New Dialkylamido Complexes of Transition Metals in Groups 4 and 5 stabilised by Terdentate Ligands†

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Application of the terdentate chelating diaminoamido ligand $^-N(CH_2CH_2NEt_2)_2$ (L) has enabled the straightforward preparation and isolation of new ternary dialkylamido complexes [MX_2L] (M = V or Ti; X = Cl, Me, or Ph), [$NbCl_2L_2$], and [$ZrCl_3L$]. These compounds are resistant to the types of rearrangements that have frustrated previous attempts to find general routes to dialkylamido complexes containing other ligands available for substitutions and other manipulations. This approach now provides access to a broad class of compounds of interest in the study of organometallic amides.

Chemistry of metal dialkylamides has centred almost entirely on metals in their higher oxidation states.[1] Ternary dialkylamides of metals in lower oxidation states containing other anionic ligands, such as halides, available for substitutions and other reactions, are rare since such complexes of electropositive metals commonly disproportionate[2] or are intractable.[3] These problems have been reduced in some cases by using bulky dialkylamido ligands [*e.g.* $(Me_3Si)_2N^-$], and this strategy has provided the only example of a tractable vanadium(III) dialkylamide,[4] prior to our present study, and also has enabled the isolation of ternary complexes containing halide ligands that are amenable to further study[5] such as C–H activation.[6]

An alternative to the use of bulky ligands is to incorporate chelating multidentate amido ligands. Of the Group 4 or 5 transition-metal complexes stabilised by chelating dialkylamido ligands,[1] few contain halide ligands and little has been reported of their chemistry. There is a recent exception that demonstrates the ability of terdentate amido ligands containing tertiary phosphine donors to stabilise Group 4 metal halide complexes,[7] as well as the utility of such compounds in the development of the chemistry of transition-metal dialkylamides.

We have reported preliminary results of our present study, including the crystal structures of [$VCl_2\{N(CH_2CH_2NEt_2)_2\}$][8] and [$VPh_2\{N(CH_2CH_2NEt_2)_2\}$].[9] In this paper we discuss the syntheses and characterisations of halide and organometallic complexes of metals in transition Groups 4 and 5, stabilised by the chelating terdentate amido ligand $^-N(CH_2CH_2NEt_2)_2$, derived from 3,9-diethyl-3,6,9-triazaundecane.

Results

Physical data are collected in the Table.

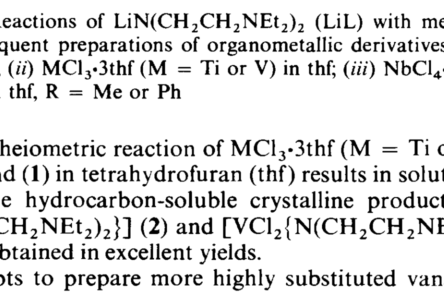
Table. Physical data for compounds (**2**)—(**9**)

Compound	$\mu_{eff.}$ [a]	M.p./°C	E.s.r.[b]	*m/e*[c]	*M*[d]
(**2**)	1.73	113	1.96	333 (2)	266 (333)
(**3**)	2.42	135		336 (2)	382 (336)
(**4**)	1.72	90	1.98		296 (292)
(**5**)	1.41	135	1.97		454 (416)
(**6**)	2.61	108		295 (57)	308 (295)
(**7**)	2.58	149		419 (3)	394 (419)
(**8**)	1.56	58	1.92		546 (592)
(**9**)		121			496 (412)

[a] Measured in the solid state at 20 °C. [b] The *g* values are referenced to diphenylpicrylhydrazyl (*g* = 2.003). [c] For observed molecular ions, with relative abundancies (%) in parentheses. [d] Calculated values in parentheses.

