AFML-TR-65-131

AD0623088

C-116

ORGANOMETALLIC COMPOUNDS AND POLYMERS BASED ON METAL-NITROGEN BOND SYSTEMS

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TECHNICAL REPORT AFML-TR-65-131

JULY 1965

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

20040301 039

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FOREWORD

This report was prepared by the University of Western Ontario under USAF Contract No. AF 33(615)-1324. This contract was initiated under Project No. 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena," Task No. 734201, "Basic Factors in the Synthesis of Macromolecular Materials". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Dr. Harold Rosenberg acting as Project Engineer.

This report covers work carried out during the year January 1st to December 31st 1964.

The experimental work was carried out by Dr. J. S. Basi, Dr. M. Howarth and Dr. S. C. Jain.

The manuscript of this report was released by the authors March 1965 for publication as an RTD Documentary Report.

This technical report has been reviewed and is approved.

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ABSTRACT

From the reaction of primary alkyl amines, with tris-(diisopropylamino)-chromium (III) the tris-(alkylamino)-chromium (III) compounds, $Cr(NHR)_3$, were obtained as pink or red, insoluble, non-volatile solids which were significantly resistant to hydrolysis. Magnetic susceptibility measurements revealed anomalously low magnetic moments μ_{eff} 2.0-2.4 B.M.) indicative of magnetically concentrated chromium atoms. It is suggested that these compounds are metal-nitrogen co-ordination polymers with octahedrally-co-ordinated chromium. With branched chain primary amines entirely different products were obtained due to steric factors.

Reactions between tetrakis-(dimethylamino)-titanium, -zirconium, or -hafnium with nickel, iron, molybdenum or tungsten carbonyls gave interesting polymeric heterometalcarbonyldimethylamides. Reactions of aniline with tetrakis-(diethylamino)-titanium or tetrakis-(diethylamino)-zirconium gave soluble polymeric compounds.

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I. INTRODUCTION

This report describes the work carried out on the synthesis of metallo-organic polymers containing metal-nitrogen bonds as a continuation of previous studies supported by Contracts AF 61-(052)-174[1], AF 33-(616)-6934[2,3] and AF 33-(657)-7675[4].

The initial work involved the synthesis of <u>tetrakis</u>-(dialkylamino)-titanium and zirconium compounds[5,6] by means of reactions between the appropriate metal chloride and lithium dialkylamide.

$$MCl_4(M = Ti, Zr) + 4LiNR_2(R = Me, Et, \underline{n}\text{-}Pr, \underline{n}\text{-}Bu) \longrightarrow 4LiCl + M(NR_2)_4 \quad \ldots\ldots\ldots\ldots \quad (1)$$

The new compounds, $M(NR_2)_4$, were very reactive towards water and hydroxylic compounds in general.

$$M(NR_2)_4 + 4R'OH \longrightarrow M(OR')_4 + 4R_2NH \quad \ldots\ldots\ldots \quad (2)$$

With the exception of <u>tetrakis</u>-(dimethylamino)-zirconium, $Zr(NMe_2)_4$, which had a degree of polymerization of 1.22 in boiling benzene, these compounds were monomeric and could be distilled <u>in vacuo</u>. The absence of polymerization suggested that steric hindrance was preventing the close approach of monomers and thus opposing the formation of intermolecular metal-nitrogen bonds. This view was supported by the behaviour of the dialkylamino-compounds when subjected to aminolysis.[6]

$$M(NR_2)_4 + 4HNR'_2 \longrightarrow M(NR'_2)_4 + 4HNR_2 \quad \ldots\ldots\ldots \quad (3)$$

In certain cases it was found that reaction (3) would not proceed to completion and products such as $M(NR_2)_x(NR'_2)_{4-x}$ were obtained which could be distilled <u>in vacuo</u>.

When niobium pentachloride was treated with lithium dimethylamide the new <u>pentakis</u>-(dimethylamino)-niobium (V) was obtained.[7]

$$NbCl_5 + 5LiNMe_2 \longrightarrow Nb(NMe_2)_5 + 5LiCl \quad \ldots\ldots\ldots \quad (4)$$

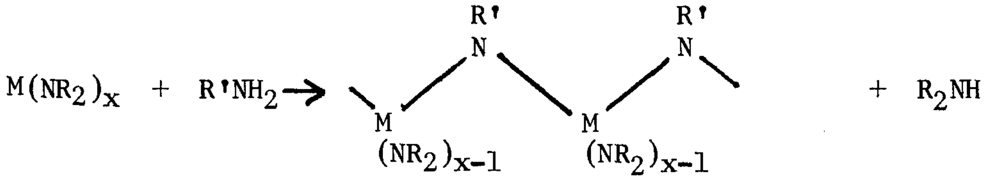
This compound was also highly reactive towards hydroxylic compounds and it could be sublimed <u>in vacuo</u>. However, extension of this reaction to the preparation of higher dialkylamino derivatives gave some unexpected results.

The products of reaction contained significant proportions of quadrivalent niobium and distillation afforded the tetrakis-(dialkylamino)-niobium (IV) compounds. The formation of tetrakis-(dialkylamino)-niobium (IV), $Nb(NR_2)_4$, was ascribed to instability of pentakis-(dialkylamino)-niobium (V), $Nb(NR_2)_5$ due to steric compression of the higher dialkylamino groups. This view was supported by the isolation of the pentakis-compounds derived from methyl-n-butylamine and from piperidine, in addition to pentakis-(dimethylamino)-niobium, $Nb(NMe_2)_5$. In these cases the steric hindrance of the ligands is much less than in the higher dialkylamino groups. Not surprisingly, aminolysis reactions gave mixed dialkylamino compounds, $Nb(NR_2)_x(NR'_2)_{(5-x)}$ and $Nb(NR_2)_y(NR'_2)_{(4-y)}$.

Similarly, from reactions involving lithium dialkylamides and tantalum pentachloride, pentakis-derivatives were obtained with dimethylamino, methyl-n-butylamino, and piperidino groups. However, with the lithium dialkylamides of the higher dialkylamines the reaction with tantalum pentachloride differed from that with niobium pentachloride. In the case of tantalum impure pentakis-derivatives were isolated which upon distillation afforded the remarkable new mono-(alkylimino)-tris-(dialkylamino)-tantalum (V) compounds, $Ta(NR)(NR_2)_3$.[8] These compounds were of special interest not only because of their unusual mode of formation but also because they contain the formal double bond between tantalum and nitrogen.

When manganese (II), iron (III), cobalt (II), and nickel (II) chlorides were treated with lithium diethylamide it was not found possible to isolate pure metal diethylamides but on heating the products volatile metallo-organic compounds of a novel kind were isolated. In the case of cobalt a compound with the formula $CoN_4C_{16}H_{32}$ was obtained and its infrared, ultraviolet, and visible absorption spectra were recorded. The compound was monomeric and its paramagnetic susceptibility (3 unpaired electrons per Co) agreed with the presence of bivalent cobalt in the tetrahedral configuration. The formation of such a compound starting from diethylamide groups is of considerable academic interest.

