β-Diiminato Complexes of V^{III} and Ti^{III} − Formation and Structure of Stable Paramagnetic Dialkylmetal Compounds

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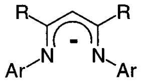
(Mono-β-diiminato)titanium(III) and -vanadium(III) dichlorides $LMCl_2$ [L = ArNC(R)CHC(R)NAr$^-$] are easily accessible from the metal trichlorides and LLi in THF. The crystal structures of $LVCl_2$ (Ar = 2,6-iPr$_2$C$_6$H$_3$, R = Me) and $LTiCl_2$ (Ar = 2,4,6-Me$_3$C$_6$H$_2$, R = Me and Ar = 2,4,6-Me$_3$C$_6$H$_2$, R = tBu) reveal tetrahedral metal environments. Treatment of $LVCl_2$ with alkyllithium reagents affords surprisingly stable dialkylvanadium(III) compounds; the structure of LV(nBu)$_2$ (Ar = 2,6-iPr$_2$C$_6$H$_3$, R = Me) is similar to that of the dichloride. The corresponding dialkyltitanium(III) compounds are less stable; only the dimethyl derivatives could be obtained in pure form (from $LTiCl_2$ and MeMgI), and only for ligands bearing 2,6-disubstituted aryl groups. The structure of $LTiMe_2$ (Ar = 2,4,6-Me$_3$C$_6$H$_2$, R = Me) is also similar to that of the dichloride. Reaction of $LTiMe_2$ with B(C$_6$F$_5$)$_3$ produces a catalyst for α-olefin polymerization, but the corresponding V^{III} derivatives are inactive.

Introduction

The development of metallocene catalysis has led to intense interest in the generation and reactivity of early transition alkylmetal compounds. Neutral dialkylmetal compounds, in particular, are of great importance as precursors of catalytically active cationic monoalkyl species. Most of the work in this area has concentrated on diamagnetic d^0 complexes of group-III and -IV metals. It is still unclear whether d^1 or d^2 complexes can be as efficient in olefin polymerization as their d^0 analogues, and this lack of insight is at least partly due to the unavailability of suitable catalyst precursors. However, work by Theopold on d^3 chromium systems demonstrates that well-defined paramagnetic homogeneous polymerization catalysts are certainly possible.[1]

We report herein on the preparation of Ti^{III} (d^1) and V^{III} (d^2) complexes containing a β-diiminato ancillary ligand. The β-diimine ligand has not been widely used in organometallic chemistry. Some Pd^{II} and Ni^{II} complexes have been prepared recently; in comparison with related α-diimine complexes they showed a much lower activity in Brookhart-type olefin polymerization.[2] Collins has recently reported the synthesis of several Zr^{IV} complexes of β-diimines.[3]

One advantage of β-diimines is that ligand variation, in both the ligand backbone and the substituent at the nitrogen atom, is relatively easy. This has allowed us to probe the consequences of steric effects in the present study (Scheme 1 shows the ligands studied and the abbreviations used here). We have concentrated on the $\mathbf{L^1}$ and $\mathbf{L^2}$ ligands, because the Ti and V dichloride and dimethyl derivatives were found to crystallize well, and only examined the use of the other ligands in selected cases.[4]



Ligand Syntheses

The two main routes for the synthesis of β-diimines are summarized in Scheme 1. The most convenient route (**A**) is condensation of a β-diketone with an (aromatic) amine.[5] The second route (**B**) is especially useful for very bulky diimines,[6] where the route **A** condensation is very sluggish. Route **B** is also applicable to the synthesis of asymmetrically substituted diimines (different Ar groups). The ligands used in the present work were all prepared by one of these two methods. Lappert has reported a more exotic synthesis of silyl-substituted diiminates from bis(trimethylsilyl)methyllithium and nitriles.[7]

Dichloride Complexes

Complexes $LMCl_2$ (M = Ti^{III}, V^{III} ; L ≠ $\mathbf{L^4}$ or $\mathbf{L^6}$) are conveniently prepared by reaction in THF of $MCl_3(THF)_3$ with the lithium salt of the β-diimine (prepared in situ from the free diimine and nBuLi). After evaporation of the solvent, the complex is extracted with toluene and purified by

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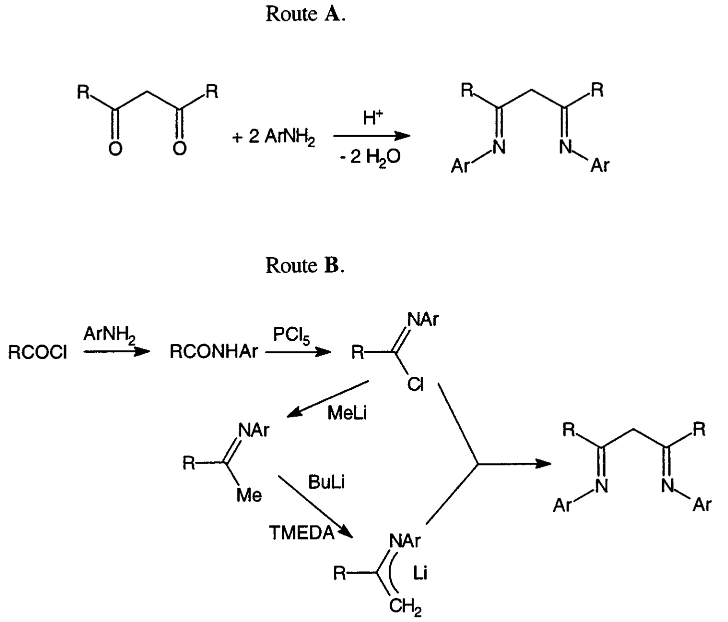
Scheme 1. β-Diimine ligand syntheses



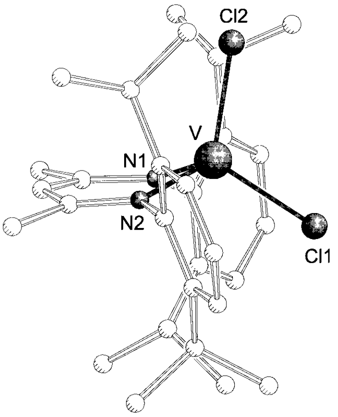
	R	Ar	ref
$\mathbf{L}^1$	Me	2,4,6-$Me_3C_6H_2$	this work
$\mathbf{L}^2$	Me	2,6-(i-Pr)$_2C_6H_3$	2
$\mathbf{L}^3$	Me	2-MeC_6H_4	this work
$\mathbf{L}^4$	Me	C_6H_5	5
$\mathbf{L}^5$	*t*-Bu	2,4,6-$Me_3C_6H_2$	this work
$\mathbf{L}^6$	*t*-Bu	2,6-(i-Pr)$_2C_6H_3$	this work

crystallization from toluene or hexane. In several instances, we initially observed formation of a THF complex; repeated distillation of toluene (at 1 bar) from a solution of the complex was found to be a convenient method for removal of this THF.

The $\mathbf{L}^4$ complexes tenaciously retain 2 molecules of complexed THF. Treatment of $VCl_3(THF)_3$ with $\mathbf{L}^4$Li in THF results in precipitation of dark-green needles of poorly soluble $\mathbf{L}^4VCl_2(THF)_2$. Most of the coordinated THF can be removed by the above-mentioned toluene distillation, but the resulting product is an ill-defined black substance. $\mathbf{L}^4TiCl_2(THF)_2$ is poorly soluble even in hot THF or toluene/THF mixtures; small amounts can be crystallized from THF as dark-brown needles. Reaction of the THF complex with Me_3SiI[8] removes the coordinated THF but also exchanges the chlorides for iodides, giving dark-red $\mathbf{L}^4TiI_2$, which is fairly soluble in toluene and diethyl ether.