3,9-*Diethyl*-6-*lithio*-3,6,9-*triazaundecane*.—The metal amides described subsequently are prepared from the lithium amide Li[$N(CH_2CH_2NEt_2)_2$] (**1**). Compound (**1**) is conveniently prepared from the corresponding secondary amine, 3,9-diethyl-3,6,9-triazaundecane, by the action of methyl-lithium (or other organometallic lithium reagents such as $LiBu^n$) in diethyl ether. The lithium amide may be readily crystallised in high yield as white prisms. It is very soluble in aromatic hydrocarbons and ethers, less soluble in aliphatic hydrocarbons. It is dimeric in benzene, although the highest peak in the mass spectrum (*m/e* 214) corresponds to [$(Et_2NCH_2CH_2)_2N$]$^+$. The fragmentation pattern for this species is also observed in the mass spectra of all the metal compounds described below. Compound (**1**) is very air and moisture sensitive as is to be expected and as are all the transition-metal derivatives discussed subsequently.

Titanium and Vanadium Compounds.—Consistent analytical data for all the new compounds mentioned below have been obtained (Experimental section). Reactions are collected in the scheme. All the transition-metal compounds below (including niobium and zirconium) are monomeric in benzene (cryoscopy).



Scheme. Reactions of $LiN(CH_2CH_2NEt_2)_2$ (LiL) with metal halides and subsequent preparations of organometallic derivatives. (*i*) $ZrCl_4$ in toluene; (*ii*) $MCl_3{\cdot}3thf$ (M = Ti or V) in thf; (*iii*) $NbCl_4{\cdot}2thf$ in thf; (*iv*) LiR in thf, R = Me or Ph

The stoicheiometric reaction of $MCl_3{\cdot}3thf$ (M = Ti or V) with compound (**1**) in tetrahydrofuran (thf) results in solutions from which the hydrocarbon-soluble crystalline products [$TiCl_2\{N(CH_2CH_2NEt_2)_2\}$] (**2**) and [$VCl_2\{N(CH_2CH_2NEt_2)_2\}$] (**3**) may be obtained in excellent yields.

Attempts to prepare more highly substituted vanadium(III)

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† *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

amides by the action of compound (**1**) occasionally have resulted in poor yields of a very soluble waxy orange material as well as more commonly crystals of the monoamide (confirmed by microanalysis). This outcome is unchanged if $VCl_3{\cdot}2NMe_3$ is used as precursor. (This amine adduct is reported to be a more successful precursor for the preparation of vanadium silylamides[4] than the tetrahydrofuran solvate.)

Both compounds (**2**) and (**3**) become yellow on exposure to air or moisture; (**3**) initially becomes purple, as do the other vanadium compounds below. They appear to be indefinitely thermally stable at room temperature and melt without decomposition. They are both monomeric in benzene and for (**2**) the molecular ion was observed in the mass spectrum. As expected (d^1), this compound is paramagnetic, the e.s.r. spectrum in frozen solution (thf, 99 K) showing no nitrogen superhyperfine structure. Such featureless e.s.r. spectra have been observed for other titanium(III) amides.[10] Compound (**3**) is e.s.r. silent. The magnetic susceptibilities are normal[11,*] and close to the spin-only values.

Organometallic derivatives may be prepared from compounds (**2**) and (**3**) by the reaction with 2 mol equivalents of the corresponding organometallic lithium reagent (methyl-lithium or phenyl-lithium) in thf. The derivatives may be obtained as hydrocarbon-soluble crystals, $[TiMe_2\{N(CH_2CH_2NEt_2)_2\}]$ (**4**), $[TiPh_2\{N(CH_2CH_2NEt_2)_2\}]$ (**5**), $[VMe_2\{N(CH_2CH_2NEt_2)_2\}]$ (**6**), and $[VPh_2\{N(CH_2CH_2NEt_2)_2\}]$ (**7**), in good yields. The molecular ions were only observed for (**5**) and (**6**) in the mass spectrum although all the organometallic derivatives are reasonably thermally stable. The e.s.r. spectra of (**4**) and (**5**) showed no nitrogen superhyperfine coupling. Again the magnetic susceptibilities were consistent.