So far the work described has resulted in the formation of monomeric molecules but these were synthesized with the view to using them as building blocks for polymers. One obvious method of polymerization is to replace the secondary amino group by a primary amino group which can act as a bridge between two metal atoms as shown in equation (5).



. . . . (5)

In this case polymerization is by primary bond formation in the metal-nitrogen bridge but this might be augmented by co-ordination polymerization. In experiments involving tetrakis-(dialkylamino)-titanium and primary amines reaction proceeded with the formation of insoluble, non volatile bis-(monoalkylamino)-titanium compounds $Ti(NR)_2$.[9]

$$Ti(NR_2)_4 + 2R'NH_2 \longrightarrow 1/n[Ti(NR')_2]_n + 4R_2NH \quad \ldots\ldots\ldots (6)$$

It was concluded that these products were highly polymeric although they were also highly reactive towards hydroxylic compounds. However, it was noteworthy that, whereas the *bis*-derivative of cyclohexylamine was highly reactive, the corresponding *bis*-(anilino)-titanium was relatively unreactive and not readily hydrolysed. This difference in behaviour was attributed to the presence of π-electrons in the aromatic ring. With this factor in mind it was decided to try the effect of a cyclic amine in which the nitrogen was actually part of the aromatic ring. Thus, the secondary amine, pyrrole (C_4H_4NH), was caused to react with *tetrakis*-(dialkylamino)-titanium compounds and gave some rather interesting results. When excess pyrrole was used a black insoluble product was obtained which seemed to consist of polymeric pyrrole containing some titanium. The compound was quite resistant to chemical attack and a satisfactory analysis has not yet been obtained for it. When very mild conditions were employed it proved possible to isolate *bis*-(pyrrolyl)-*bis*-(dialkylamino)-titanium compounds, $Ti(NC_4H_4)_2(NR_2)_2$, (where R = Me, Et, *n*-Pr, *n*-Bu).

$$Ti(NR_2)_4 \; + \; 2C_4H_4NH \longrightarrow Ti(NC_4H_4)_2 \; + \; 2R_2NH \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (7)$$

There seemed to be a definite preference for disubstitution to take place and it was also found that in aminolysis reactions the dialkylamino groups were replaceable but not the pyrrolyl groups.

$$Ti(NC_4H_4)_2(NR_2)_2 \; + \; 2R'_2NH \longrightarrow Ti(NC_4H_4)_2(NR'_2)_2 \; + \; 2R_2NH \; . \; . \; . \; . (8)$$

The preferential formation of the *bis*-pyrrolyl-derivative raises the possibility that the pyrrole groups are π-bonded to the titanium as in *bis*-(π-cyclopentadienyl)-derivatives. Unfortunately these compounds were not very stable so their interest is mainly academic.

In the reactions involving primary amines and *tetrakis*-(diethylamino)-titanium it was found that with *n*-butylamine some soluble polymeric products, $Ti_x(NBu)_{(2x-2)}(NEt_2)_4$, were obtained.[9] However, with tertiary butylamine a volatile, dimeric product, $Ti_2(NMe_2)_2(NCMe_3)_2(HNCMe_3)_2$, was isolated although a large excess of tertiary butylamine was employed. This behaviour was considered indicative of the importance of steric factors in controlling the formation of polymers.

Preliminary experiments[4] using primary amines and *tris*-(diisopropylamino)-chromium (III) gave insoluble non-volatile products which appeared to be polymeric *tris*-(monoalkylamino)-chromium (III) compounds, $[Cr(NHR)_3]_n$, in which the primary amine behaves as a monofunctional group.

Another remarkable discovery in the previous work was the formation of addition compounds between *tetrakis*-(dimethylamino)-titanium and either nickel tetracarbonyl or iron pentacarbonyl. These products were surprisingly unreactive and seemed worthy of further study.

Work on the current contract has continued in three main areas:- (i) further investigation of *tris*-(monoalkylamino)-chromium (III), $[Cr(NHR)_3]_n$, polymers; (ii) further work on the metal dimethylamide-metal carbonyl polymers; (iii) controlled aminolysis of *tetrakis*-(dialkylamino)-titanium compounds using aniline.

II. RESULTS AND DISCUSSION

A. Reactions involving tris-(diisopropylamino)-chromium (III) and Primary amines.

In a previous Report[4] we described the reaction of tris-(diisopropylamino)-chromium with n-propyl-, i-propyl-, n-butyl-, isobutyl-, and t-butylamines. In some cases pink, insoluble compounds, $Cr(NHR)_3$ (where R = n-propyl, n-butyl, isobutyl), were obtained which were relatively unreactive. With isopropylamine or t-butylamine the replacement of diisopropylamino groups was incomplete and soluble, black products were obtained which were highly reactive. This work has been extended by carrying out reactions with liquid ammonia, methylamine, ethylamine, and n-amylamine. The products were either pink or red and required heating in vacuo to remove addended amine. The following series of compounds, $Cr(NHR)_3$, where R = H, Me, Et, n-Pr, n-Bu, i-Bu, n-Am, are thus known. A striking feature is that all of these compounds contain alkylamino, NHR, groups bonded to chromium in contrast to the behaviour shown by titanium which replaces both NH-hydrogens of a primary alkylamine, RNH_2. The chromium compounds were all insoluble in common organic solvents and were non-volatile and it is concluded that they are highly polymeric. Moreover, they were apparently unaffected by cold water in contrast to the titanium compounds, $[Ti(NR)_2]_n$, which were very vigorously hydrolysed. The chromium compounds were hydrolysed by hot water and were dissolved by dilute sulphuric acid. The low reactivity towards water suggests that the chromium is octahedrally co-ordinated by nitrogen and this would result in a polymeric structure.

Magnetic susceptibility measurements showed that the compounds were paramagnetic but the magnetic moments of the chromium atoms were in the range 2.0-2.4 Bohr Magnetons which is anomalously low for chromium (III) (spin only value for d^3 ion is 3.87 B.M.). It was concluded that the polymeric nature of these compounds with chromium-nitrogen bridges brought the chromium atoms sufficiently close for spin-interaction to occur between the d-electrons on adjacent chromium atoms. Infrared spectra on the tris-(monoalkylamino)-chromium(III), compounds confirmed the presence of NH bonds.

Entirely different products were obtained from the reactions involving isopropylamine, sec-butylamine or t-butylamine with tris-(diisopropylamino)-chromium. The replacement of diisopropylamine was incomplete and the dark brown products were soluble in hexane and extremely reactive in striking contrast to the properties of the pink tris-(monoalkylamino)-chromium(III), $Cr(NHR)_3$, compounds. The ease of oxidation and hydrolysis of the dark brown compounds precluded accurate analyses and prevented the determination of reliable molecular weights or magnetic susceptibilities. However, it is believed that the dark brown compounds have the formula $(\underline{i}\text{-Pr})_2NCrNR$ and are probably dimers or tetramers. The high chemical reactivity suggests that the chromium is not 6-coordinated in these compounds and there is little doubt that this is due to the steric hindrance to polymerization caused by the branched chain primary amines (cf. behaviour of titanium[9]).