All the dichlorides are stable at room temperature, but are highly sensitive to air and moisture. They are paramagnetic and exhibit strongly broadened NMR spectra that could not be fully interpreted. Complexes $\mathbf{L}^2VCl_2$ (Figure 1), $\mathbf{L}^1TiCl_2$ (Figure 2), and $\mathbf{L}^5TiCl_2$ (Figure 3) were characterized by X-ray diffraction. They are monomeric and show the expected distorted tetrahedral surrounding of the metal center. In the case of the bulky $\mathbf{L}^2$ ligand, the metal atom has moved out of the NCCCN plane of the ligand. This allows the aryl groups at the nitrogen atoms to tilt, thus relieving steric repulsion between the chlorides and the isopropyl substituents. Movement of the metal atom out of the NCCCN plane has also been observed in the sterically hindered zirconium complex [$Me_3SiNC(t$Bu)CHC(tBu)N-$SiMe_3]ZrCl_3$[7] and in the tin derivative [$Me_3SiNC(t$Bu)CHC(tBu)$NSiMe_3]SnMe_2Cl$,[7] whereas the unhindered tin complex [HNC(tBu)CHC(tBu)NH]$SnMe_2Cl$[7] and the lanthanide complex [PhNC(Me)CHC(Me)NPh]$GdBr_2(THF)_2$[9] have essentially planar skeletons. The *neutral* β-diimine complex (H$\mathbf{L}^2$)$NiBr_2$ and the *C*-metallated $[Pd(NCMe)_3][\mu\text{-C:N,N}'\text{-}\mathbf{L}^2][Pd(NCMe)_2]^{3+}$ also have non-planar diimine skeletons.[2] The strongly non-planar structure recently reported for ($\mathbf{L}^4$)(indenyl)$ZrCl_2$ by Collins was described as partially η^5;[3] the nonplanarity of our $\mathbf{L}^2VCl_2$ complex is clearly not pronounced enough to warrant such a description.

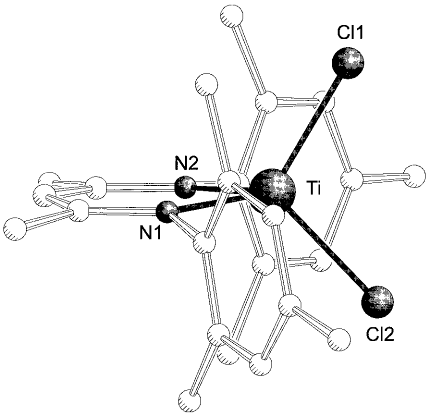
Figure 1. X-ray structure of L^2VCl_2[a]



[a] Selected structure data: V−N1 1.940(2), V−N2 1.963(2), V−Cl1 2.242(1), V−Cl2 2.234(1) Å; N1−V−N2 94.0(1), Cl1−V−Cl2 114.3(1)°.

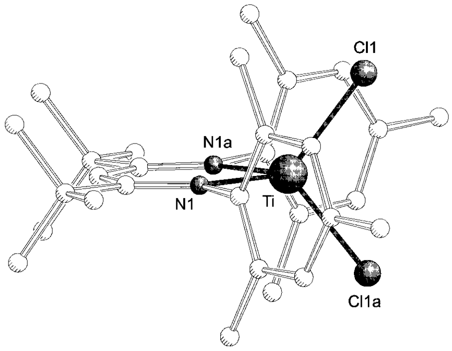
Surprisingly, we were unable to prepare transition metal complexes of the bulkiest ligand ($\mathbf{L}^6$). Neither the lithium salt nor the potassium salt reacted with $TiCl_3$ in refluxing THF, despite the fact that in the less hindered systems ligand transfer occurs even at room temperature. With VCl_3, some kind of reaction took place, but no vanadium diiminate was formed. It occurred to us that the steric repulsion between the backbone *t*Bu groups and the substituents at the nitrogen atoms might destabilize the geometry needed

Figure 2. X-ray structure of L^1TiCl_2[a]



[a] Selected structure data: Ti−N1 1.983(3), Ti−N2 1.964(3), Ti−Cl1 2.294(1), Ti−Cl2 2.295(1) Å; N1−Ti−N2 84.2(1), Cl1−Ti−Cl2 106.34(5)°.

Figure 3. X-ray structure of L^5TiCl_2[a]



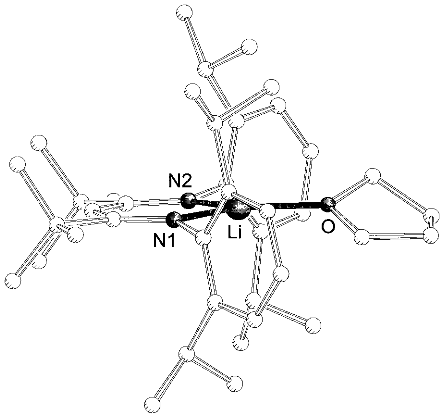
[a] Selected structure data: Ti−N1 1.986(1), Ti−Cl1 2.2966(6) Å; N1−Ti−N1a 83.88(8), Cl1−Ti−Cl1a 104.57(3)°.

for chelation, for example by enforcing a *trans* arrangement of the *t*Bu and diisopropylphenyl groups around the C=N bonds. However, the X-ray structure of the salt **L⁶**Li(THF) (Figure 4) shows a normal chelate structure. The most likely explanation for the failure to form Ti and V complexes is still a steric one. The *t*Bu groups enforce a larger C−N−C angle [compare the values of 119 and 120° in $\mathbf{L^2}VCl_2$ and 121 and 122° in $\mathbf{L^1}TiCl_2$ to 128° in $\mathbf{L^5}TiCl_2$ and 127 and 129° in $\mathbf{L^6}$Li(THF)], thus restricting the amount of space in the open "wedge" between the aryl groups. Also, the possibility of strain relief by aryl group tilting as found in $\mathbf{L^2}VCl_2$ is probably limited by the *t*Bu groups. Thus, there is still enough space in the center of the open wedge for the single THF molecule in $\mathbf{L^6}$Li(THF), but the isopropyl groups might cause severe repulsion at the two tetrahedral positions of the chlorides in a hypothetical $\mathbf{L^6}MCl_2$ molecule.

Dialkylvanadium(III) Compounds

Treatment of complexes $LVCl_2$ with alkyllithium compounds (MeLi, *n*BuLi) in diethyl ether affords easy access to dialkylmetal compounds LVR_2. These complexes were found to be unexpectedly stable. For example, $\mathbf{L^2}$V(*n*Bu)$_2$, which is formally a 10-*e* complex (or at most a 14-*e* complex, if π-donation from both nitrogen atoms is included in the count) and contains 4 β-hydrogen atomss, could be crystallized from warm (50°C) hexane without significant decomposition. The X-ray structure of this complex (Figure 5) shows a tetrahedral environment of the metal centre, similar to that in the dichloride. There is some disorder in one of the *n*-butyl groups, but the structure is otherwise unremarkable. There is no evidence for significant agostic interactions or short intermolecular contacts.

Figure 4. X-ray structure of L^6Li(THF)[a]



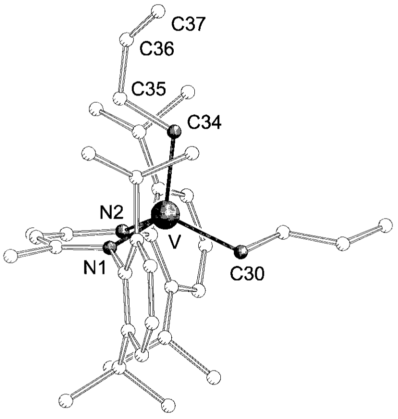
[a] Selected structure data: Li−N1 1.927(6), Li−N2 1.927(6), Li−O 1.910(6) Å; N1−Li−N2 100.2(3), N1−Li−O 130.9(3), N2−Li−O 128.8(3)°.

Not many dialkylvanadium(III) compounds are known. Two examples bearing tridentate amido ligands have been reported: Edwards obtained a compound formulated as $[(Me_2PCH_2CH_2)_2N]VMe_2$ as an oil from the reaction of the dichloride with MeLi;[10] he also obtained the crystalline complex $[(Et_2NCH_2CH_2)_2N]VMe_2$ in a similar manner.[11] $CpVMe_2(PMe_3)_2$[12] and $CpVR_2(PMe_3)$ (R = CH_2CMe_3, CH_2CMe_2Ph, CH_2SiMe_3)[13] have been reported by the group of Teuben. None of these complexes have been characterized by X-ray diffraction, but the crystal structure of the metallated alkyl-aryl complex CpV(CH_2CMe_2-*o*-C_6H_4)$(PMe_3)_2$ has been determined and shows a rather long V−C(alkyl) distance of 2.194(3) Å.[13] The *tri*alkyl complex $[(Me_3CCH_2)_3V]_2(\mu\text{-}N_2)$ has much shorter V−C bonds [2.026(2) Å];[14] those in our complex $\mathbf{L^2}V(n\mathrm{Bu})_2$ are intermediate [2.062(5) Å].