Solutions of compound (**6**) in hydrocarbons or ethers are dichroic (exhibiting the chartreuse[12] effect) as a result of two absorbances in the visible region, one sharp and relatively intense (λ = 505 nm, ε = 85 $dm^3\ mol^{-1}\ cm^{-1}$), the other broad and relatively weak (λ = 730 nm, ε = 39.5 $dm^3\ mol^{-1}\ cm^{-1}$). The colour of the bulk solution is orange, but thin films (*e.g.* the meniscus) are pink.

Niobium and Zirconium.—If $NbCl_4{\cdot}2thf$ is treated with 2 mol equivalents of compound (**1**) in thf an orange-brown crystalline material $[NbCl_2\{N(CH_2CH_2NEt_2)_2\}_2]$ (**8**) may be isolated in good yield. The compound becomes blue upon exposure to air as the solid or in solution. Magnetic susceptibility confirms the presence of d^1 Nb^{IV} and the e.s.r. spectrum (thf, 293 K) displays a ten-line pattern coupled to ^{93}Nb ($I = \frac{9}{2}$) with no nitrogen superhyperfine structure. The molecular ion is not observed in the mass spectrum.

The material obtained in this way is commonly contaminated by small quantities of green needles that may be separated by fractional crystallisation from toluene. If, however, aluminium-free $NbCl_4{\cdot}2thf$ (prepared according to the procedure of Nielson and co-workers[13]) is used, compound (**8**) may be obtained in high yield uncontaminated. The nature of the green needles is as yet undetermined. Attempts to prepare niobium compounds with different halide-to-amide ratios have resulted only in the isolation of (**8**) in poor yields, even with a deficiency of (**1**).

The reaction of 1 mol equivalent of compound (**1**) with zirconium tetrachloride in toluene enables the isolation of $[ZrCl_3\{N(CH_2CH_2NEt_2)_2\}]$ (**9**) as white needles. If the reaction is performed in thf the product may be obtained in a similar manner but is more difficult to crystallise and purify; the yield is also poor.

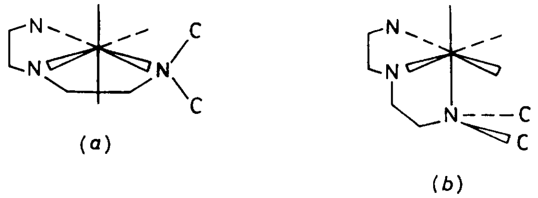

Figure 1. Possible structures for compound (**9**). The ethyl methylene carbons are included for one terminal amino nitrogen only in each case, for the sake of clarity

Discussion

For compound (**9**) analysis of the ^1H, ^{13}C-$\{^1H\}$, and ^{13}C n.m.r. spectra provides detailed information on the stereochemistry in solution. Thus the ^1H n.m.r. spectrum consists of five resonances: a triplet (δ 0.92, 12 H), two six-line multiplets (δ 2.75, 4 H; 3.43, 4 H the lines in each multiplet having relative intensity 1:3:4:4:3:1), and a pattern of two unsymmetrical triplets (δ 2.95, 4 H; 3.04, 4 H), displaying a second-order 'roofing' effect (inner lines > outer). From decoupling experiments it may be shown that the triplet (δ 0.92) and six-line multiplets are coupled (the multiplets collapse to two doublets when the triplet is irradiated), and the two unsymmetrical triplets (δ 2.95 and 3.04) are coupled, one collapsing to a singlet when the other is irradiated. This indicates that the backbone methylene protons give rise to the two second-order triplets consistent with an ABCD pattern where $J_{AB} = J_{CD} \approx 0$ Hz, so this part of the spectrum appears limited to an AA′BB′ pattern, *i.e.* the protons on each carbon are equivalent on the n.m.r. time-scale. The triplet (δ 0.92) represents the methyl protons, the multiplets (δ 2.75 and 3.43) therefore represent the methylene protons of the ethyl groups, the doublet in the decoupled spectrum inicating that the protons on these carbons are diastereotopic. Since both meridional and facial isomers (Figure 1) of compound (**9**) should have diastereotopic ethyl methylene protons and since the backbone methylene protons should conform to an ABCD pattern in both isomers, the apparent simplicity of the observed pattern for these protons may be more likely for the structure in Figure 1(*a*) but is not definitive.