B. The preparation of Heterometalcarbonyldialkylamides.

Further work on reactions between dialkylaminometal compounds and metal carbonyls[4] has shown that the combination of these compounds is general and leads to the formation of polymeric heterometalcarbonyldialkylamides, $M_aM_b(CO)_c(NR_2)_d$. With but few exceptions reaction appears to occur without displacement of carbon monoxide and this is very remarkable. Owing to analytical problems the formulae of these compounds are not all known with certainty. Most of these new compounds are surprisingly unreactive considering the high chemical reactivity of the compounds from which they were formed. Unfortunately these compounds are all insoluble in common organic solvents and it is thus difficult to determine structural information. However, in most cases infrared spectra and magnetic susceptibilities have been determined.

It has been found that the *tetrakis*-(dimethylamino)-derivatives of titanium, zirconium and hafnium each react with either nickel tetracarbonyl, iron pentacarbonyl, molybdenum hexacarbonyl or tungsten hexacarbonyl. A number of the new compounds were found to be paramagnetic although all the reactants were diamagnetic. Evidently some profound changes have occurred in these reactions. Some properties of these new materials are listed in Table 1.

Table 1

HETEROMETALCARBONYLDIALKYLAMIDES

Probable Formula	Colour	Action of Heat	Magnetic Susceptibility
$Ti(NMe_2)_4.2Ni(CO)_4$	Brown	Begins decomposing at 150° does not melt	1.7 B.M.
$Ti(NMe_2)_4.2Fe(CO)_5$	Red-brown	Not investigated	-
$Ti(NMe_2)_4.Mo_3(CO)_6$ *	Brown	Fuses at 145-155°	0.5 B.M.
$Ti(NMe_2)_4.W_2(CO)_4$ *	Brown	Not investigated	1.4 B.M.
$Zr(NMe_2)_4.2Ni(CO)_4$	Brown	Blackens at 140-150°, does not melt	1.7 B.M.
$Zr(NMe_2)_4.2Fe(CO)_5$	Brown	Darkens above 100°, does not melt	1.7 B.M.
$Zr(NMe_2)_4.Mo(CO)_6$	Yellow	Blackens at 250°, does not melt	0.5 B.M.
$Zr(NMe_2)_4.W(CO)_6$ *	Yellow	Darkens at 250°, does not melt	Diamag.

$Hf(NMe_2)_4.2Ni(CO)_4$	Brown	Darkens at 140-150°, does not melt	1.5 B.M.
$Hf(NMe_2)_4.2Fe(CO)_5$	Brown	Darkens at 200°, does not melt	1.4 B.M.
$Hf(NMe_2)_4.2Mo(CO)_6$	Yellow	Darkens at 160-200°, does not melt	Diamag.

* Analysis incomplete and unreliable.

A significant feature of these results is the preponderance of compounds of the general formula $M(NMe_2)_4.2M'(CO)_x$. It seems possible that pairs of dimethylamino groups attached to the metal, M, are also co-ordinated to the other metal, M', but there are several ways in which this and other changes may occur and the present physical evidence does not discriminate. Several plausible polymeric structures were indicated in the previous Report[4] and there is nothing further which can be usefully added at this juncture. However, it is clear that these fascinating compounds deserve further investigation.

C. Titanium and Zirconium Polymers containing Anilino groups.

When excess of aniline was added to tetrakis-(dimethylamino)-titanium a black, insoluble bis-(anilino)-titanium compound was isolated[9] which was of interest because of its relatively high resistance towards hydrolysis compared to that of the polymers, $[Ti(NR)_2]_n$(where R = aliphatic group). It seemed worthwhile to attempt the preparation of lower polymers, $Ti_x(NC_6H_5)_{(2x-2)}(NEt_2)_4$, by means of reactions involving aniline and tetrakis-(diethylamino)-titanium. Experiments were carried out with molar ratios of 1 : 1 and 1 : 2 (aniline:titanium compound). In both cases the non-volatile residue remaining after evaporation of the solvent and drying at 200°C *in vacuo* was a shiny black compound which was soluble in benzene, cyclohexane, methylene chloride and carbon tetrachloride. In the case of the 1 : 2 molar ratio about half of the tetrakis-(diethylamino)-titanium originally taken was recovered as a distillate and hence the titanium residue in fact resulted effectively from a 1 : 1 molar ratio reaction. The analytical results for the two products were similar as shown in Table 2.

Table 2

ANILINO-TITANIUM COMPOUNDS

Molar Ratio $C_6H_5NH_2:Ti(NEt_2)_4$	%Ti	%N	%C	%H	Mol.Wt.
1 : 1	20.5	12.4	50.1	6.32	1100
1 : 2	23.0	12.3	46.2	6.14	2100
Calc. for $Ti(NC_6H_5)_2$	20.8	12.2	62.6	4.38	-
Calc. for $Ti(NC_6H_5)(NEt_2)$	22.7	13.3	56.9	7.15	-
Calc. for $TiH(NEt_2)(NC_6H_5)$	22.6	13.2	56.6	7.59	-
Calc. for $Ti(NC_6H_5)(NEt)$	28.2	16.5	49.4	5.93	-

It would seem from the titanium and nitrogen analyses that these compounds were close in composition to bis-(anilino)-titanium. However, a material balance of reactants and products clearly showed that the ratio of anilino groups per titanium in the products could not exceed 1 : 1 while it was also found that these products were quite soluble whereas $[Ti(NC_6H_5)_2]_n$ is insoluble. It seems reasonable to suppose that the first stage of reaction involves the formation of bis-(diethylamino)-mono-(anilino)-titanium.

$$Ti(NEt_2)_4 + C_6H_5NH_2 \longrightarrow Ti(NC_6H_5)(NEt_2)_2 + 2Et_2NH \quad \ldots\ldots\ldots (9)$$

This compound would probably not be monomeric but could exist as a dimer or higher polymer. It is further supposed that the action of heat causes a decomposition to give the observed product with the nitrogen:titanium ratio of approximately 2 : 1. One possibility is the liberation of one diethylamino group leaving a tervalent titanium compound.

$$Ti(NC_6H_5)(NEt_2)_2 \longrightarrow Ti(NC_6H_5)(NEt_2) + NEt_2 \quad \ldots\ldots\ldots (10)$$

$$2NEt_2 \longrightarrow HNEt_2 + CH_3CH{:}NEt \quad \ldots\ldots\ldots (11)$$

It is also possible that diethylamine and ethylene are eliminated and mono-(ethylamino)-(monoanilino)-titanium formed.

$$Ti(NC_6H_5)(NEt_2)_2 \longrightarrow Ti(NC_6H_5)(NEt) + Et_2NH + C_2H_4 \quad \ldots\ldots\ldots (12)$$

