METALLO-ORGANIC COMPOUNDS CONTAINING METAL-NITROGEN BONDS.

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ABSTRACT

By means of reactions involving transition metal chlorides MC_{x} and
lithium dialkylamides a number of new dialkylamino-derivatives of titanium,
zirconium, vanadium, zirconium, tantalum, chromium, molybdenum and tungsten have
been prepared. Aminolysis of some of these compounds involved considerable
steric effects due to shielding of the metal atom. In the case of quinque-
valent zirconium and tantalum the steric effect precluded the formation of
pentakis-derivatives except with dimethylamino-, N-methyl-N-butyramino-, and
piperidino-groups. With higher dialkylamines the products were Nb(NR_{3})_{5} and
Mo-Ta(NR_{3})_{3}. Studies on the reactions of dialkylamino-titanium compounds
with primary amines showed that polymeric compounds may be obtained.
INTRODUCTION

The dialkylamino- compounds of the transition metals were of special interest since they bridge the gap between the relatively stable metal alkoxides and the generally unstable metal alkyls. In addition there was the possibility that metal-nitrogen polymers would be formed, either by coordination-polymerisation (I) in which the lone-pair of electrons on the nitrogen forms an intermolecular coordinate bond, or by using the bifunctional primary amine as in (II).

\[
\begin{align*}
\text{(I)} & \quad \text{R} \quad \text{R} \\
& \quad \text{N} \\
& \quad \text{H} \\
\text{(II)} & \quad \text{R} \\
& \quad \text{N} \\
& \quad \text{H}
\end{align*}
\]

In the case of the primary amino-derivatives there was the further possibility that coordination-polymerisation would also take place. There were also some factors which might operate against polymerisation. Thus in the dialkylamino-derivatives the intermolecular bond (I) might be prevented by steric effects or by "intramolecular coordination" involving d-or p-π bonds H\text{NH}_2. In the case of primary amino-derivatives there was the further possibility that only one of the hydrogens of the NH\textsubscript{2} group would be replaceable by metal and this would prevent polymerisation by mechanism (II). Prior to 1959 the only binary dialkylamino-compound of a transition metal or actinide element reported was the tetrakis-(diethylamino)-uranium (IV) obtained by Gilman and coworkers\textsuperscript{1} from the reaction involving uranium tetrachloride and lithium diethylamide. Berner and Ferrel\textsuperscript{2} prepared Ti[\text{N(C}_2\text{H}_5)_2]_2 by treating titanium tetrachloride with sodium diphenylamide.

We have shown that the lithium dialkylamide-metal chloride reaction (I) is suitable for the synthesis of numerous dialkylamino-derivatives of titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.

\[
\text{MCl}_x + x\text{LiNR}_2 \rightarrow \text{M(NR}_2)_x + x\text{LiCl}
\]

Most of the dialkylamino-derivatives may be distilled under reduced pressure although in some cases [e.g. Nb(IV), Ta(V) compounds] interesting thermal decomposition occurs. The aliphatic dialkylamino-compounds were readily hydrolysed or alcoholysed but arylaminio-derivatives were relatively more stable. Some interesting steric effects were observed in the dialkylamino-compounds whilst in the primary amino-compounds a number of polymeric derivatives were obtained.

Titanium and Zirconium Compounds


Some data on tetrakis-(dialkylamino)-titanium and zirconium compounds\textsuperscript{3} are presented in Table 1.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Appearance</th>
<th>Boiling point (°C mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(NMe₂)₄</td>
<td>Yellow liquid</td>
<td>10/0.05</td>
</tr>
<tr>
<td>Ti(NBu₂)₄</td>
<td>Orange liquid</td>
<td>112/0.1</td>
</tr>
<tr>
<td>Ti(NPr₂)₂</td>
<td>Red liquid</td>
<td>150/0.1</td>
</tr>
<tr>
<td>Ti(NBu₂)₂</td>
<td>Red liquid</td>
<td>170/0.1</td>
</tr>
<tr>
<td>Zr(NMe₂)₂</td>
<td>White solid (mp 70°)</td>
<td>80/0.05</td>
</tr>
<tr>
<td>Zr(NPr₂)₂</td>
<td>Green liquid</td>
<td>120/0.1</td>
</tr>
<tr>
<td>Zr(NBu₂)₂</td>
<td>Green liquid</td>
<td>165/0.1</td>
</tr>
<tr>
<td>Zr(NBu₂)₄</td>
<td>Green solid</td>
<td>180/0.1 (sublimes)</td>
</tr>
</tbody>
</table>