The ^{13}C-$\{^1H\}$ n.m.r. spectrum, however, does indicate the solution stereochemistry since only four resonances are seen (δ 55.5, 54.3, 49.0, and 9.5 p.p.m.) and the ethyl carbons must be pairwise equivalent. This is only consistent with the meridional structure, Figure 1(*a*). Assignments and the virtual equivalence of the backbone methylene protons are confirmed in the ^{13}C n.m.r. spectrum since the three lower-field resonances appear as triplets and the last as a quartet. The proposed stereochemistry is intuitively sensible since the meridional isomer will have all three nitrogens and the zirconium atom in a plane enabling the central amido nitrogen atom to double bond to zirconium becoming formally a π-bonding four-electron donor, adopting a trigonal planar conformation and providing zirconium with 14 valence electrons. The facial isomer [Figure 1(*b*)] requires that the amido nitrogen will tend to act as a σ-bonding two-electron donor (leaving zirconium with only 12 valence electrons), since models indicate that a planar conformation will be somewhat strained. Models also indicate a very close contact between one ethyl group on each tertiary amino function for this isomer, so steric forces are probably also contributory to the relative stability of (*a*) *vs.* (*b*).

The fact that this amido ligand can bind in such a fashion with all three nitrogens and the metal atom in a plane and with the amido nitrogen π-bonded to the metal is precedented.[8] It is indeed the only mode of binding known for this ligand.

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* For example, for $VX_3{\cdot}2L$ (X = halide, L = nitrogen or sulphur donor), $\mu_{eff.}$ varies from 2.5 to 2.7 and for $TiX_3{\cdot}2L$ or $TiX_3{\cdot}3L$ (L = nitrogen or oxygen donor) $\mu_{eff.}$ is very close to the spin-only value.

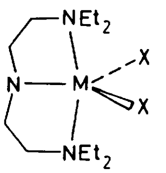

Figure 2. Proposed structure of compounds (**2**) and (**4**)—(**6**) (M = Ti or V; X = Cl, Me, or Ph)

The structures of the vanadium compounds (**3**) and (**7**) are distorted trigonal bipyramidal, with the anionic ligands in the trigonal plane. Distortions from pure geometry are due to differences in the V–C or V–Cl and the V–N bond lengths and to the chelate restrictions forcing the axial N–V–N angle to be less than 180°. The general structure is shown in Figure 2 and is likely to be representative of all titanium and vanadium compounds since this structure is also precedented for Ti^{III}.[14]

Preparation of these 'ternary' complexes demonstrates the stabilising effect of the chelating ligand since the resultant complexes are quite resistant to disproportionations and ligand rearrangements. This is most marked for V^{III} for which attempts to prepare dialkylamides result in compounds that readily disproportionate[2] to vanadium-(IV) and -(II) species. An exception is $[V\{N(SiMe_3)_2\}_3]$[4] which presumably owes its stability to the bulk of its ligands. This is also generally true for Ti^{III}.

This kinetic stabilisation of 'ternary' complexes now provides access to a wide range of new compounds. We are currently investigating the chemistry of these organometallic derivatives.