A third possibility is the formation of a hydrido compound, $TiH(NEt_2)(NC_6H_5)$, by elimination of ethylidene ethylimine.

$$Ti(NC_6H_5)(NEt_2)_2 \longrightarrow TiH(NEt_2)(NC_6H_5) + CH_3CH{:}NEt \quad \ldots\ldots\ldots (13)$$

Unfortunately there are doubts concerning the commercial analyses for C, H, and N, because the total elemental analysis for both compounds is less than 90%. Therefore it is not possible at this stage to determine the composition of the products. However, it was noticed that the products reacted slowly with water giving initially a bluish solid which slowly became white and this is suggestive of tervalent titanium as required by equation (10). Moreover, diethylamine was detected as a volatile product but this could result from reactions (9), (10) or (12). After hydrolysis of the polymer, aniline but not monoethylamine was detected by gas chromatography. Both compounds were slowly hydrolysed by water or alcoholysed but were rapidly dissolved by acids. Also their infrared spectra were remarkably alike. It was noteworthy that the molecular weight of one compound was almost double that of the other. According to the titanium analyses and molecular weights the degree of polymerization of one compound was five and of the other was ten. It is clear that these experiments have led to the formation of some interesting new soluble polymers and the work requires further investigation.

Some preliminary work on the aniline-tetrakis-(diethylamino)-zirconium system gave, from a reaction of 1 : 1 molar proportions, a dark brown solid which was more readily hydrolysed than the titanium compounds and rather sparingly soluble in hydrocarbon solvents. The total elemental analysis was only 90% and it is not possible to determine the nature of the compound, although it seems to be similar to that of the titanium compounds. The infrared spectrum of the zirconium compound was also similar to the spectra of the titanium compounds.

III. CONCLUSIONS

The primary aim of the past year's work was the synthesis of polymers containing transition metals bonded to nitrogen and this report shows that notable success has been achieved. The results obtained have also posed some interesting and as yet unsolved problems.

The work on chromium compounds was rewarding. It has shown that comparatively chemically inert polymers can be obtained although the pink tris-(monoalkylamino)-chromium (III), $Cr(NHR)_3$, compounds are rather intractable. Moreover, this work has emphasized the powerful effect of steric factors on both structure and reactivity and holds promise that the structural features of metal-nitrogen polymers may be controlled. From the academic viewpoint the contrast in reactions of primary amines with titanium and chromium is rather interesting.

The work on reactions involving dialkylamino-metal compounds and metal carbonyls has revealed a new field of polymers which may be called heterometalcarbonyldialkylamides. It is obvious that further work in this exciting new field is mandatory.

Finally, it may be noted that although the reactions between aniline and the tetrakis-(diethylamino)-titanium or -zirconium did not give the originally desired products, nevertheless the compounds formed were soluble polymers and this field looks promising for further studies.

IV. EXPERIMENTAL

A. General Details

Reactions were carried out in all-glass apparatus fitted with standard interchangeable joints and special precautions were taken to exclude moisture. Apparatus was dried at 120-130°C, all chemicals were rigorously dried, and the experiments were carried out under an atmosphere of dry nitrogen. Transfer of materials was usually carried out in an efficient "dry-box".

Carbon, hydrogen, nitrogen, and oxygen analyses were determined commercially in the laboratories of A. Bernhardt, Mülheim (Ruhr). Metal analyses were determined by conventional methods.

Infrared absorption spectra were obtained using special cells fitted with KBr windows. The "rock salt" region of the spectrum was obtained using the Beckman IR-7 or IR-5 instruments while, for longer wavelengths, the Beckman IR-5A (CsBr optics) instrument was used.

The magnetic susceptibility measurements were determined using a Gouy magnetic balance operating at room temperature.

B. Reactions involving Tris-(diisopropylamino)-chromium (III) and Primary amines.

In most experiments an excess of the primary amine was added dropwise with stirring to a solution of *tris*-(diisopropylamino)-chromium (III) in *n*-hexane. The volatile products were evaporated *in vacuo* and the residue was heated to remove the last traces of tenaciously-bound amine. Ammonia and the volatile amines methylamine and ethylamine were condensed on to the chromium alkylamide at the temperature of boiling nitrogen and the systems allowed to attain room temperature. In Table 3 are presented the results on the "pink" products.

Table 3

ANALYTICAL DATA FOR $Cr(NHR)_3$

R	Colour	Temp. of drying (^oC)	% Cr		% N		Ratio N:Cr
			Found	Calc	Found	Calc	
H	Red	50	51.8	52.0	41.2	42.0	2.94
CH_3	Pink	70	36.4	36.6	28.8	29.5	2.94
C_2H_5	Pink	100	28.1	28.2	22.5	22.8	2.97
$\underline{n}$-C_3H_7	Pink	120	22.8	23.0	18.3	18.5	2.98
$\underline{n}$-C_4H_9	Pink	160	19.1	19.4	15.3	15.6	2.98
$\underline{i}$-C_4H_9	Pink	160	19.15	19.4	15.3	15.6	2.98
$\underline{n}$-C_5H_{11}	Dark red	160	16.8	16.8	-	-	-

In all cases it was established by gas chromatographic analysis of the amine released by hydrolysis that no diisopropylamine was present. All of the compounds listed in Table 3 were insoluble in common organic solvents and were non-volatile. Infrared spectra on Nujol mulls or hexachlorobutadiene mulls gave in all cases absorption around 3300 cm^{-1}, indicative of the presence of N-H bonds.

Magnetic susceptibilities were determined at 26° and the results are presented in Table 4.

Table 4

MAGNETIC SUSCEPTIBILITIES OF $Cr(NHR)_3$

Compound	χ_g (cgs. x 10^6)	χ_M (cgs. x 10^6)	Mag. Moment (μ_{eff} B.M.)
$Cr(NH_2)_3$	+20.2	+2045	2.22
$Cr(NHCH_3)_3$	+11.7	+1719	2.02
$Cr(NHC_2H_5)_3$	+11.15	+2135	2.25
$Cr(NH$-$\underline{n}$-$C_3H_7)_3$	+10.3	+2459	2.40
$Cr(NH$-$\underline{n}$-$C_4H_9)_3$	+7.1	+2053	2.21
$Cr(NH$-$\underline{i}$-$C_4H_9)_3$	+8.08	+2320	2.37

The values for the magnetic moment of chromium are all 2.2 ± 0.2 B.M. and it is doubtful whether the accuracy of the determinations would justify interpreting the variations. The main point is that a much higher value (3.87 B.M.) is required for an atom with a d^3 configuration by the "spin only" formula.

When primary amines containing secondary or tertiary alkyl groups were added to tris-(diisopropylamino)-chromium the reactions did not lead to complete replacement of diisopropylamine. The products were highly reactive and in some cases were spontaneously inflammable in the air. Also they were soluble in n-hexane. Some data are given in Table 5.