Dialkyltitanium(III) Compounds

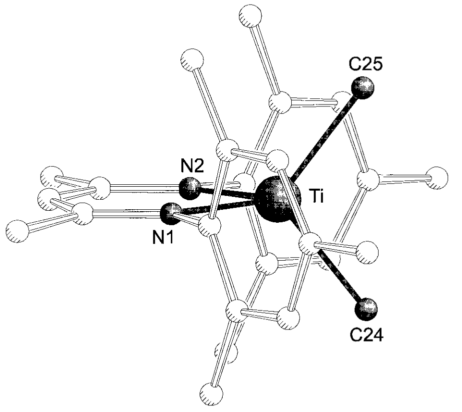
The related dialkyltitanium(III) compounds were found to be less stable. For ligands bearing 2,6-disubstituted aryl groups, $LTiMe_2$ complexes are best prepared from $LTiCl_2$ and MeMgI in diethyl ether. Addition of 1 equiv. of dioxane, evaporation of the solvent, and extraction with hexane gave an impure product, which could be purified further by crystallization from hexane. The $LTiMe_2$ complexes all have an intense dark-blue colour. The structure of $\mathbf{L^1}TiMe_2$ (Figure 6) shows the expected tetrahedral environment of the metal centre and is very similar to that of

Figure 5. X-ray structure of $L^2V(nBu)_2$[a]



[a] Selected structure data: V−N1 1.997(4), V−N2 1.991(4), V−C30 2.062(5), V−C34 2.062(5) Å; N1−V−N2 94.5(2), C30−V−C34 109.6(2)°; the apparent near-eclipsed confirmation of the C34−C37 butyl chain is caused by a disorder in the positions of C35 and C36, probably between two possible *gauche* conformations.

Figure 6. X-ray structure of L^1TiMe_2[a]



[a] Selected structure data: Ti−N1 1.989(2), Ti−N2 1.989(2), Ti−C24 2.131(3), Ti−C25 2.123(3) Å; N1−Ti−N2 85.33(7), C24−Ti−C25 104.5(1)°.

the dichloride. Paramagnetic alkyltitanium compounds are relatively rare, and only a few examples not bearing cyclopentadienyl substituents have been described. Arnold has reported the synthesis of a *mono*methyltitanium(III) benzamidinate complex, $[PhC(NSiMe_3)_2]_2TiMe$,[15] and suggested that the unusually short Ti−C bond in this complex, 2.120(5) Å, was due to the low coordination number (5) of the Ti atom. The coordination number of Ti in $\mathbf{L^1}TiMe_2$ is even lower (4), but the Ti−C bond lengths [2.123(3) and 2.131(3) Å] are not shorter than those in the benzamidinate compound. However, the benzamidinato ligand should be "harder" than the diiminato ligand, and this is reflected in much longer Ti−N bonds [2.104(3), 2.164(3), 2.095(3), and 2.160(3) Å, vs. 1.989(2) Å in $\mathbf{L^1}TiMe_2$], which might compensate for the difference in coordination number. Cummins has reported the X-ray structure of $[\eta^1\text{-}(t\mathrm{Bu})(\mathrm{Ar})\mathrm{N}][\eta^3\text{-}(t\mathrm{Bu})(\mathrm{Ar})\mathrm{N}]\mathrm{TiCH}(\mathrm{SiMe_3})_2$ (Ar = $3,5\text{-}Me_2C_6H_3$), which has a Ti−C distance of 2.137(7) Å.[16] Edwards has reported the preparation of $[(Et_2NCH_2CH_2)_2N]TiMe_2$, which was characterized by elemental analysis and ESR; no further details of its stability and reactivity were given.[11] Gambarotta has prepared several anionic dialkyltitanium(III) compounds $(R_2N)_2Ti(\mu\text{-}R')_2Li(TMEDA)$ and $[(R_2N)_2Ti(R')_2]^-[Li(TMEDA)_2]^+$.[17]

The presence of sufficient steric shielding appears to be essential for the stability of the product. Whereas $LTiMe_2$ complexes bearing *2,6-disubstituted* aryl groupss were found to be reasonably stable at room temperature, the bis(*o-tolyl*) ($\mathbf{L^3}$) derivative decomposes within 1 h (an impure product could be obtained by carrying out the reaction and isolation at −10°C). The di*phenyl* ($\mathbf{L^4}$) derivative was initially formed upon addition of MeMgI to $LTiCl_2$ (as indicated by the deep-blue colour), but within ca. 10 seconds the colour had changed to green-brown, indicating rapid decomposition. We could not find any conditions under which the rate of formation was sufficiently high and the decomposition slow enough to allow isolation of $\mathbf{L^4}TiMe_2$.

Higher alkyl derivatives are less stable than the methyl complexes. A few large, dark-blue crystals of what appeared to be $\mathbf{L^1}TiEt_2$ were obtained by rapid work-up of the reaction product from $\mathbf{L^1}TiCl_2$ and EtMgBr in Et_2O, but even during crystallization at −20°C the initially blue hexane solution turned green, indicating partial decomposition. The crystals themselves were fully decomposed after 1 night at room temperature. No further attempts were made to prepare higher alkyl compounds.

Polymerization Experiments

Even though they are coordinatively unsaturated, the dialkylmetal compounds themselves were found to be unreactive towards olefins. Treatment with MAO or $EtAlCl_2$ resulted in transfer of the β-diimine ligand to Al, and no significant polymerization activity was observed. The reaction of $LVMe_2$ complexes with 1 equiv. of $B(C_6F_5)_3$ produced a brown solution, possibly containing the ionic species, but no polymerization activity was observed with propene, and only a very low activity with ethene.

The corresponding Ti complexes proved to be significantly more active. Reaction of $\mathbf{L^1}TiMe_2$ with $B(C_6F_5)_3$ in benzene produced a red-brown solution, possibly containing $\mathbf{L^1}TiMe^+MeB(C_6F_5)_3^-$. This solution was found to be active in the polymerization of propene and 1-hexene, producing atactic materials, although activities in propene polymerization (see Table 1) are not very high compared to those of metallocene catalysts. The molecular weight distribution is rather narrow ($M_w/M_n \approx 1.58-1.78$) indicating relatively slow chain transfer. The polymerization is not "living", since propene absorption almost stopped after 15 min. The stoichiometry of the reaction indicates the formation of ca. 1 chain per metal atom. NMR analysis of the product did not reveal any unsaturated end groups. These facts suggest that the polymerization does *not* terminate by β-elimination, but by a different mechanism which prevents initiation of a new chain. One possibility is reaction with impurities in the feed (since there is no scavenger present

Table 1. Propene polymerization experiments[a]

Entry	Cat.	Co-cat.	Solvent	Time [min]	Activity[b][c]	Remarks
1	**L^1**$TiMe_2$	$B(C_6F_5)_3$	benzene	30	62000/96000	
2		$B(C_6F_5)_3$	benzene	120	25000	0.05 mmol cat, co-cat.
3		$B(C_6F_5)_3$	benzene	30	14000/33000	50°C; exotherm
4		$B(C_6F_5)_3$	toluene	10	−	
5		$B(C_6F_5)_3$	bromobenzene	10	−	
6		$Ph_3C^+B(C_6F_5)_4^-$	benzene	30	−	
7		$PhMe_2NH^+ B(C_6F_5)_4^-$	benzene	30	53000/101000	
8		$PhMe_2NH^+ B(C_6F_5)_4^-$	benzene	30	2000/8100	0.05 mmol cat, co-cat.
9	**L^5**$TiMe_2$	$B(C_6F_5)_3$	benzene	30	0/2000/10000	
10	**L^2**$TiMe_2$	$B(C_6F_5)_3$	benzene	30	2000	

[a] 0.1 mmol of cat. and co-cat., 25 ml of solvent, 5−6 bar propene, room temperature. − [b] (g olefin)/(mol Ti)·h. − [c] Multiple entries are results from separate experiments.

in this system), but alkyl transfer to the ligand cannot be excluded: Floriani observed transfer of alkyl groups from Zr^{IV} to the imine carbon atoms of the macrocyclic bis(diiminato) ligand tmtaa.[18] Reproducibility of the activities is poor (see the different activities given for entries 1, 3, 7, 8, 9 in the table). We found that the time taken to prepare the catalyst mixture and the laboratory temperature had a significant influence, indicating that the catalyst is not very stable.

Curiously, polymerization activity is virtually zero if toluene is used as the solvent instead of benzene (entries 1 and 3). Inhibition of polymerization by toluene has been noted for a closely related Ti^{IV} di*amide* catalyst by McConville,[19] but he did not report on the effect of benzene in the same system. McConville attributed the effect of toluene to the formation of a toluene complex. Our observed difference between benzene and toluene might have a similar cause, since toluene is a somewhat stronger donor than benzene. However, we do not consider this very likely since some activity was observed when the reaction was carried out at a lower temperature in toluene. Chemical reaction with toluene (e.g. benzylic C−H activation) could be an alternative explanation.