Experimental

All manipulations were performed using a Vacuum Atmospheres HE-43-2 glove-box or standard Schlenk-line techniques under high-purity nitrogen and an efficient gas purifier of local design. Zirconium tetrachloride (Aldrich) was sublimed prior to use. The compounds VCl_3·3thf, $TiCl_3$·3thf, and $NbCl_4$·2thf were prepared from vanadium trichloride (Alfa), titanium trichloride (Aldrich), and niobium pentachloride (Aldrich) respectively using standard literature routes.[13,15] Yields quoted are for the analytically pure material. Tetrahydrofuran, diethyl ether, and hexane were refluxed over sodium–potassium alloy and benzophenone, benzene over sodium–potassium alloy, and toluene over sodium. Solvents were distilled just prior to use.

Carbon, hydrogen, and nitrogen analyses were by Mikroanalytisches Labor Pascher (Bonn), Butterworth Laboratories (Middlesex), or CHN Analysis Ltd. (Leicester). N.m.r. spectra were obtained on a Bruker WM-360 spectrometer (360 MHz, ^{1}H; 90 MHz, ^{13}C) in C_6D_6 and were referenced to residual protic impurity (^{1}H, δ 7.27) or the solvent carbons (^{13}C, δ 128.8 p.p.m.). E.s.r. spectra were obtained on a Varian E109 *X*-band instrument. Infrared spectra were obtained on a Perkin-Elmer 783 spectrometer and referenced to polystyrene (1 601 cm^{-1}), magnetic susceptibility on a Johnson-Matthey magnetic susceptibility balance. Melting points were measured in sealed tubes and are not corrected. Mass spectra (chemical ionisation, CH_4) were obtained on VG micromass 7070 spectrometer or at the S.E.R.C. mass spectrometry centre at Swansea using a VG Mass Lab GC/MS instrument; samples were introduced as diethyl ether solutions. Molecular weights were measured by the cryoscopic method in benzene. Deuteriated benzene was dried over activated 4A molecular sieves and freeze–thaw degassed just prior to use.

All the organometallic derivatives are conveniently prepared directly from $TiCl_3$·3thf or VCl_3·3thf as described below, however similar results are obtained in all cases if compounds (**2**) or (**3**) are used as precursors.

3,9-*Diethyl*-3,6,9-*triazaundecane*, $HN(CH_2CH_2NEt_2)_2$.—Our preparation is an adaptation from that of Marxer and Miescher.[16]

Bis(2-chloroethyl)amine hydrochloride (100 g, 0.56 mol), ethanol (300 cm^3), diethylamine (300 cm^3, 2.92 mol), and sodium iodide (1.5 g, 0.01 mol) were placed in a flask (3 l) and refluxed (72 h). Sodium (50 g, 2.17 mol) was dissolved in an excess of ethanol (1.5 l) and the solution was added to the reaction mixture at room temperature. The mixture was filtered and ethanol and diethylamine removed on a rotary evaporator. The remaining material was extracted with diethyl ether (4 × 200 cm^3) and filtered, the ether was then evaporated, and the remaining oil transferred to a distillation flask. The ether was distilled at atmospheric pressure. All volatile materials with a boiling point up to 130 °C (0.01 mmHg) were collected by low-pressure distillation. Subsequent fractional distillation of this phase enabled collection of the product at 50—55 °C (0.01 mmHg) [yield 23%, 27.7 g, based on bis(2-chloroethyl)amine hydrochloride]. The i.r. spectrum was recorded for the neat liquid: 3 460m, br, 3 300m, br, 2 985s, 2 950s, 2 885s, 2 805s, 1 680w, br, 1 470s, 1 461s, 1 450s, 1 382s, 1 371s, 1 360w, 1 345w, 1 335w, 1 294s, 1 261m, 1 225w, 1 204s, 1 190w, 1 169w, 1 145m, 1 138m, 1 085s, 1 070s, 995w, 975w, 945w, 920w, 860w, br, 800m, br, 780m, br, 735s, 535m, br, 486m, br, 395w, br, and 305w, br cm^{-1}.

