n_2, *ca.* 1%. Calc. for $Ti(OBu)_4$: Ti, 14·1%].

The authors thank the Wright Air Development Centre of the Air Research and Development Command, U.S. Air Force, who supported this work through their European Office.

BIRKBECK COLLEGE, MALET STREET, LONDON, W.C.1.
[Present addresses: THE UNIVERSITY OF WESTERN ONTARIO, LONDON,
ONTARIO, CANADA].

[*Received, March* 18*th*, 1960.]

---

[6] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.
[7] Bradley, Wardlaw, and Whitley, *J.*, 1956, 5.