The catalyst system used here allows only a limited amount of “tuning”. Increasing the steric hindrance at the metal centre was found to have a deleterious effect on activity (compare entries 1 and 10). *Reduction* of steric hindrance was not possible since the required $LTiMe_2$ precursors are unstable (see above). Use of the less coordinating anion $B(C_6F_5)_4^-$ also decreased activity (entries 1 and 6), possibly because of faster catalyst decomposition. Activity is also lower at higher temperature (entries 1 and 3), again indicating catalyst decomposition. Thus, the scope of this Ti^{III} catalyst appears to be rather limited.

Conclusions

β-Diimine complexes $LMCl_2$ of Ti^{III} and V^{III} are easily prepared. The corresponding dialkylmetal compounds are unexpectedly stable when M = V, but they do not seem to give rise to active polymerization catalysts. The corresponding dialkyltitanium(III) compounds are much less stable, but catalysts generated from $LTiMe_2$ and $B(C_6F_5)_3$ show activity in α-olefin polymerization. The reasons for these differences are unclear and point out the need for a more detailed understanding of the reactivity of paramagnetic non-d^0 systems

Experimental Section

General: All manipulations involving lithium, potassium, and transition metal compounds were performed in standard Schlenk glassware under an inert atmosphere. Reagents were used as received. Solvents were dried by distillation from sodium under argon prior to use. − ^1H- and ^{13}C-NMR spectra were recorded using Varian XL-200 and Varian VXR-300 instruments, respectively. − The metal chlorides $TiCl_3(THF)_3$ and $VCl_3(THF)_3$[20], the ligands **L^2**H[2] and **L^4**H[5] and the borane $B(C_6F_5)_3$[21] were prepared according to literature methods. For some syntheses of vanadium compounds, $VCl_3(THF)_3$ was prepared in situ by refluxing anhydrous VCl_3 in THF prior to reaction with a lithium β-diiminate.

***L^2**Li:* 76 g of **L^2**H was dissolved in 200 ml of THF. To a cooled solution of 10.2 g of *n*BuLi in 250 ml of hexane was added 25 ml of diisopropylamine, and this solution was slowly added to the cooled solution of **L^2**H. The mixture was warmed to room temperature and the solvents were removed in vacuo. The crude product was crystallized from hexane (+65°C/−20°C) to give light-yellow crystals of the composition **L^2**Li(THF) (by NMR) (ca. 70 g, 80%). − ^1H NMR (C_6D_6): δ = 7.28 (*m*-H), 7.20 (*p*-H), 5.14 (C*H*C=N), 2.03 (C*H*$_3$C=N), 1.30, 1.40, 3.55 (*i*Pr), 1.02, 2.83 (THF). − ^{13}C NMR ([D$_8$]THF): δ = 150.3 (*i*-C), 141.4 (*o*-C), 123.4 (*m*-C), 123.1 (*p*-C), 163.4 (*C*=N), 92.7 (*C*HC=N), 28.4 (*C*H$_3$C=N), 24.8, 24.0 (*C*H$_3$CH), 23.3 (*C*HCH$_3$).

***L^1**H* was prepared by a similar route to that used for **L^2**H:[2] A mixture of 25.03 g of acetylacetone (0.25 mol), 67.6 g of 2,4,6-trimethylaniline (0.5 mol), and 20.8 ml of 12 N hydrochloric acid (0.25 mol) was heated to 120°C for 4 h. Water was allowed to distil from the reaction mixture and heating was continued at 140°C overnight. Thereafter, the solids produced were crystallized from refluxing ethanol. Two fractions were collected, the second fraction after treatment with diethyl ether. Yield of crude **L^1**H·HCl: 87.6 g (94%). − ^1H NMR ($CDCl_3$): δ = 2.65 (1-H), 4.29 (3-H), 6.74 (*m*-H), 1.94 (α*o*-H), 2.23 (α*p*-H), 4.88 (NH). − ^{13}C NMR ($CDCl_3$): δ = 21.1 (C-1), 171.5 (C-2), 90.5 (C-3), 139.7 (*i*-C), 135.5 (*o*-C), 130.0 (*m*-C), 132.7 (*p*-C), 17.5 (α*o*-C), 21.2 (α*p*-C). A mixture of 60.2 g of crude **L^1**H·HCl (162 mmol), 30 ml of triethylamine (218 mmol), 200 ml of dichloromethane, and 100 ml of water was stirred for 1 h until all solids had dissolved and a clear separation of the two layers had occurred. The organic phase was removed, dried with magnesium sulfate, filtered, and the solvent was removed in vacuo. The resulting thick oil was dried in vacuo at 100°C for 4 h (to remove small amounts of 2,4,6-trimethylaniline). The crude product **L^1**H was isolated as a brown solid, yield 46.2 g (85%), and was used as such, without further purification, for reaction with transition metal chlorides. − ^{1}H NMR ($CDCl_3$): δ = 1.68 (1-H), 4.85 (3-H), 6.85 (*m*-H), 2.25 (α*o*-H), 2.11 (α*p*-H). − ^{13}C NMR ($CDCl_3$): δ = 20.3 (C-1), 160.9 (C-2), 93.3 (C-3), 141.1 (*i*-C), 131.8 (*o*-C), 128.4 (*m*-C), 133.4 (*p*-C), 18.2 (α*o*-C), 20.8 (α*p*-C).

L^{5}H was prepared by procedures similar to those used by Knorr and Weiss for bulky diimines.[6] − (a) To a mixture of 67.6 g of 2,4,6-trimethylaniline (0.5 mol) and 50.6 g of triethylamine (0.5 mol) in 800 ml of dichloromethane was slowly added a solution of 60.3 g of pivaloyl chloride (0.5 mol) in 200 ml of dichloromethane. After the addition was completed, the reaction mixture was refluxed for 1 h and then extracted with 2 × 250 ml water. The organic fraction was dried with magnesium sulfate, filtered, and the solvent was removed in vacuo. The resulting yellow oil was treated with diethyl ether, yielding a white, microcrystalline powder. This powder was filtered off and dried. Yield: 96 g (88%) of crude 2,2-dimethyl-*N*-(2,4,6-trimethylphenyl)propionamide. − ^{1}H NMR ($CDCl_3$): δ = 1.32 (3-H), 6.86 (*m*-H), 2.14 (α*o*-H), 2.25 (α*p*-H). − ^{13}C NMR ($CDCl_3$): δ = 176.5 (C-1), 39.2 (C-2), 27.8 (C-3), 136.6 (*i*-C), 135.1 (*o*-C), 128.8 (*m*-C), 131.3 (*p*-C), 18.1 (α*o*-C), 20.9 (α*p*-C).

(b) To a slurry of 96 g (438 mmol) of the crude amide in 1 l of toluene, 91.15 g of phosphorus pentachloride (438 mmol) was added in small portions. During the course of the addition, HCl gas was liberated and the reaction mixture became a clear yellow solution. After the addition was completed, the reaction mixture was stirred overnight. The solvent was distilled off, first toluene followed by the formed $POCl_3$. Finally, the product was distilled at 85°C (4 mbar oil pump). Yield: 88.8 g (85%) of 1-chloro-2,2-dimethyl-1-(2,4,6-trimethylphenylimino)propane. − ^{1}H NMR ($CDCl_3$): δ = 1.43 (3-H), 6.88 (*m*-H), 2.03 (α*o*-H), 2.29 (α*p*-H). − ^{13}C NMR ($CDCl_3$): δ = 155.3 (C-1), 43.8 (C-2), 28.5 (C-3), 143.1 (*i*-C), 125.9 (*o*-C), 128.4 (*m*-C), 133.1 (*p*-C), 17.5 (α*o*-C), 20.8 (α*p*-C).

(c) To 32.5 g of 1-chloro-2,2-dimethyl-1-(2,4,6-trimethylphenylimino)propane (137 mmol) in 200 ml of diethyl ether was added 170 ml of 1.6 M methyllithium in diethyl ether (274 mmol). The solution became warm and methane gas was evolved. The reaction mixture was stirred for 1 h at room temperature. After careful hydrolysis with water and subsequent extraction, the organic fraction was dried with magnesium sulfate, filtered, and distilled at 106−108°C (3 mbar oil pump). Yield: 27.6 g (93%) of 3,3-dimethyl-2-(2,4,6-trimethylphenylimino)butane. − ^{1}H NMR ($CDCl_3$): δ = 1.61 (1-H), 1.27 (4-H), 6.81 (m-H), 1.93 (α*o*-H), 2.25 (α*p*-H). − ^{13}C NMR ($CDCl_3$): δ = 15.2 (C-1), 177.0 (C-2), 40.3 (C-3), 28.0 (C-4), 146.3 (*i*-C), 125.1 (*o*-C), 128.4 (*m*-C), 131.2 (*p*-C), 17.5 (α*o*-C), 20.7 (α*p*-C).