Bis(2-*diethylaminoethyl*)*amidolithium*, $Li[N(CH_2CH_2NEt_2)_2]$ (**1**).—3,9-Diethyl-3,6,9-triazaundecane (8.4 g, 0.039 mol) and diethyl ether (50 cm^3) were placed in a Schlenk flask and cooled (−78 °C). Methyl-lithium (in diethyl ether, 28.5 cm^3; 0.039 mol) was added *via* a syringe dropwise with stirring. The mixture was allowed to warm (20 °C) and was stirred (3 h). The volatile materials were removed *in vacuo*. Hexane (200 cm^3) was added, and the solution was filtered and concentrated until saturated. After cooling (−20 °C), large white prisms separated and were collected. Several consecutive crops were collected by further concentration and cooling. Yield 86%, 7.41 g (based on 3,9-diethyl-3,6,9-triazaundecane). The amide may also be conveniently prepared by the addition of other alkyl-lithium reagents in place of methyl-lithium.

The lithium amide was used as a 0.25 mol dm^{-3} solution in toluene for the following preparations. I.r.: 2 680s, 2 615s, 1 385m, 1 300m, 1 260m, 1 230s, 1 195s, 1 175w, 1 148s, 1 125w, 1 083s, 1 069s, 1 052w, 1 001m, 922s, 900w, 851s, 810m, 796m, 781m, 738s, 600w, 572w, 540s, br, 505s, 454w, 412w, and 380s, br cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*dichlorotitanium*(III), $[TiCl_2\{N(CH_2CH_2NEt_2)_2\}]$ (**2**).—To a suspension of $TiCl_3$·3thf (0.30 g, 0.81 mmol) in tetrahydrofuran (20 cm^3) at −78 °C was added lithium amide solution (3.2 cm^3, 0.81 mmol) with stirring. The solution was allowed to warm (20 °C) and was then stirred (3 h). It was taken to dryness, and the residue extracted with hexane (50 cm^3) and filtered. The blue-green solution was concentrated until saturated, and cooled (−20 °C). Blue-green prisms separated and were collected. Yield 96%, 0.26 g (based on $TiCl_3$·3thf) (Found: C, 43.00; H, 8.65; N, 13.00. $C_{12}H_{28}Cl_2N_3Ti$ requires C, 42.25; H, 8.45; N, 12.60%). I.r.: 1 404w, 1 331m, 1 305w, br, 1 260m, 1 232m, 1 179w, 1 162vw, 1 150m, 1 129vw, 1 108m, 1 087m, 1 070vw, 1 065vw, 1 037w, 1 027m, 997m, 942m, 937m, 908vw, 868m, 816m, 800w, br, 782m, 731s, 545s, 472m, 350m, br, 324s, and 251s cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*dichlorovanadium*(III), $[VCl_2\{N(CH_2CH_2NEt_2)_2\}]$ (**3**).—As for (**2**) above, from