Some tetrakis-(diethylamino)-titanium and -zirconium compounds

Only in the case of Zr(NMe₂)₄ was there any evidence of polymerization at the boiling point of benzene and it is noteworthy that the compound is significantly less volatile than the corresponding titanium derivative. From a consideration of the steric effects demonstrated in the aminolysis of these tetrakis-(diethylamino)-derivatives it was deduced that the absence of polymerization was a consequence of the powerful shielding of the central atom by the dialkylamino groups. In the aminolysis reactions an excess of a higher boiling amine was added to the tetrakis-(diethylamino)-derivative and the liberated lower boiling amine was fractionated off until it appeared that the reaction was complete. The extent of these reactions is shown in the following equations.

\[
\begin{align*}
\text{Ti(NMe}_2\text{)}_4 + \text{Et}_2\text{NH} &\rightarrow \text{Ti(NMe}_2\text{)(NMe}_2\text{)}_3, \text{ (bp. 95°/0.05 mm.)} \quad (2) \\
\text{Ti(NMe}_2\text{)}_4 + \text{Pr}_2\text{NH} &\rightarrow \text{Ti(NMe}_2\text{)(NPr}_2\text{)}_3, \text{ (bp. 135°/0.05 mm.)} \quad (3) \\
\text{Ti(NMe}_2\text{)}_4 + \text{Bu}_2\text{NH} &\rightarrow \text{Ti(NMe}_2\text{)(NBu}_2\text{)}_3, \text{ (bp. 170°/0.1 mm.)} \quad (4) \\
\text{Ti(NMe}_2\text{)}_4 + \text{Piperidine} &\rightarrow \text{Ti(NC}_2\text{H}_4\text{)}_4, \text{ (bp. 180°/0.1 mm.)} \quad (5) \\
\text{Ti(NMe}_2\text{)}_4 + 2\text{-methyl piperidine} &\rightarrow \text{Ti(NMe}_2\text{)(NC}_2\text{H}_5\text{Me})_3, \text{ (bp. 160°/0.1 mm.)} \quad (6) \\
\text{Ti(NMe}_2\text{)}_4 + 2,6-\text{dimethyl piperidine} &\rightarrow \text{Ti(NMe}_2\text{)(NC}_2\text{H}_5\text{Me})_3, \text{ (bp. 120°/0.05 mm.)} \quad (7) \\
\text{Ti(NMe}_2\text{)}_4 + \text{Piperidine} &\rightarrow \text{Ti(NC}_2\text{H}_5\text{)}_4, \text{ (bp. 190°/0.05 mm.)} \quad (8) \\
\text{Zr(NMe}_2\text{)}_4 &\rightarrow \text{Zr(NMe}_2\text{)}_4 \quad (9)
\end{align*}
\]

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The above reactions are readily interpreted as controlled by steric factors. For example in the case of titanium compounds it is clear that the dimethylamino-groups in Ti(NMe₂)₄ are equally replaced by diethylamino-, di-n-propylamino-, or di-iso-butylamino-groups although the experimental conditions were not strictly comparable. However, when di-isopropylamine was used only a small amount of Ti(NMe₂)₂(NPr₃)₂ was formed in a reaction lasting 6 days. Even more striking was the behaviour of piperidine, 2-ethyl piperidine, and 2,6-dimethyl piperidine. In the reaction with piperidine all of the dimethylamino-groups were replaced because piperidine exerts a smaller steric effect than the di-n-alkylamino-groups (excepting Me₂N). When 2-methyl piperidine was used substitution was limited to the formation of Ti(NMe₂)(NC₃H₇Me)₂ whilst with 2,6-dimethyl piperidine steric hindrance to substitution was so powerful that only one dimethylamino-group could be replaced. Nevertheless, it was evident that the steric effect of di-isopropylamine was greater than that of 2,6-dimethyl piperidine. The behaviour of tetraakis(dimethylamino)-zirconium was also in accordance with steric control of substitution. It would be predicted that the zirconium atom being larger than titanium would cause Zr(NMe₂)₄ to be more prone to nucleophilic reagents than Ti(NMe₂)₄. The velocity of this prediction was well established by the fact that complete substitution of dimethylamino-groups was achieved by Et₂N⁺, Pr⁴⁺, and Bu₃N⁺ groups in the case of zirconium in contrast to trisubstitution in the case of titanium. The complete substitution of dimethylamino-groups attached to zirconium by piperidine, 2-methyl piperidine, or 2,6-dimethyl piperidine emphasizes the importance of steric effects in these reactions. Only in the reaction of di-isopropylamine with Zr(NMe₂)₄ was it restricted to disubstitution there, evidence of steric hindrance to substitution of tetraakis(dimethylamino)-zirconium. On the other hand it would be expected that the greater steric effect of diethylamino-groups would lead to greater steric hindrance to substitution of Zr(NEt₂)₄. This was strikingly proved in the reaction with di-isopropylamine which was confined to mono-substitution.