(d) To a cooled (−78°C) mixture of 10.85 g of 3,3-dimethyl-2-(2,4,6-trimethylphenylimino)butane (50 mmol) and 5.8 g of *N,N,N′N′*-tetramethylethylenediamine (TMEDA) (50 mmol) in 100 ml of hexane was added 31.25 ml of 1.6 M *n*-butyllithium in hexane (50 mmol). The reaction mixture was allowed to warm to room temperature and was then stirred overnight, resulting in a cloudy, slightly yellow slurry. To this was added dropwise 11.875 g of 1-chloro-2,2-dimethyl-1-(2,4,6-trimethylphenylimino)propane (50 mmol) in 75 ml of hexane. The reaction temperature was maintained below reflux temperature with water-bath cooling. After the addition was completed, the mixture was refluxed for 1 h. Then, 100 ml of water and 100 ml of diethyl ether were added and the product was extracted. The aqueous layer was extracted once with 100 ml of diethyl ether. The combined organic fractions were dried with magnesium sulfate, filtered, and the solvent was evaporated in vacuo. The product was crystallized from refluxing ethanol. Yield: 15.88 g (76%). The NMR spectra show separate peaks due to the imine-enamine and bis(imine) (minor component) forms. − ^{1}H NMR ($CDCl_3$) of imine-enamine form: δ = 1.14 (1-H), 5.43 (4-H), 6.71 (*m*-H), 2.20 (α*o*-H), 2.14 (α*p*-H), 13 (NH); of bis(imine) form (all peaks broad): δ = 0.8−1.4 (1-H), 3.2 (4-H), 1.9 (α*o*-H), 2.23 (α*p*-H), 6.75 (*m*-H). − ^{13}C NMR ($CDCl_3$) of imine-enamine form: δ = 30.4 (C-1), 40.3 (C-2), 170 (C-3), 91 (C-4), 143 (*i*-C), 131.3 (*o*-C), 128.7 (*m*-C), 132.7 (*p*-C), 19.2 (α*o*-C), 20.9 (α*p*-C).

L^{6}H was prepared by a route similar to that used for **L^5**H. − (a) To a mixture of 44.3 g of 2,6-diisopropylaniline (0.25 mol) and 25.3 g of triethylamine (0.25 mol) in 400 ml of dichloromethane was slowly added a solution of 30.145 g of pivaloyl chloride (0.25 mol) in 100 ml of dichloromethane. After the addition was completed, the reaction mixture was refluxed for 1.5 h. It was then diluted with 500 ml of dichloromethane and extracted with water (3 × 100 ml). The organic fraction was dried with magnesium sulfate, filtered, and the solvent was removed in vacuo. The resulting yellow oil was treated with diethyl ether to yield a white microcrystalline powder. This powder was filtered off and dried. Yield: 65.5 g (100%) of crude *N*-(2,6-diisopropylphenyl)-2,2-dimethylpropionamide. − ^{1}H NMR ($CDCl_3$): δ = 1.36 (3-H), 7.15−7.25 (*m*-, *p*-H), 3.00 (α-H), 1.19 (β-H), 6.8 (NH). − ^{13}C NMR ($CDCl_3$): δ = 177.1 (C-1), 39.2 (C-2), 28.7 (C-3), 131.4 (*i*-C), 146.1 (*o*-C), 123.3 (*m*-C), 128.0 (*p*-C), 23.5 (α-C), 27.8 (β-C).

(b) To a slurry of 65.5 g of *N*-(2,6-diisopropylphenyl)-2,2-dimethylpropionamide (0.25 mol) in 500 ml of benzene, 52 g of phosphorus pentachloride (0.25 mol) was added in small portions. During the course of the addition, HCl gas was liberated and the reaction mixture became a clear yellow solution. After the addition was completed, the reaction mixture was stirred for 1 h. The solvent was then distilled off, first benzene followed by the formed $POCl_3$. Finally, the product was distilled at 85°C (4 mbar oil pump). Yield: 54.4 g (78%) of 1-chloro-1-(2,6-diisopropylphenylimino)-2,2-dimethylpropane.[22] − ^{1}H NMR ($CDCl_3$): δ = 1.44 (3-H), 7.14 (*m*-, *p*-H), 2.75 (α-H), 1.2 (β-H). − ^{13}C NMR ($CDCl_3$): δ = 154.6 (C-1), 43.9 (C-2), 28.4 (C-3), 143.1 (*i*-C), 136.4 (*o*-C), 122.9 (*m*-C), 124.4 (*p*-C), 23 (α-, β-C).

(c) To 32.76 g of 1-chloro-1-(2,6-diisopropylphenylimino)-2,2-dimethylpropane (117 mmol) in 100 ml of diethyl ether was added a large excess of 200 ml of 1.6 M methyllithium in diethyl ether (320 mmol). The solution became warm and methane gas was evolved. The reaction mixture was stirred for 3 h at room temperature and then carefully (!) hydrolysed with water. After extraction, the organic fraction was dried with magnesium sulfate, filtered, and distilled at 75°C (2 mbar oil pump). Yield: 27.9 g (92%) of 2-(2,6-diisopropylphenylimino)-3,3-dimethylbutane. − ^{1}H NMR ($CDCl_3$): δ = 1.7 (1-H), 1.3 (4-H), 7.0−7.3 (*m*-, *p*-H), 2.71 (α-H), 1.15, 1.18 (β-H). − ^{13}C NMR ($CDCl_3$): δ = 15.9 (C-1), 176.4 (C-2), 40.4 (C-3), 28.0 (C-4), 146.6 (*i*-C), 135.7 (*o*-C), 122.7 (*m*-C), 122.6 (*p*-C), 27.8 (α-C), 22.8, 23.0 (β-C).

(d) To a cooled (−78°C) mixture of 27.9 g 2-(2,6-diisopropylphenylimino)-3,3-dimethylbutane (107.5 mmol) and 12.5 g of *N,N,N′N′*-tetramethylethylenediamine TMEDA (107.5 mmol) in 100 ml of hexane was added 67.5 ml of 1.6 M *n*-butyllithium in hexane (107.5 mmol). The reaction mixture was allowed to warm to room temperature and then stirred overnight. A sticky white slurry was obtained, which was treated dropwise with 30.1 g of 1-chloro-1-(2,6-diisopropylphenylimino)-2,2-dimethylpropane (107.5 mmol) in 75 ml of hexane. The reaction temperature was maintained below reflux temperature with water-bath cooling. After the addition was completed, the mixture was refluxed for 1 h. Then, 100 ml of water and 100 ml of diethyl ether were added and the product was extracted. The aqueous layer was extracted once with 100 ml of diethyl ether. The combined organic fractions were dried with magnesium sulfate, filtered, and the solvent was evaporated in vacuo. The product was crystallized from refluxing hexane. Two fractions of white crystals (35.86 and 7.47 g) were collected; combined yield 43.33 g (80%) of $\mathbf{L^6}$H. The NMR spectra show separate peaks due to the imine-enamine and bis(imine) (minor component) forms. − ^{1}H NMR ($CDCl_3$) of imine-enamine form: δ = 1.08 (1-H), 5.42 (4-H), 6.94 (*m*-, *p*-H), 3.26 (α-H), 1.02, 1.22 (β-H), 4.9 (NH); of bis(imine) (all peaks broad): δ = 0.8−1.4 (1-H, β-H), 2.4−2.8 (α-H), 6.9−7.2 (*m*-, *p*-H). − ^{13}C NMR ($CDCl_3$) of imine-enamine form: δ = 31.3 (C-1), 41.3 (C-2), 169.3 (C-3), 94.7 (C-4), 142.7 (*i*-C), 141.3 (*o*-C), 123.1 (*m*-C), 122.9 (*p*-C), 28.9 (α-C), 22.5, 25.8 (β-C).