VCl_3·3thf (1.42 g, 3.83 mmol) was obtained 0.62 g of compound (**3**) (48% based on VCl_3·3thf) as orange prisms by cooling (−20 °C) the saturated hexane extract (Found: C, 42.75; H, 8.70; N, 12.35. $C_{12}H_{28}Cl_2N_3V$ requires C, 42.85; H, 8.40; N, 12.50%). I.r.: 1 400w, 1 350w, 1 329m (sh), 1 313w, 1 305w, br, 1 242w, 1 223m (sh), 1 180w, 1 155m, 1 148m, 1 138m, 1 130m, 1 102m (sh), 1 086m (sh), 1 069w, 1 059w, 1 045w, 1 034m, 1 023m, 995w, 939m, 926m, 910w, 865m (sh), 813m, 780m, 740s (sh), 571m, 550m, 471w, 402m, 388m, 318m (sh), 287w, 268m, and 220w cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*dimethyltitanium*(III), $[TiMe_2\{N(CH_2CH_2NEt_2)_2\}]$ (**4**).—A solution of compound (**2**) in thf was prepared as described from $TiCl_3$·3thf (5.00 g, 13.5 mmol). It was cooled (−78 °C) and methyl-lithium (in diethyl ether, 28.9 cm^3; 27.0 mmol) was added with stirring. The solution was warmed to room temperature and stirred (3 h). The volatile materials were removed *in vacuo*, and the solid extracted into hexane (200 cm^3) and filtered. The blue-green solution provided several crops of blue-green crystals upon successive concentration and cooling (−20 °C) cycles. Yield 60%, 2.36 g (based on $TiCl_3$·3thf) (Found: C, 57.65; H, 11.50; N, 14.50. $C_{14}H_{34}N_3Ti$ requires C, 57.55; H, 11.65; N, 14.40%). I.r.: 1 401w, 1 349w, 1 329s (sh), 1 308w, 1 300w, 1 261s (sh), 1 242w, 1 228m (sh), 1 202w, 1 182m, 1 171s, 1 151s, 1 130w, 1 105s, 1 089s, 1 071w, 1 063w, 1 050vw, 1 040m, 1 028m, 999m, 969w, 939s (sh), 925s (sh), 908w, 864s (sh), 815w, 795m, 785m, 735s, 639w, 602m, 570m, 538s, br, 480s, br, 431m, br, 295w, and 238s cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*diphenyltitanium*(III), $[TiPh_2\{N(CH_2CH_2NEt_2)_2\}]$ (**5**).—A thf solution of compound (**2**), prepared from $TiCl_3$·3thf (4.00 g, 10.8 mmol) and used directly, was cooled to −78 °C and phenyl-lithium (in diethyl ether, 17.3 cm^3; 21.6 mmol) was added with stirring. The solution was warmed to room temperature and stirred for 3 h. The volatile materials were removed *in vacuo*, and the residue extracted into hexane (250 cm^3) and filtered. The green-yellow solution was concentrated and cooled (−20 °C) whereupon dark green needles were collected in one crop. Yield 83%, 3.73 g (based on $TiCl_3$·3thf) (Found: C, 69.15; H, 9.20; N, 9.95. $C_{24}H_{38}N_3V$ requires C, 69.20; H, 9.20; N, 10.10%). I.r.: 3 100w, 3 019w, 1 548w, 1 408w, 1 329m (sh), 1 304w, br, 1 260m, 1 222m, 1 168m, 1 148m, 1 130w, 1 105m, 1 083m, 1 052m, 1 023m, 998m, 988w, 965w, br, 932m, 920m, 905w, 890w, 860m, 815w, 803w, 781w, 731s, 702s, 671w, 540s, 528s, 469m, 441s, 322s, br, and 252s cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*dimethylvanadium*(III), $[VMe_2\{N(CH_2CH_2NEt_2)_2\}]$ (**6**).—The preparation of this compound is essentially identical to that of the titanium analogue. Thus from VCl_3·3thf (0.74 g, 1.98 mmol) orange-red prisms of (**6**) were obtained. Yield 70%, 0.41 g (based on VCl_3·3thf) (Found: C, 56.80; H, 11.50; N, 14.40. $C_{14}H_{34}N_3V$ requires C, 56.95; H, 11.60; N, 14.20%). I.r.: 1 397w, 1 328s (sh), 1 302w, br, 1 260m, 1 240vw, 1 222m, 1 182w, 1 169s, 1 152s, 1 128w, 1 116vw, 1 103s, 1 086m, 1 070w, 1 039m, 1 027m, 998m, 967w, br, 938m, 925m, 906w, 862s (sh), 813m, 781m, 733s, 602w, 577s, 559s, 537s, 486vw, 462vw, 438w, 390vw, 340vw, br, 298w, 250m, 240m, and 220w cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*diphenylvanadium*(III), $[VPh_2\{N(CH_2CH_2NEt_2)_2\}]$ (**7**).—This preparation again is essentially identical to that of the titanium analogue. The product may be obtained as yellow-green needles in 61% yield (0.69 g), starting from and based on VCl_3·3thf (1.00 g, 2.68 mmol) from the hexane (60 cm^3) extract after concentration and cooling (−20 °C) (Found: C, 68.25; H, 9.35; N, 10.05. $C_{24}H_{38}N_3V$ requires C, 68.70; H, 9.15; N, 10.00%). I.r.: 3 100vw, 3 018m, 3 012m, 1 580w, 1 558m (sh), 1 550w, 1 411w, 1 400w, br, 1 300s (sh), 1 307w, br, 1 260m, 1 226m, 1 180vw, 1 164m, 1 147m, 1 131m, 1 102m, br, 1 087m, 1 068vw, 1 052m, 1 047w, 1 038w, 1 025m, 998m, 937m, 926m, 917w, 862m, 818w, 805w, br, 784w, 735s (sh), 719s, 708s, 645vw, 640w, 603vw, 567vw, 552s, 542s, 478w, 453s (sh), 345m, br, 288w, and 258s, br cm^{-1}.