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2. Derivatives of Primary amines.

When either $\text{Ti}(\text{NMMe}_2)_4$ or $\text{Ti}(\text{NHBu}_2)_4$ were treated with excess of the primary amine $\text{NR}_2$, where $R = \text{Ph}^t$, $\text{Ph}^t$, $\text{Bu}^t$, $\text{Bu}^t$, $\text{Bu}^s$, or cyclohexyl, a coloured solid approximating to the limiting formula $\text{Ti}(\text{NR})_2$ was formed. The colours ranged from orange through red to brown and the compounds were practically insoluble and non-volatile. These properties suggested that the compounds were highly polymeric due to metal-nitrogen bridges ($\text{Ti}$). It is clear that the primary amines are behaving as bifunctional reactants in the aminolysis:

$$\text{Ti}(\text{NMMe}_2)_4 + 2\text{NR}_2 \rightarrow [\text{Ti}(\text{NR})_2]_4 + 4\text{Me}_2\text{NH} \quad \text{(17)}$$

The primary amino-derivatives were all readily hydrolysed or alcoholysed.

When $\text{Ti}(\text{NMMe}_2)_4$ was treated with excess tertiary butylamine only displacement occurred with the formation of the dimer $\text{Ti}_2(\text{NMMe}_2)_2(\text{NHBu}^t)_2$, which probably has the formula (III):

$$[\text{Me}_2\text{N}]_2 \quad \text{III}$$

Once again it appeared that steric factors controlled the extent of the reaction. Prolonged treatment of (III) with excess of tertiary butylamine failed to produce any higher polymers although some replacement of dimethylamino-groups took place. Instead the volatile (sublimes $140-150^\circ$ C, 0.1 mm.) deep red solid dimer $\text{Ti}_2(\text{NMMe}_2)_2(\text{NHBu}^t)_2$ was obtained which may well have structure (IV):

$$[\text{Me}_2\text{N}]_2 \quad \text{IV}$$

In the reactions involving $\text{Ti}(\text{NHBu}_2)_4$ and $\text{p}$-butylamine it was possible to isolate a number of soluble polymers of the general formula $\text{Ti}_n(\text{NHBu}^t)_2\text{en}_{n-2}(\text{NHBu}_2)_4$.

$$n\text{Ti}(\text{NHBu}_2)_4 + (2n-2)\text{Bu}^t\text{NH}_2 \rightarrow \text{Ti}_n(\text{NHBu}^t)_2\text{en}_{n-2}(\text{NHBu}_2)_4 + (4n-4)\text{Et}_2\text{NH} \quad \text{(18)}$$

It is believed that these compounds are polymers involving tetrahedrally 4-coordinated titanium with terminal $\text{Et}_2\text{N}$- groups acting as chain stoppers as in (V).

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These products were dark red non-voluble solids and polymers containing 6, 14, 16 and ca 100 titanium atoms per molecule were obtained.

A significant result was obtained from the reaction involving Ti(NEt₂)₄ and aniline. A black microcrystalline non-volatile solid corresponding in analysis to Ti(NC₆H₅)₄ remained after drying at 215°C/0.1 mm. It was most interesting to find that this compound was noticeably less readily hydrolysed than any of the aliphatic primary amino-derivatives.

3. Tris-(diethylamino)-titanium (III).

From the reaction involving titanium trichloride and lithium diethylamine a brown liquid was obtained. From the analysis it was deduced that the compound was substantially the tervalent titanium derivative Ti(NEt₂)₃ containing some coordinated amine. When heated under reduced pressure the compound disproportionated to give tetrakis-(diethylamino)-titanium (IV) and left a non-volatile residue containing lower valency compounds of titanium.