L^6Li: To a cooled (−78°C) mixture of 1.0 g of $\mathbf{L^6}$H (2 mmol) and 202 mg of diisopropylamine in 15 ml of THF was added 1.25 ml 1.6 of M *n*BuLi in hexane. The reaction mixture was allowed to warm to room temperature and then refluxed for a short time (10 min). The solvent was evaporated in vacuo and the product was crystallized from refluxing hexane, yielding beautiful yellow crystals of $\mathbf{L^6}$Li·THF. − ^{1}H NMR (C_7D_8): δ = 1.26 (1-H), 5.11 (4-H), 6.8−7.0 (*m*-, *p*-H), 3.36 (α-H), 1.03, 1.29 (β-H). − ^{13}C NMR (C_7D_8): δ = 33.3 (C-1), 44.1 (C-2), 170.1 (C-3), 92.2 (C-4), 150.9 (*i*-C), 139.5 (*o*-C), 122.9 (*m*-C), 121.6 (*p*-C), 27.9 (α-C), 23.1, 25.3 (β-C).

L^6K: To a stirred suspension of 0.16 g (4 mmol) of KH (dispersion in mineral oil, washed with hexane to remove the oil) in 25 ml of THF, 1.0 g (2 mmol) of $\mathbf{L^6}$H was added in small portions. The yellowish solution was stirred at 65°C for 1 h and then filtered. The THF was removed in vacuo, and the product was washed with hexane to give off-white $\mathbf{L^6}$K (0.9 g, 90%). − ^{1}H NMR ([D_8]THF): δ = 1.16−1.19 (1-H, β-H), 3.85 (4-H), 6.84 (*m*-H), 6.51 (*p*-H), 3.35 (α-H). − ^{13}C NMR ([D_8]THF): δ = 31.4 (C-1), 42.2 (C-2), 168 (br., C-3), 88.4 (C-4), 153.7 (*i*-C), 137.8 (*o*-C), 122.3 (*m*-C), 117.0 (*p*-C), 28.1 (α-C), 23.8, 25.4 (β-C).

L^3H: (a) A mixture of 46.9 g of *o*-toluidine (438 mmol) and 48.2 g of acetylacetone (481 mmol) in 500 ml of toluene, plus a few drops of H_2SO_4, was heated under reflux in a Dean-Stark apparatus for the azeotropic removal of water. After 16 h, the reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The product was distilled at 118°C (5 mbar) to give 4-*o*-tolylamino-3-penten-2-one as a light-yellow oil (75.3 g, 91%). − ^{1}H NMR ($CDCl_3$): δ = 1.86 ($CH_3C{=}N$), 2.10 ($CH_3C{=}O$), 2.27 (*o*-CH_3), 5.19 (C*H*), 7.0−7.3 (Ar-H), 12.3 (NH). − ^{13}C NMR ($CDCl_3$): δ = 29.0 ($CH_3C{=}O$), 196.0 ($CH_3C{=}O$), 97.0 (*C*H), 161.1 ($CH_3C{=}N$), 19.5 ($CH_3C{=}N$), 137.4 (arom. C-1), 133.8 (arom. C-2), 130.7 (arom. C-3), 126.2 (arom. C-4), 126.3 (arom. C-5). 126.2 (arom. C-6), 18.0 (*o*-CH_3).

(b) A mixture of 47.3 g of 4-*o*-tolylamino-3-penten-2-one (250 mmol) and 35.9 g of *o*-toluidine hydrochloride (250 mmol) was refluxed in the minimum volume of ethanol for dissolution of both components. Cooling the reaction mixture to room temperature yielded yellow crystals of the monohydrochloride of 2,4-di-*o*-tolyliminopentane (63.1 g, 80%). − ^{1}H NMR (CD_3OD): δ = 2.68 ($CH_3C{=}N$), 2.06 (*o*-CH_3), 4.64 (CH), 4.89 (NH), 6.8−7.3 (Ar-H). − ^{13}C NMR (CD_3OD): δ = 22.0 ($CH_3C{=}N$), 171.5 ($CH_3C{=}N$), 92.4 (*C*H), 136.5 (arom. C-1), 135.6 (arom. C-2), 132.2 (arom. C-3), 127.7 (arom. C-4), 129.8 (arom. C-5), 128.2 (arom. C-6), 17.4 (*o*-CH_3).

(c) A mixture of 7.87 g of 2,4-di-*o*-tolyliminopentane·HCl (25 mmol), 7 ml of triethylamine (50 mmol), 100 ml of dichloromethane, and 100 ml of water was stirred for 1 h until all solids had dissolved and a clear separation of the two layers had occurred. The organic phase was removed, dried with magnesium sulfate, filtered, and the solvent was removed in vacuo. The resulting thick yellow oil was dried in vacuo for 16 h. The product was isolated as a yellow oil (6.36 g, 91%). − ^{1}H NMR ($CDCl_3$): δ = 1.97 ($CH_3C{=}N$), 2.27 (*o*-CH_3), 4.98 (CH), 12.6 (NH), 6.9−7.3 (Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 20.7 ($CH_3C{=}N$), 159.8 ($CH_3C{=}N$), 96.5 (*C*H), 144.6 (arom. C-1), 130.7 (arom. C-2), 130.2 (arom. C-3), 123.6 (arom. C-4), 126.1 (arom. C-5), 123.0 (arom. C-6), 16.3 (*o*-CH_3).

L^1VCl_2: Vanadium trichloride (7.865 g, 50 mmol) was refluxed for 3 h in 100 ml of THF to form $VCl_3(THF)_3$. A solution of 16.725 g (50 mmol) of $\mathbf{L^1}$H in 100 ml of THF was cooled to −78°C. To this was added 31.4 ml (50 mmol) of 1.6 M *n*-butyllithium in hexane, and the mixture was allowed to warm to room temperature. The orange/yellow solution thus obtained was added to the pink/red slurry of $VCl_3(THF)_3$ resulting in an immediate colour change to an intense dark brown-red. The reaction mixture was refluxed for an additional 1 h. The solvent was then removed in vacuo, and the residue was dried at 80°C in vacuo. It was then washed with 50 ml of hexane, dried, and extracted with 200 ml of toluene. The product was crystallized from toluene as red crystals. Two fractions were obtained (7.425 g and 5.4 g). Yield: 12.825 g (56%). − $C_{23}H_{29}Cl_2N_2V$ (455.34): calcd. C 60.67, H 6.42, Cl 15.57, N 6.15, V 11.19; found C 60.39, H 6.26, Cl 15.45, N 6.00, V 10.95.

L^1VMe_2: To a suspension of 9.3 g of $\mathbf{L^1}VCl_2$ (20.4 mmol) in 150 ml of diethyl ether, cooled to −78°C, was slowly added 25.65 ml of a solution of methyllithium in diethyl ether (1.6 M, 40.8 mmol). The mixture was allowed to warm to room temperature and the solvent was removed in vacuo. Crystallization from hexane (+40°C/−20°C) gave dark-brown crystals. Yield: 5.42 g (64%). − $C_{25}H_{35}N_2V$ (414.51): calcd. C 72.44, H 8.51, N 6.76, V 12.29; found C 72.18, H 8.33, N 6.71, V 12.10, Cl < 0.1.

L^1TiCl_2: To a solution of 6.69 g of **L1**H (20 mmol) in 50 ml of THF, cooled to −78°C, was added 6.3 ml (20 mmol) 1.6 of M *n*BuLi in hexane, and the mixture was allowed to warm to room temperature. Then, 3.7 g of solid $TiCl_3(THF)_3$ (20 mmol) was added and the reaction mixture was refluxed overnight. A colour change from green to dark brown took place. The solvent was then removed in vacuo and 100 ml of toluene was added. The resulting solution was reduced in volume by 20 ml by distillation of toluene along with residual THF and/or hexane. The warm, deep-red solution was filtered and the filtrate was concentrated, at reflux temperature, until crystals appeared. After leaving the solution to stand overnight, deep-red crystals were collected. Yield: 7.32 g (81%). − $C_{23}H_{29}Cl_2N_2Ti$ (452.30): calcd. C 61.08, H 6.46, Cl 15.68, N 6.19, Ti 10.59; found C 60.90, H 6.62, Cl 15.76, N 6.03, Ti 10.45.