Table 5

PROPERTIES OF Cr(NR)(N-i-Pr_2)

R in Cr(NR)(N-i-Pr_2)	Colour	% Cr		% N		Ratio N:Cr
		Found	Calc.	Found	Calc.	
i-C_3H_7	Dark brown	25.6	24.8	16.5	13.4	2.3
s-C_4H_9	Dark brown	23.3	23.3	14.0	12.5	2.2
t-C_4H_9	Black	23.0	23.3	11.9	12.5	1.9

The product from the reaction involving t-butylamine contained some tris-(diisopropylamino)-chromium which was removed by sublimation at 80°C in vacuo. The very reactive nature of these compounds has so far obviated the determination of molecular weights or magnetic susceptibilities and it is likely that the analytical results are subject to a higher margin of error than usual.

C. Preparation of Heterometalcarbonyldialkylamides

(i) Reaction of tetrakis-(dimethylamino)-titanium

Tetrakis-(dimethylamino)-titanium (3.6 g., 0.016 g. mol.) and molybdenum hexacarbonyl (6 g., 0.0227 g. mol.) were brought together in petrol (25 cc., boiling range 110-120°C) and the immediate yellow colour gradually darkened. The system was refluxed for 24 hours and became dark brown. The solvent was then evaporated off and the excess molybdenum hexacarbonyl removed by sublimation at 60-65°C in vacuo.

The dark brown product slowly changed to yellow-brown and smelled of amine when exposed to the atmosphere. The product was insoluble in cyclohexane and slightly soluble in methylene chloride or acetone. The compound reacted slowly with water, dilute hydrochloric or dilute sulphuric acids forming yellow turbid solutions. The compound reacted more rapidly with nitric acid.

The compound did not melt sharply but fused over a temperature range (145-155°C) to a dark viscous liquid.

To date a satisfactory method of analysing the compound for titanium and molybdenum has not been found and the tentative formula, $Ti(NMe_2)_4 : Mo_3(CO)_6$, is based on the carbon, hydrogen, nitrogen, and oxygen analyses.

Found: C, 24.70 ; H, 3.61 ; N, 8.88 ; O, 14.44%.
$Ti(NMe_2)_4 : Mo(CO)_6$ requires: C, 23.22 ; H, 4.63 ; N, 8.86 ; O, 19.94 %

It is noteworthy that the agreement between observed and calculated elemental analyses is poor for hydrogen and oxygen and the tentative formula is probably incorrect.

An infrared spectrum was determined on a Nujol mull and the data are given in Table 6.

Table 6

INFRARED SPECTRUM OF $Ti(NMe_2)_4.Mo(CO)_6$

2070 *w*	1815 *sh*	1417 *w*	1112 *sh*	865 *sh*
2050 *w*	1760 *sh*	1400 *w*	1092 *m*	840 *sh*
2045 *s*	1697 *m*	1375 *s*	1050 *w* (*sh*)	800 *m*
2000 *sh*	1642 *m*	1365 *sh*	1040 *m*	725 *m*
1985 *s*	1595 *w*	1275 *s*	1017 *sh*	637 *w*
1977 *w* (*sh*)	1550 *m*	1220 *s*	950 *s*	620 *w*
1935 *m*	1495 *s*	1182 *sh*	917 *m*	
1870 *m*	1460 *s*	1140 *w*	902 *sh*	

The nine bands from 2070 - 1815 cm^{-1} are almost certainly due to CO stretching vibrations with the possibility that the bands at 1870 and 1815 cm^{-1} are due to bridging CO groups. The strong bands at 1460 and 1375 cm^{-1} are due to the asymmetric and symmetric C-H deformation modes (CH_3-N). The four bands from 1220 - 1112 cm^{-1} are probably C-N vibrations whilst the strong band at 950 cm^{-1} is most likely a Ti-N-C vibration.

(ii) Reaction of *tetrakis*-(dimethylamino)-titanium with Tungsten Hexacarbonyl

Tetrakis-(dimethylamino)-titanium (2.5 g., 0.011 g. mol.) in petrol (20 cc., boiling range 100-120°C) was added to tungsten hexacarbonyl (8 g., 0.0227 g. mol.) with magnetic stirring. There was a colour change to dark red but no gas was evolved. After refluxing the system for 10 hours the solvent was evaporated off and the excess tungsten hexacarbonyl sublimed *in vacuo* at 65-70°C leaving a dark brown solid.

On exposure to the atmosphere the compound became light brown and smelled of amine. It was sparingly soluble in acetone or methylene chloride giving brown solutions which became turbid. The compound reacted slowly with dilute hydrochloric acid and rapidly with dilute nitric acid and in both cases evolved a gas and gave turbid white solutions. The formula, $Ti(NMe_2)_4 . W_2(CO)_4$, was tentatively assigned on the basis of the following analytical data.

Found: Ti, 6.4 ; N, 7.97 ; C, 20.34 ; O, 10.23 %.
$Ti(NMe_2)_4 . W_2(CO)_4$ requires: Ti, 6.8 ; N, 7.96 ; C, 20.44 ; O, 9.06 %.

The infrared spectrum was taken on a Nujol mull and the data are recorded in Table 7.

Table 7

INFRARED SPECTRUM OF $Ti(NMe_2)_4.W_2(CO)_4$

2270 w
2050 m
1978 vs
1913 s
1850 vs
1806 s
1700 m
1640 m
1598 w
1550 sh
1495 m
1460 s
1420 w
1402 w
1376 s
1278 s
1222 m
1190 w
1150 w
1100 m
1052 m
1045 sh
1022 w
950 s
875 w
840 sh
800 m
752 sh
732 s
630 m
615 w

The general pattern of this spectrum is fairly similar to that for $Ti(NMe_2)_4.Mo_3(CO)_6$ but with less bands in the CO stretching region. The characteristic strong absorptions at 1460 (asym. C-H defmn.), 1376 (sym. C-H defmn.), and 950 cm^{-1} (Ti-N-C banding) are present in both compounds.

(iii) Reaction of tetrakis-(dimethylamino)-zirconium with Nickel Carbonyl

Nickel carbonyl (8 g., 0.0469 g. mol.) in cyclohexane (20 cc.) was treated with tetrakis-(dimethylamino)-zirconium (3.8 g., 0.0142 g. mol.) in cyclohexane (10 cc.) and gave an immediate exothermic reaction. The colour of the solution changed slowly from yellow to red to dark brown but no carbon monoxide was evolved. On standing for 42 hours in the dark a brown solid deposited leaving a clear light brown supernatent liquor. Evaporation of solvent and excess nickel carbonyl *in vacuo* left a dark brown solid which darkened at 140-150°C and became black but did not melt up to 300°C. When finely divided, the solid fumed on exposure to air, became hot, and changed to charcoal black. It reacted slowly with water or dilute hydrochloric or sulphuric acids giving turbid solutions. It dissolved readily in dilute nitric acid evolving a gas and giving a clear green solution.

The compound was insoluble in benzene, cyclohexane or carbon tetrachloride.