Bis[*bis*(2-*diethylaminoethyl*)*amido*]*dichloroniobium*(IV), $[NbCl_2\{N(CH_2CH_2NEt_2)_2\}_2]$ (**8**).—To a suspension of $NbCl_4$·2thf (0.86 g, 2.27 mmol) in thf (80 cm^3) at −78 °C was added lithium amide solution (18.2 cm^3, 4.54 mmol) with stirring. The solution was warmed to room temperature, and stirred (3 h). Volatile materials were removed *in vacuo*, and the remaining solid extracted with hexane (50 cm^3) and filtered. The brown solution was concentrated until saturated and cooled (−20 °C). Orange-brown prisms separated and were collected. Yield 52%, 0.70 g (based on $NbCl_4$·2thf) (Found: C, 48.75; H, 9.45; N, 14.10. $C_{24}H_{56}Cl_2N_6Nb$ requires C, 48.65; H, 9.45; N, 14.20%). I.r.: 1 351w, 1 340m, 1 315w, 1 300w, 1 285s, 1 260m, 1 248w, 1 233m, 1 222w, 1 198m, 1 178m, 1 148m, 1 133w, 1 102s, 1 080s, 1 060s, 1 042s, 1 026s, 1 012s, 995w, 935w, 922m, 893w, 879s, 852m, 820m, 798s, 788m, 733vs, 638m, 618m, 580s, 518s, 490w, 475m, 465w, 445w, 430w, 415w, 395m, 312s, 281s (sh), 274s, and 258m cm^{-1}.

[*Bis*(2-*diethylaminoethyl*)*amido*]*trichlorozirconium*(IV), $[ZrCl_3\{N(CH_2CH_2NEt_2)_2\}]$ (**9**).—To a suspension of $ZrCl_4$ (1.00 g, 4.29 mmol) in toluene (30 cm^3) at −78 °C was added lithium amide solution (17.2 cm^3, 4.29 mmol) with stirring. The solution was warmed to room temperature, and stirred (24 h). The mixture was evaporated to dryness and the residue washed with light petroleum (20 cm^3) and extracted with toluene (40 cm^3). The filtered solution was concentrated until saturated and cooled (−20 °C). The resulting white needles were collected. Yield 60%, 1.05 g (based on $ZrCl_4$) (Found: C, 34.90; H, 6.80; N, 10.10. $C_{12}H_{28}Cl_3N_3Zr$ requires C, 35.00; H, 6.85; N, 10.20%). I.r.: 1 410vw, 1 336w, 1 310w, 1 265m, 1 240m, 1 228w, 1 181m, 1 158vw, 1 144vw, 1 132vw, 1 108m, 1 091w, 1 081vw, 1 070w, 1 045vw, 1 032w, 1 019m, 1 005m, 970w, 938m, 921m, 902w, 880m, 812m, 786m, 730s, br, 580w, 546m, 539m, 516s, 461s, 340vs, br, 315vs, br, and 290vs, br cm^{-1}.

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