Vanadium, Niobium and Tantalum Compounds

1. Vanadium Compounds.

Vanadium tetrachloride reacted with lithium dialkylamides to form tetrakis-(dialkylamino)-vanadium (IV) derivatives. For example, V(NEt₂)₄ was obtained as a green solid (mp. 40°C; bp. 60°C/1.0 mm.) and V(NEt₃), was a dark green liquid (bp. 110°C/0.05 mm.). Alcoholysis of the tetrakis-(dialkylamino)-vanadium derivatives afforded the vanadium tetraalkoxides.

Vanadium trichloride reacted with lithium diethylamine to form a dark brown liquid which was substantially tris-(diethylamino)-vanadium (III) with some coordinated diethylamine. This product resembled the corresponding titanium compound by undergoing disproportionation when heated in vacuo.

2. Niobium Compounds.

Studies of the reactions of niobium pentachloride with lithium dialkylamides led to some interesting results. In the case of lithium dimethylamide the product was substantially pentakis-(dimethylamino)-niobium (V) with <10% of quadrivalent niobium present. The pure Nb(NMe₂)₅ was isolated by vacuum sublimation. With the higher dialkylamides the amount of quadrivalent niobium in the crude products increased steadily with length of the alkyl chain (i.e. Et₃, 60%; Pr₃, 85%; Bu₃, 91% reduction). In each case the tetrakis-(dialkylamino)-niobium (IV) compound was obtained by vacuum distillation. Some data on niobium compounds are given in Table 2.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Appearance</th>
<th>Boiling point (°C/mm.Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb(NMe₂)₃</td>
<td>Brown solid</td>
<td>sublimes 100/0.1</td>
</tr>
<tr>
<td>Nb(NMeBu)₃</td>
<td>Red liquid</td>
<td>decomp. 150/0.1</td>
</tr>
<tr>
<td>Nb(NC₅H₄Me)₂</td>
<td>Yellow crystals</td>
<td>decomp. 170/0.1</td>
</tr>
<tr>
<td>Nb(NC₅H₄Me)₃</td>
<td>Brown liquid</td>
<td>120/0.1</td>
</tr>
<tr>
<td>Nb(NPr₂)₃</td>
<td>Red liquid</td>
<td>155/0.1</td>
</tr>
<tr>
<td>Nb(NBu₂)₃</td>
<td>Red liquid</td>
<td>175/0.1</td>
</tr>
<tr>
<td>Nb(NBuMe)₃</td>
<td>Red liquid</td>
<td>150/0.1</td>
</tr>
<tr>
<td>Nb(C₂H₅O)₃</td>
<td>Brown liquid</td>
<td>decomp. 170/0.1</td>
</tr>
</tbody>
</table>

**Table 2**

Some Alkylamino-niobium Compounds.

We have interpreted the breakdown of pentakis-(diethylalaminio)-niobium (V) compounds as being caused by steric compression within the molecules. Obviously the intramolecular compression will become more severe as the size of the di-n-alkylamino- group is increased. This is in accord with the increasing percentage of Nb(IV) found in the initial products from the NbCl₅-LAN₃ reactions. This view is also supported by the additional facts that pentakis-derivatives were also obtained with N-methyl-n-butylamino- and piperidino- groups. Our work on titanium and zirconium compounds showed very clearly that the steric effect of the piperidino- group was significantly less than that of the diethylamino- and higher di-n-alkylamino- groups. Moreover, there can hardly be any doubt that the steric effect of the MeBuN₄- group must be less than that for diethylamino- groups because the methyl group being small allows the n-buty1 group to bend away from the centre of the Nb(NMeBu)₃ molecule.

Further evidence for the existence of powerful steric effects was forthcoming from some reactions involving Nb(NMe₂)₃ and diethyldiamine. In one case the reagents were maintained at the boiled point of diethyldiamine for 2 hours and the liberated dimethyldiamine was fractionated off. No reduction of niobium occurred but aminolysis was restricted to disubstitution.

\[
\text{Nb(NMe₂)₃} + 2\text{Et₂NH} \rightarrow \text{Nb(NMe₂)₂(NEt₂)₂} + 2\text{Et₂NH}
\]

In another experiment continued for 9 days the replacement of dimethylamino-groups was still incomplete and about 30% reduction of niobium occurred. Distillation of the product gave the quadravalent compound Nb(NMe₂)(NEt₂₂) as a red liquid (bp. 125°/0.1 mm). Evidently the niobium can accommodate three dimethylamino- and two diethyldiamino- groups but the introduction of the third or fourth diethyldiamino- groups leads to instability.