L^1TiMe_2: 1. *Using MeLi:* To a stirred suspension of 1.0 g (2.2 mmol) of $\mathbf{L^1}TiCl_2$ in 20 ml of diethyl ether, cooled to −80°C, was slowly added 2.8 ml (4.4 mmol) of a 1.6 M solution of MeLi in diethyl ether. The mixture was allowed to warm to 0°C, whereupon a deep-blue colour appeared. The solvent was then removed in vacuo, and the residue was quickly extracted with two 15-ml portions of hexane. The combined hexane fractions were concentrated in vacuo to a volume of ca. 2.5 ml and after storage overnight at

-20°C, a dark-blue crystalline solid was isolated. The yield of this synthesis was rather variable, but was usually in the range 10−50%. The isolated product was found to be stable at room temperature, both in solution and in the solid state. Crystals for X-ray diffraction were obtained by recrystallization from pentane (+25°C/−20°C).

2. *Using MeMgI:* To a stirred suspension of 1.0 g (2.2 mmol) of $\mathbf{L^1}TiCl_2$ in 20 ml of diethyl ether was slowly added a solution of 1.06 g (4.4 mmol) of $MeMgI(Et_2O)$ in 15 ml of diethyl ether. The mixture immediately turned deep-blue. The solvent was removed in vacuo, and the residue was extracted with two 15-ml portions of hexane. Concentration of the solution and cooling to −20°C gave dark-blue crystals of the product (0.64 g, 70%).

Attempted Synthesis of $\mathbf{L^1}$*TiEt*$_2$*:* To a stirred suspension of 1.0 g (2.2 mmol) of $\mathbf{L^1}$TiCl2 in 20 ml of diethyl ether, cooled to −20°C, was slowly added a solution of 0.92 g (4.4 mmol) of $EtMgBr(Et_2O)$ in 15 ml of diethyl ether. The mixture immediately turned deep-blue. It was allowed to warm to 5°C and then cooled once more to −20°C. The solvent was then removed in vacuo, and the residue was quickly extracted with two 15-ml portions of hexane. Concentration of the combined extracts at −20°C and storage at this temperature overnight gave a few very large, dark-blue crystals of the product. These decomposed within a day at room temperature, both in solution and in the solid state, leading to unidentified brown products with liberation of ethane.

$\mathbf{L^2}$*VCl*$_2$*:* Vanadium trichloride (7.865 g, 50 mmol) was refluxed for 2 h in 150 ml of THF to form $VCl_3(THF)_3$. To this was added a solution of 24.84 g of $\mathbf{L^2}Li(THF)$ (50 mmol) in 50 ml of THF and the reaction mixture was refluxed for 30 min resulting in a deep brown-red colouration. The solvent was then removed in vacuo and the residue was dried at 100°C, whereupon it slowly turned dark green. It was then washed with 25 ml hexane, dried, and crystallized from toluene as very dark-green crystals. Yield: 22.15 g (82%). − $C_{29}H_{41}Cl_2N_2V$ (539.50): calcd. C 64.56, H 7.66, Cl 13.14, N 5.19, V 9.44; found C 64.30, H 7.52, Cl 13.00, N 5.03, V 9.55.

$\mathbf{L^2}$*VMe*$_2$: To a solution of 2.7 g of $\mathbf{L^2}VCl_2$ (5 mmol) in 25 ml of diethyl ether, cooled to −80°C, was slowly added 6.28 ml of methyllithium in diethyl ether (1.6 M, 10 mmol). The stirred mixture was allowed to warm to room temperature and then refluxed for 1.5 h. The resulting solution was filtered through a fine frit and the solvent was removed in vacuo. Crystallization from hexane gave dark-brown crystals. Yield: 1.12 g, second crop 0.4 g, total yield: 1.52 g (61%).

$\mathbf{L^2}$*V(nBu)*$_2$*:* To a suspension of 1.0 g of $\mathbf{L^2}VCl_2$ (1.7 mmol) in 10 ml of toluene, cooled to −80°C, was slowly added 2.1 ml of a solution of *n*BuLi (1.6 M in hexane). The stirred mixture was allowed to warm to room temperature. The solvents were then removed in vacuo, and the product was extracted with a small amount of warm hexane. After leaving the resulting solution to stand for 1 week at −20°C, large, dark-brown crystals were deposited.

$\mathbf{L^2}$*TiCl*$_2$*:* A solution of 4.967 g of $\mathbf{L^2}Li(THF)$ (20 mmol) and 3.7 g of $TiCl_3(THF)_3$ in 50 ml of THF was refluxed overnight. The colour of the reaction mixture changed from light green to dark green. The solvent was then removed in vacuo and 75 ml of toluene was added. The resulting solution was reduced in volume by 20 ml by distillation of toluene along with residual THF and/or hexane. A further 20 ml of fresh toluene was added and distilled off once more. The warm, deep-red/brown solution was filtered and the filtrate was concentrated, at reflux temperature, until crystals appeared. After storage overnight, deep-red/brown crystals were deposited. Yield: 2.85 g (53%).

$\mathbf{L^2}$*TiMe*$_2$*:* This was prepared in the same manner as $\mathbf{L^1}$TiMe2 (Grignard route). The residue after the reaction was sticky, and extraction with hexane was far from complete; from 1.0 g of $\mathbf{L^2}TiCl_2$, we obtained only 0.09 g (10%) of $\mathbf{L^2}TiMe_2$ as dark-blue needles from hexane.

$\mathbf{L^5}$*VCl*$_2$*:* Vanadium trichloride (1.57 g, 10 mmol) was refluxed for 2 h in 25 ml of THF to form $VCl_3(THF)_3$. A solution of 4.19 g (10 mmol) of $\mathbf{L^5}H$ in 25 ml of hexane was cooled to −78°C. To this was added 6.25 ml (10 mmol) of 1.6 M *n*-butyllithium solution in hexane and the mixture was allowed to warm to room temperature. The reaction mixture slurry was stirred overnight and then a small amount of THF was added until a clear yellow solution was obtained. This yellow solution was added to the pink/red slurry of $VCl_3(THF)_3$ and the mixture was refluxed for 1 d. The solvent was then removed in vacuo and the residue was crystallized from toluene (30 ml) to afford dark-red crystals. Yield: 2.07 g (38%). − $C_{29}H_{41}Cl_2N_2V$ (539.50): calcd. C 64.56, H 7.66, Cl 13.14, N 5.19, V 9.44; found C 64.81, H 7.72, Cl 12.93, N 5.18, V 9.55.

$\mathbf{L^5}$*TiCl*$_2$*:* To a mixture of 5.66 g of $\mathbf{L^5}H$ (13.5 mmol) in 30 ml of hexane was added 8.5 ml (13.5 mmol) of 1.6 M *n*BuLi in hexane. The reaction mixture was allowed to warm to room temperature and then stirred overnight. The initially clear yellow solution became a yellow slurry. To this, 5.0 g of $TiCl_3(THF)_3$ (13.5 mmol) and 30 ml of THF were added and the mixture was refluxed overnight. The solvent was then removed in vacuo and 75 ml of toluene was added. The resulting solution was reduced in volume by 10 ml by distillation of toluene along with residual THF and/or hexane. The warm, deep-red solution was filtered and the filtrate was concentrated, at reflux temperature, until crystals appeared. After storage overnight, deep-red crystals separated. Yield: 4.36 g (74%). − $C_{29}H_{41}Cl_2N_2Ti$ (536.46): calcd. C 64.93, H 7.70, Cl 13.22, N 5.22, Ti 8.93; found C 64.89, H 7.56, Cl 13.32, N 5.18, Ti 8.79.

$\mathbf{L^5}$*TiMe*$_2$*:* This was prepared in the same manner as $\mathbf{L^1}TiMe_2$ (MeLi route) but crystallized more easily and was typically obtained in 70% yield as dark-blue crystals.

Attempted Synthesis of $\mathbf{L^3}$*TiMe*$_2$*:* $\mathbf{L^3}TiCl_2$ was prepared in the same manner as $\mathbf{L^1}TiCl_2$. However, the compound did not crystallize well from toluene, and so an excess of hexane was added to the dark-brown toluene solution to precipitate the product as a brown-green powder. To a stirred suspension of 1.0 g (2.5 mmol) of crude $\mathbf{L^3}TiCl_2$ in 20 ml of diethyl ether, cooled to −10°C, was slowly added a cooled solution of 1.21 g (5.1 mmol) of MeMgI-(Et_2O) in 15 ml of diethyl ether. The solution turned deep-blue. After 1 min, 0.43 ml of 1,4-dioxane was added, the solvent was removed in vacuo, and the residue was extracted with two cold (−10°C) 15-ml portions of hexane. Evaporation of the solvent left a dark-blue solid, which upon hydrolysis produced variable amounts of methane (but always less than 2 equivalents based on $\mathbf{L^3}TiMe_2$). All attempts at purification or crystallization resulted in the disappearance of the blue color, indicating decomposition.