Except for the carbon, hydrogen, and oxygen figures the analytical results agree with the formula, $Zr(NMe_2)_4.2Ni(CO)_4$.

Found: Zr, 15.19 ; Ni, 19.07 ; N, 9.07 ; C, 28.43 ; H, 5.08 ; O, 24.16 %.
Calc: Zr, 14.98 ; Ni, 19.29 ; N, 9.20 ; C, 31.54 ; H, 3.94 ; O, 21.03 %.

The results of an infrared spectrum (Nujol mull) are given in Table 8.

Table 8

INFRARED SPECTRUM OF $Zr(NMe_2)_4.2Ni(CO)_4$

2200 m
2042 m
2000 sh
1970 m
1942 sh
1882 w
1885 w
1820 w
1785 w
1645 sh
1620 w
1532 m
1462 s
1402 m
1380 s
1345 sh
1275 s
1215 sh
1140 sh
1110 m
1073 m
1045 sh
975 w
900 w
845 w
798 w
770 w
742 w
725 m
675 w
662 w
632 sh

The pattern of the spectrum is generally similar to that for $Ti(NMe_2)_4 \cdot 2Ni(CO)_4$ with characteristic CO bands (2200 - 1785 cm^{-1}) and strong bands at 1462 (asym. C-H defmn.) and 1380 cm^{-1} (sym. C-H defmn.).

(iv) Reaction of *tetrakis*-(dimethylamino)-zirconium with Iron Pentacarbonyl

Addition of *tetrakis*-(dimethylamino)-zirconium (2.5 g., 0.0094 g. mol.) in cyclohexane (20 cc.) to iron pentacarbonyl (4.38 g., 0.0224 g. mol.) in cyclohexane (20 cc.) caused an immediate exothermic reaction but no evolution of gas. The colour of the solution became brown and the system was kept in the cark for two days. Evaporation of solvent and excess iron pentacarbonyl *in vacuo* left a brown solid which darkened above 100°C but did not melt up to 300°C.

The product slowly lightened in colour when exposed to air and reacted slowly with water or dilute hydrochloric or sulphuric acids. It reacted rapidly with nitric acid evolving a gas. It was partially soluble in alcohol, methylene chloride, or tetrahydrofuran, and insoluble in benzene, cyclohexane, or carbon tetrachloride.

The analytical results, while leaving much to be desired, suggest the formula, $Zr(NMe_2)_4 \cdot 2Fe(CO)_5$.

Found: Fe, 16.21 ; $Fe_2O_3 + ZrO_2$, 42.16 ; N, 7.10 ; C, 31.49 ; H, 5.06 ; O, 20.40%.

Calc: Fe, 16.95 ; $Fe_2O_3 + ZrO_2$, 42.95 ; N, 8.49 ; C, 32.77 ; H, 3.64 ; O, 24.28%.

The iron was determine by permanganate titration of the acid solution reduced by the Jones' Reductor and the total oxides by precipitation with aqueous ammonia solution.

The infrared spectrum, determined on a Nujol mull, is recorded in Table 9.

Table 9

INFRARED SPECTRUM OF $Zr(NMe_2)_4 \cdot 2Fe(CO)_5$

2220 w	1560 sh	1270 sh	975 w	682 sh
2045 s	1510 s	1260 s	938 m	673 s
2038 s	1463 s	1215 s	895 w	668 sh
2015 s	1405 sh	1200 sh	882 w	650 sh
2000 s	1382 s	1110 s	842 w	635 s
1940 sh	1370 sh	1050 m	795 w	
1910 w	1345 w	1032 sh	725 m	
1655 w	1295 sh	1020 sh	698 w	

The noteworthy features of these data are the CO bands at 2220 - 1910 cm^{-1} and the strong C-H deformation frequencies at 1463 cm^{-1} (asym.) and 1382 cm^{-1}(sym.).

(v) Reaction of *tetrakis*-(dimethylamino)-zirconium and molybdenium hexacarbonyl

Tetrakis-(dimethylamino)-zirconium (2 g., 0.008 g. mol.) and molybdenium hexacarbonyl (3.4 g., 0.0128 g. mol.) were mixed and the pale colour of the zirconium compound was immediately replaced by a bright yellow. Petrol (20 cc., b.p. 110-120°C) was then added and the mixture stirred in the dark for 15 hours. Finally the solution was refluxed at 110°C for 5 hours and the solvent was then evaporated off. The excess molybdenum hexacarbonyl was sublimed off in vacuo at 60-65°C.

The product was a yellow powder which darkened rapidly on exposure to air and gave off fumes. The product blackened at about 250°C but did not melt up to 300°C. The substance reacted readily with nitric acid, smoothly with dilute and violently with concentrated acid. After removing molybdenum by the α-benzoin oxime method, the zirconium was determined on the filtrate. The analytical results suggest the formula, $Zr(NMe_2)_4 \cdot Mo(CO)_6$.

Found: Zr, 16.55 ; Mo, 17.26 ; N, 10.35 ; C, 31.46 ; H, 4.47 ; O, 15.68%.
Calc: Zr, 17.17 ; Mo, 18.06 ; N, 10.54 ; C, 31.62 ; H, 4.55 ; O, 18.07%.

The results of an infrared spectrum (Nujol mull) are given in Table 10.

Table 10

INFRARED SPECTRUM OF $Zr(NMe_2)_4 \cdot Mo(CO)_6$

2060 m	1650 m	1367 sh	1022 sh	720 m
2016 m	1617 w	1280 s	972 w (sh)	670 w
1985 s	1575 w	1227 m	945 sh	665 w
1925 s	1550 w	1170 w	912 w	640 m
1873 s	1500 m	1145 w	870 w	620 m
1650 sh	1462 s	1100 m	842 w	
1807 s	1404 w	1060 sh	797 m	
1700 m	1378 s	1045 m	770 w	

The eight bands in the region 2060 - 1700 cm^{-1} are due to CO stretching vibrations. The characteristic C-H deformation modes CH_3-N are also present at 1462 (asym.) and 1378 cm^{-1} (sym.).

(vi) Reaction of tetrakis-(dimethylamino)-zirconium and tungsten hexacarbonyl

Tetrakis-(dimethylamino)-zirconium (2 g., 0.008 g. mol.) was added to tungsten hexacarbonyl (5.7 g., 0.016 g. mol.) and the pale yellow colour immediately changed to a deep bright yellow but although the reaction was exothermic no gas was evolved. Petrol (25 cc., boiling range 100-120°C) was added and the system was stirred for 25 hours and then refluxed for 7 hours. After removal of solvent the excess tungsten hexacarbonyl was sublimed away at 65-70°C.

The product retained its bright yellow colour for several hours whilst exposed to air. It darkened at 250°C but did not melt up to 300°C. The limited analytical data suggest a formula, $Zr(NMe_2)_4 \cdot W(CO)_6$ but this must be considered provisional in the absence of metal analyses.

Found: N, 8.95 ; C, 26.95 ; H, 3.81 ; O, 17.85%.