3. Thermal decomposition of pentakis-(diethylamino)-niobium compounds.

The formation of tetrakis-(diethylamino)-niobium (IV) compounds by thermolysis of the pentakis-(diethylamino)-niobium (V) is extremely interesting and raises the question of mechanisms. Although the mechanism of the thermolysis has not yet been studied some useful observations may be made. Thus it was noticed that secondary amines was also liberated in the reaction and this suggests that the diethylamino-radical is involved in hydrogen abstraction. The following equations suggest possible mechanisms for the thermolysis.
\[ \text{Nb}[\text{N}(\text{C}_6\text{H}_5)_2]_5 \rightarrow \text{Nb}[\text{N}(\text{C}_6\text{H}_5)_2]_4 + (\text{C}_6\text{H}_5)_2\text{N} \]  

\[ 2(\text{C}_6\text{H}_5)_2\text{N} \rightarrow (\text{C}_6\text{H}_5)_2\text{NH} + \text{CH}_3\text{CH} = \text{C} = \text{NH} \]  

An interesting feature of the thermolysis of \( \text{Nb}(\text{NMeBu}^I)_5 \) was the formation of \( \text{Bu}^N\text{Nb}(\text{NMeBu}^I)_3 \) in addition to \( \text{Nb}(\text{NMeBu}^I)_6 \). This was the only case in which the quinquevalent \( \text{RN}^\text{III} \text{Nb}(\text{NMe})_5 \) was found because there was no evidence for the formation of such compounds in the thermolysis of the dialkyaminoderivatives.

4. Tantalum Compounds.

The reactions of tantalum pentachloride with various lithium dialkylamides \( \text{Li} \) \( X \), where \( X = \text{NMe}_{2}, \text{NEt}_{2}, \text{NP} \text{Pr}^I, \text{NMeBu}^I \) and \( \text{N} \text{C} \text{H} \text{Cl} \), were studied. From these reactions the corresponding pentakis-derivatives were obtained, in contrast to the behaviour of niobium pentachloride. However, only the pentakis-dimethylamino-derivative \( \text{Ta}(\text{NMe})_5 \) could be sublimed without decomposition and this calls to mind the behaviour of \( \text{Nb}(\text{NMe})_5 \). When the higher pentakis-(dialkyaminol) compounds of tantalum were heated in vacuo thermolysis took place with the formation of substantially the interesting quinquevalent compounds \( \text{RN}^\text{III} \text{Ta}(\text{NR}^\text{III})_3 \) together with some tetraakis-(dialkyaminol)-tantalum (IV). Some data on the tantalum compounds are presented in Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Appearance</th>
<th>Boiling point (°C/mm.Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ta}(\text{NMe})_5 )</td>
<td>Yellow crystals</td>
<td>sublimes 100/0.1</td>
</tr>
<tr>
<td>( \text{EtN-Ta(NR}^\text{III})_3 )</td>
<td>Yellow liquid</td>
<td>120/0.1</td>
</tr>
<tr>
<td>( \text{Pr}^\text{III} \text{N-Ta(NPr}^I)_3 )</td>
<td>Orange liquid</td>
<td>150/0.1</td>
</tr>
<tr>
<td>( \text{Bu}^N \text{N-Ta(NBu}^I)_3 )</td>
<td>Yellow liquid</td>
<td>180/0.1</td>
</tr>
<tr>
<td>( \text{Ta(NC} \text{H} \text{Cl})_5 )</td>
<td>Yellow solid</td>
<td>-</td>
</tr>
<tr>
<td>( \text{Bu}^N \text{N-Ta(NMeBu}^I)_3 )</td>
<td>Orange liquid</td>
<td>decomp. 160/0.1</td>
</tr>
<tr>
<td>( \text{Ta(NMeBu}^I)_5 )</td>
<td>Red liquid</td>
<td>150-155/0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>155-180/0.1</td>
</tr>
</tbody>
</table>

Some Alkyllamino-compounds of Tantalum.