Calc: N, 9.00 ; C, 27.13 ; H, 3.87 ; O, 15.51%.

The infrared data (Nujol mull) are presented in Table 11.

Table 11

INFRARED SPECTRUM OF $Zr(NMe_2)_4 \cdot W(CO)_6$

2200 *w*	1800 *sh*	1375 *s*	1042 *w*	795 *w*
2055 *m*	1698 *m*	1365 *sh*	1017 *w*	720 *m*
2015 *w*	1650 *w*	1280 *s*	1000 *w* (*sh*)	670 *w*
1980 *s*	1555 *w*	1220 *s*	970 *w*	665 *w*
1910 *s*	1495 *m*	1165 *w* (*sh*)	945 *w*	634 *w*
1860 *s*	1462 *s*	1100 *m*	900 *w*	620 *w*
1835 *sh*	1402 *sh*	1057 *w*	875 *w*	

The general pattern of this spectrum is similar to that for $Zr(NMe_2)_4 \cdot Mo(CO)_6$ with CO bands at 2200-1800 cm^{-1} and the C-H deformation modes at 1462 and 1375 cm^{-1}.

(vii) Reaction of tetrakis-(dimethylamino)-hafnium with nickel carbonyl

Tetrakis-(dimethylamino)-hafnium (2.5 g., 0.007 g. mol.) in cyclohexane (15 cc.) was added to nickel carbonyl (6.8 g., 0.04 g. mol.) and caused a mildly exothermic reaction with an accompanying change of colour from yellow to brown. Although the colour eventually became almost black during 24 hours and some dark brown solid was deposited, there appeared to be no evolution of gas. The solvent and excess nickel carbonyl were evaporated off under reduced pressure leaving a dark brown solid.

The solid darkened at 140-150°C and gradually blackened but did not melt up to 300°C. On exposure to the air the substance slowly changed to light brown and finally to off-white. Dilute hydrochloric or nitric acids gave yellowish solutions which became turbid on standing. Nitric acid reacted vigorously forming a clear green solution and evolving gas. The compound appeared to be partially soluble in methylene chloride. The analytical data favoured the formula, $Hf(NMe_2)_4 \cdot 2Ni(CO)_4$.

Found: Hf, 25.35 ; Ni, 16.15 ; N, 7.82 ; C, 24.01 ; H, 4.38 ; O, 20.61%.

Calc: Hf, 25.65 ; Ni, 16.87 ; N, 8.05 ; C, 27.61 ; H, 3.47 ; O, 18.39%.

The infrared spectrum (Nujol mull) is recorded in Table 12.

Table 12.

INFRARED SPECTRUM OF $Hf(NMe_2)_4 \cdot 2Ni(CO)_4$

2200 *w*	1675 *w*	1370 *w* (*sh*)	1040 *w*	725 *m*
2045 *m*	1650 *w*	1280 *m*	1020 *w*	692 *w*
2006 *s*	1600 *vs*	1242 *w*	997 *w*	675 *w*
1962 *sh*	1550 *sh*	1225 *sh*	970 *sh*	665 *w*
1937 *sh*	1457 *s*	1142 *w*	950 *m*	630 *w*
1855 *sh*	1418 *w*	1110 *m*	902 *w*	
1818 *w*	1200 *sh*	1075 *m*	845 *w*	
1690 *vs*	1380 *s*	1062 *sh*	765 *m*	

This spectrum was similar to that given by $Zr(NMe_2)_4 \cdot 2Ni(CO)_4$ and calls for no special comment.

(viii) Reaction of tetrakis-(dimethylamino)-hafnium with iron pentacarbonyl

Addition of *tetrakis*-(dimethylamino)-hafnium (3.0 g., 0.0085 g. mol.) in cyclohexane (15 cc.) to iron pentacarbonyl (4.38 g., 0.0224 g. mol.) caused an exothermic reaction and the mixture changed colour to brown. A brown solid was precipitated during two days when the mixture was shielded from the light but no carbon monoxide was evolved. The solvent and excess iron pentacarbonyl were evaporated off *in vacuo* leaving a dark brown solid.

The substance changed colour to light brown when exposed to the air. It darkened at about 200°C (under nitrogen) and turned black at higher temperature but did not melt below 300°C. The product was hydrolysed by water and it reacted with dilute hydrochloric and sulphuric acids giving yellowish-green solutions. Reaction with nitric acid was rapid and a yellow solution was formed.

The substance was insoluble in ether, benzene, cyclohexane, or carbon tetrachloride and was partially soluble in methylene chloride or tetrahydrofuran. The analytical data suggested the formula, $Hf(NMe_2)_4\cdot 2Fe(CO)_5$.

Found: Hf, 23.64 ; Fe, 15.42 ; N, 7.11 ; C, 28.41 ; H, 3.62 ; O, 21.80%.

Calc: Hf, 23.92 ; Fe, 14.96 ; N, 7.51 ; C, 28.95 ; H, 3.22 ; O, 21.45%.

The infrared data (Nujol mull) are given in Table 13.

Table 13

INFRARED SPECTRUM OF $Hf(NMe_2)_4\cdot 2Fe(CO)_5$

2220 *w*
2045 *s*
2037 *s*
2020 *s*
2000 *s*
1940 *sh*
1910 *s*
1700 *m*
1637 *m*
1560 *sh*
1507 *s*
1460 *s*
1405 *w*
1380 *s*
1370 *sh*
1345 *w*
1290 *sh*
1260 *s*
1238 *sh*
1235 *sh*
1220 *s*
1192 *sh*
1185 *s*
1107 *s*
1050 *m*
1020 *w*
950 *s*
904 *w*
880 *m*
862 *w*
840 *w*
798 *w*
785 *sh*
722 *m*
698 *w*
682 *sh*
670 *s*
632 *vs*

The spectrum was very similar to that found for $Zr(NMe_2)_4\cdot 2Fe(CO)_5$.

(ix) Reaction of *tetrakis*-(dimethylamino)-hafnium with molybdenum hexacarbonyl

Addition of *tetrakis*-(dimethylamino)-hafnium (3 g., 0.00846 g. mol.) in cyclohexane (25 cc.) to molybdenum hexacarbonyl (5 g., 0.0189 g. mol.) caused an exothermic reaction and a colour change to yellow but no evolution of gas. After refluxing the system for four hours the solvent and excess molybdenum hexacarbonyl were evaporated off *in vacuo*.

The finely divided yellow product was pyrophoric in air but in bulk it changed colour to brown and smelled of amine on exposure. It became dark at about 158°C and blackened above 240°C but did not melt up to 300° C. It reacted with nitric acid evolving gas and forming a yellow solution. The substance was insoluble in benzene, cyclohexane, carbon tetrachloride, or tetrahydrofuran. It seemed partially soluble in methylene chloride or alcohol.

The analytical data were limited by our failure to determine hafnium and molybdenum separately, but the formula, $Hf(NMe_2)_4 \cdot 2Mo(CO)_6$, seems appropriate.

Found: $HfO_2 + Mo_2O_3$, 51.66 ; N, 6.87 ; C, 21.96 ; H, 3.84 ; O, 21.51%.

Calc: $HfO_2 + Mo_2O_3$, 53.50 ; N, 6.35 ; C, 27.19 ; H, 2.72 ; O, 21.76%.

The infrared spectrum (Nujol mull) is recorded in Table 14.

Table 14

INFRARED SPECTRUM OF $Hf(NMe_2)_4 \cdot 2Mo(CO)_6$

2075 m
1987 s
1925 s
1875 s
1850 s
1812 s
1702 m
1657 w
1590 sh
1550 sh
1500 m
1462 s
1400 sh
1380 s
1282 s
1222 s
1142 w
1102 m
1062 w
1042 m
1025 sh
1002 sh
955 m
918 w
907 w (sh)
875 w
848 w
800 w
775 w
725 m
675 w
665 w
645 m
632 m

The spectrum was similar in pattern to that for $Zr(NMe_2)_4 \cdot Mo(CO)_6$.

(x) Magnetic Susceptibilities of Heterometalcarbonyldialkylamides

The susceptibility data obtained at 26°C are presented in Table 15.

Table 15

MAGNETIC SUSCEPTIBILITIES OF HETEROMETALCARBONYLDIALKYLAMIDES

Compound	χ_g(cgs. x 10^6)	χ'_M(cgs. x 10^6)	μ_{eff}(B.M.)
$Ti(NMe_2)_4 \cdot 2Ni(CO)_4$	+1.83	+1253	1.74
$Zr(NMe_2)_4 \cdot 2Ni(CO)_4$	+1.59	+1190	1.69
$Hf(NMe_2)_4 \cdot 2Ni(CO)_4$	+0.95	+879	1.46
$Zr(NMe_2)_4 \cdot 2Fe(CO)_5$	+1.55	+1154	1.74
$Hf(NMe_2)_4 \cdot 2Fe(CO)_5$	+0.75	+790	1.38
$Ti(NMe_2)_4 \cdot Mo(CO)_6$	-0.18	+94	0.48
$Zr(NMe_2)_4 \cdot Mo(CO)_6$	-0.19	+94	0.47
$Hf(NMe_2)_4 \cdot 2Mo(CO)_6$	-0.52	-197	Diamagnetic
$Ti(NMe_2)_4 \cdot W_2(CO)_4$	+0.92	+826	1.41
$Zr(NMe_2)_4 \cdot W(CO)_6$	-0.35	-15	Diamagnetic

D. Reactions of Aniline with *tetrakis*-(diethylamino)-titanium and *tetrakis*-(diethylamino)-zirconium

(i) Reaction of Aniline (1 mol.) with *tetrakis*-(diethylamino)-titanium (1 mol.)

Aniline (7.06 g., 1 g. mol.) in dioxan (75 cc.) was added to *tetrakis*-(diethylamino)-titanium (25.6 g., 1 g. mol.) at room temperature and a deep red colour developed and an oily precipitate formed. After refluxing for six hours the solvent was evaporated off and the residue heated at 200°C /0.1 mm. This gave a distillate (2.3 g.) of impure *tetrakis*-(diethylamino)-titanium (Found: Ti, 15.6 ; Calc: 14.2%) and left a black shiny solid (I), 16.4 g. (Found: Ti, 20.5 ; N, 12.4 ; C, 50.1 ; H, 6.32%). The cold-trap contained some diethylamine.

The black solid reacted slowly with water giving a bluish solid which slowly changed to white. The compound dissolved readily in acids. It was soluble in benzene, cyclohexane, methylene chloride and carbon tetrachloride. Its molecular weight (1100) was determined cryoscopically in benzene.

The infrared spectrum was obtained on a solution in carbon tetrachloride and the spectral data are given in Table 16.

Table 16

INFRARED SPECTRUM OF COMPOUND I

3049 *m*	1623 *s*	1361 *m*	1072 *w*
2967 *s*	1524 *s*	1325 *m*	1030 *w*
2924 *m*	1479 *vs*	1242 *s*	1000 *w*
2882 *m*	1379 *m*	1179 *m*	

Aniline was detected by gas chromatographic analysis in the hydrolysis products but no evidence for primary ethylamine was found.

(ii) Reaction of Aniline (1 mol.) with *tetrakis*-(diethylamino)-titanium (2 mol.)

A solution of aniline (3.83 g., 0.5 g. mol.) in dioxan (50 cc.) was added dropwise to a solution of *tetrakis*-(diethylamino)-titanium (27.6 g., 1 g. mol.) at room temperature. The colour of the solution slowly darkened and on refluxing became very deep red. After evaporation of the solvent the residue was heated *in vacuo* and gave a distillate of *tetrakis*-(diethylamino)-titanium (14.8 g., 0.536 g. mol.; Found: Ti, 14.7%) and a shiny black solid (II) (7.3 g.; Found: Ti, 23.0 ; N, 12.3 ; C, 46.2 ; H, 6.14%). Compound II was slowly hydrolysed by cold water and reacted rapidly with acids. It was soluble in benzene, cyclohexane, methylene chloride and carbon tetrachloride. Its molecular weight (2100) was determined cryoscopically in benzene.

Its infrared spectrum was determined on a solution in carbon tetrachloride and the results are given in Table 17.

Table 17

INFRARED SPECTRUM OF COMPOUND II

3058 m
2976 m
2924 m
2874 m
1529 m
1481 vs
1377 m
1361 m
1325 m
1242 s
1175 m
1073 w
1030 m
1000 m
892 m

The spectrum for compound II was very similar to that of compound I.

(iii) Reaction of Aniline (1 mol.) with tetrakis-(diethylamino)-zirconium (1 mol.)

Aniline (4.00 g., 1 g. mol.) in dioxan (50 cc.) was added to tetrakis-(diethylamino)-zirconium (16.4 g., 1 g. mol.) in dioxan (75 cc.). A mildly exothermic reaction occurred with some darkening of colour. After refluxing for two hours the solvent was evaporated off and residue heated at 200°C/0.1 mm. A small amount of tetrakis-(diethylamino)-zirconium, 1.89 g., (Found: Zr, 24.1 ; Calc: Zr, 24.0%) was recovered and a dark brown solid (9.9 g.) remained as compound (III) (Found: Zr, 35.5 ; N, 10.3 ; C, 40.0 ; H, 5.19%).

Compound III was more readily hydrolysed by water than compounds I or II and it was also less soluble in organic solvents. The infrared spectral data given in Table 18 were obtained on a carbon tetrachloride solution of III.

Table 18

INFRARED SPECTRUM OF COMPOUND III

3067 m
3003 m
2976 s
2924 s
2849 s
1605 m
1502 m
1488 vs
1479 vs
1453 s
1377 m
1362 m
1227 s
1185 s
1147 m
1031 m
1000 w
876 s

The spectrum for compound III was generally like the spectra of compounds I and II.

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