The detailed mechanism of the formation of the quinquevalent derivatives \( \text{RN}^\text{III} \text{Ta}(\text{NR}^\text{III})_3 \) is as yet obscure but from product analysis it appears that secondary amine and olefin are also produced in the thermolysis of \( \text{Ta}(\text{NR}^\text{III})_5 \) compounds. We suggest as a tentative explanation that the pentakis-derivative dissociates to the tetraakis-derivative and a dialkyaminol radical.

\[ \text{Ta(NR}^\text{III})_5 \rightarrow \text{Ta(NR}^\text{III})_4 + \text{R}_2\text{N} \]  

Further it is suggested that the quadrivalent tantalum compound is so unstable that it reacts with the radical before the latter becomes "free". A possible sequence would be hydrogen abstraction by the radical followed by the elimination of olefin.

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\[
\text{(Bu}_3\text{N})_2\text{Ta-N}^+\text{Bu}^+ + \text{Bu}_3\text{N}^- \rightarrow \text{(Bu}_3\text{N})_2\text{Ta-N}^+\text{Bu}^+ + \text{Bu}_3\text{NH}
\]

\[
\text{(Bu}_3\text{N})_2\text{Ta}=\text{NR}^+\text{Bu}^+ \rightarrow \text{(Bu}_3\text{N})_2\text{Ta-N}^+\text{Bu}^+ + \text{CH}_2=\text{CH}_2\text{Bu}^+ \rightarrow \text{(Bu}_3\text{N})_2\text{Ta-N}^+\text{Bu}^+ + \text{CH}_2=\text{CH}_2\text{NH}
\]

The thermalysis of Ta(NMeBu)\text{NR}_2 was of added interest because of the choice of alkyl groups attached to the nitrogen. The formation of Ta(NMeBu)\text{NR}_2 and Bu\text{NR}_2Ta(NMeBu)\text{NR}_2 suggest that a methyl group in Ta(NMeBu)\text{NR}_2 is preferentially attacked by the N-methyl-N-butylamino-radical. It is pertinent to examine the evidence on which the formula for the R\text{NR}_2Ta(NR)_2 derivatives is based. Firstly there is the analytical data for tantalum and nitrogen. However, the analytical figures for R\text{NR}_2Ta(NR)_2 are fairly near to those for Ta(NR)_2. The second factor is the determination of the average valency of the tantalum by a chemical method. This ruled out the quadrivalent formula Ta(NR)_2. The third and decisive piece of evidence was forthcoming from the identification of the primary amine R\text{NH}_2 in addition to the secondary amine among the products of alcoholysis.

\[
\text{R\text{NR}_2Ta(NR)_2 + 5ROH} \rightarrow \text{Ta(OR)_5 + R\text{NH}_2 + 3ROH}
\]

However, there remains the possibility that the compound is the dimer Ta\text{NR}_2(NR)_2 with a double primary amino-bridge as in (VI).

\[
(\text{R}_3\text{N})_2\text{Ta} = \text{NR}_2\text{NR}_2
\]

(VI)

The dimeric structure (VI) was ruled out by the volatility of the compounds which were close to the volatilities of the monomeric tetraakis-(dialkylamino)-niobium (IV) compounds. Consequently we assign the monomeric formula R\text{NR}_2Ta(NR)_2, which contains the metal-nitrogen n-bond.

**Chromium, Molybdenum and Tungsten Compounds**

When chromium trichloride was treated with lithium diethylamide a small yield of tris-(diethylamino)-chromium (III) was ultimately obtained as a volatile (bp. 900/0.1 mm.) green liquid.

From the reaction involving molybdenum pentachloride and lithium diethylamide a very small yield of substantially pure tetakis-(diethylamino)-molybdenum (IV) was obtained as a volatile (bp. 1100/0.1 mm.) violet liquid.

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From molybdenum trichloride an impure tris-(diethylamino)-molybdenum (III) was obtained as a non-volatile brown gum.

When tungsten hexachloride was allowed to react with lithium diethylamido some tetrakis-(diethylamino)-tungsten (IV) was obtained as a volatile (bp. 120°/0.1 mm.) red liquid. All of these chromium, molybdenum and tungsten compounds were readily hydrolysed.

References
6 Bradley, D.C., and Thomas, I.M., to be published.