$\mathbf{L^4}$*VCl*$_2$*(THF)*$_2$*:* Vanadium trichloride (7.9 g, 50 mmol) was refluxed for 3 h in 100 ml of THF to form $VCl_3(THF)_3$. A slurry of 14.3 g (50 mmol) of $\mathbf{L^4}H \cdot HCl$ in 100 ml of THF was cooled to −78°C. To this was added 63 ml (100 mmol) of 1.6 M *n*-butyllithium in hexane, and the mixture was allowed to warm to room temperature. The resulting orange/yellow solution was added to the cooled, pink/red slurry of $VCl_3(THF)_3$. An immediate colour change to very dark green was observed and small crystals were formed. After leaving the mixture to stand overnight, the supernatant was decanted, the crystals were washed with 50 ml of THF, and dried in vacuo. Yield: 20.8 g (81%). − $C_{25}H_{33}N_2VO_2Cl_2$

(515.40): calcd. C 58.26, H 6.45, Cl 13.76, N 5.44, V 9.88; found C 57.93, H 6.23, Cl 14.01, N 5.60, V 10.10.

$\mathbf{L^4}$VMe$_2$: To a slurry of 1.03 g (2 mmol) of $\mathbf{L^4}$VCl2(THF)$_2$ in 30 ml of THF, cooled to −78°C, was added 2.5 ml (4 mmol) of 1.6 M methyllithium in diethyl ether. The reaction mixture was allowed to warm to room temperature, whereupon the colour changed from dark green/blue to dark red. The solvent was then removed in vacuo, and the product was redissolved in diethyl ether. Filtration of the resulting solution and evaporation of the solvent yielded the product as a solid foam. Because of its high solubility, we were unable to purify the product further; the number of methyl groups still present in the complex was determined by controlled hydrolysis. A 430-mg (1.3 mmol) portion of the solid foam was dissolved in the minimum volume of dichloromethane and the complex was deliberately decomposed with 1 ml of methanol. The volume of evolved gas was measured as 58 cm^3 (2.6 mmol).

$\mathbf{L^4}$TiCl$_2$(THF)$_2$: To a solution of *n*BuLi (2.6 ml of a 1.6 M solution in hexane; 4.2 mmol) in 15 ml of THF, cooled to −40°C, was added 0.7 ml (4.8 mmol) of diisopropylamine. The resulting mixture was added to a solution of 1.0 g (4.0 mmol) of $\mathbf{L^4}$H in 15 ml of THF and the solvent was removed in vacuo (50°C, 1 h). The residue was taken up in 10 ml of THF, and the resulting solution was slowly added to a suspension of 1.48 g (4.0 mmol) of TiCl$_3$(THF)$_3$ in 25 ml of THF. The mixture was heated to 50°C and after 10 min the solvent was removed in vacuo. The residue was quickly[23] extracted with two 25-ml portions of toluene. After the addition of 1 ml of THF to the combined extracts and leaving the solution to stand, brown crystals of $\mathbf{L^4}$TiCl$_2$(THF)$_2$ were deposited (1.4 g, 70%). The product could be recrystallized from toluene/THF mixtures, but its solubility is low even in hot solvent mixtures.

$\mathbf{L^4}$TiI$_2$: To a suspension of $\mathbf{L^4}$TiCl$_2$(THF)$_2$ (0.5 g, 1 mmol) in 25 ml of benzene was added 0.78 g (0.56 mmol) of Me$_3$SiI. The mixture was stirred for 4 h at 70°C, during which it turned violet. The solvent was then removed in vacuo, the residue was washed with hexane, and crystallized from toluene/hexane to give red-purple crystals of $\mathbf{L^4}$TiI$_2$ (0.43 g, 80%).

Polymerization Experiments: Under argon, a glass Büchi miniclave was charged with benzene (21 ml) followed by 41 mg of tris(pentafluorophenyl)borane (0.1 mmol) in 2 ml of benzene. The solvent was then saturated with propene and the dimethyltitanium compound (0.1 mmol) in 2 ml of benzene was introduced. The dark blue/green colour of the diminatodimethyltitanium compound immediately disappeared and a clear, red solution was formed. The propene pressure was maintained at 5−6 bar for 30 min. The propene pressure was then released and the solution was poured into 200 ml of methanol. The polymer produced was filtered off and dried in vacuo at 100°C.

X-ray Structure Determinations: All crystals were mounted in thin-walled glass capillaries under N$_2$ and held in place with silicone grease. Diffraction measurements were made with a Siemens P3m diffractometer fitted with an LT-1 crystal cooling device, using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit cell dimensions were determined from carefully centered reflections in the range 15.0° < 2θ < 40.0°. Diffracted intensities were measured in a unique volume of reciprocal space for 4.0° < 2θ < 50.0° by Wyckoff ω scans. Three check reflections were measured again after every 100 ordinary data over the period of data collection in order to monitor and correct for crystal decay and long term intensity fluctuations. Duplicate and equivalent measurements were averaged and systematic absences were deleted. Absorption corrections were applied based on azimuthal scan data and Lorentz and polarization corrections were applied. The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters and all hydrogen atoms were given fixed isotropic displacement parameters and constrained to idealized geometries (C−H 0.96 Å, methyl H−C−H 109.5°). Full-matrix least-squares refinements were against F_o or $F_o{}^2$. Weights, *w*, were adjusted to minimize the variation in *S* as a function of F_o . Final difference electron density maps showed no

Table 2. Details of X-ray structure determinations

Compound	$\mathbf{L^2}$VCl$_2$	$\mathbf{L^1}$TiCl$_2$	$\mathbf{L^5}$TiCl$_2$	$\mathbf{L^6}$Li(THF)	$\mathbf{L^2}$V(*n*Bu)$_2$	$\mathbf{L^1}$TiMe$_2$
Formula	$C_{29}H_{41}Cl_2N_2V$	$C_{23}H_{29}Cl_2N_2Ti$	$C_{29}H_{41}Cl_2Ti$	$C_{39}H_{61}LiN_2O$	$C_{37}H_{59}N_2V$	$C_{25}H_{35}N_2Ti$
Mass	539.5	452.3	536.4	580.8	582.8	411.5
T [K]	200	213	200	200	200	200
Crystal size [mm]	0.25 × 0.65 × 0.7	0.3 × 0.6 × 0.6	0.6 × 0.55 × 0.45	0.4 × 0.5 × 0.6	0.4 × 0.4 × 0.65	0.45 × 0.45 × 0.75
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group[25]	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a [Å]	17.177(5)	8.198(3)	14.592(3)	9.541(3)	12.903(3)	8.233(3)
b [Å]	13.170(4)	8.719(3)	9.096(2)	17.911(6)	13.042(4)	23.097(7)
c [Å]	13.842(4)	17.859(6)	21.727(5)	21.711(7)	21.489(7)	12.598(3)
α [°]	90	90.68(3)	90	90	90	90
β [°]	109.11(2)	93.43(3)	95.43(2)	95.44(2)	92.85(2)	94.60(3)
γ [°]	90	113.91(3)	90	90	90	90
V [Å^3]	2958.8(15)	1163.9(7)	2870.9(11)	3694(2)	3612(2)	2387.9(13)
Z	4	2	4	4	4	4
$d_{calcd.}$ [g cm^{-3}]	1.21	1.29	1.24	1.05	1.07	1.14
Transmission (min./max.)	0.755/0.917	0.722/0.921	0.574/0.618	(no correction, μ = 0.61 cm^{-1})	0.737/0.808	0.733/0.821
F(000)	1144	474	1140	1280	1272	884
Measured	5703	4076	2614	7197	6913	4555
Unique	5225	4067	2520	6495	6310	4186
Used	4119, $I > 2\sigma(I)$	4056, $I > -3\sigma(I)$	2519, $I > -3\sigma(I)$	3607, $I > 2\sigma(I)$	3859, $I > 2\sigma(I)$	4184, $I > -3\sigma(I)$
Parameters	337	253	161	388	361	295
R	0.041	0.048 [3611 data with $I > 2\sigma(I)$]	0.033 [2266 data with $I > 2\sigma(I)$]	0.063	0.070	0.038 [3562 data with $I > 2\sigma(I)$]
wR	0.049	0.142 (all data)	0.038 (all data)	0.065	0.071	0.108 (all data)
S	1.42	1.16	1.52	1.45	1.59	1.13

chemically significant features (with one exception noted below). All calculations were carried out using programs of the SHELXTL-PLUS and SHELXL-93 packages.[24] Complex neutral-atom scattering factors were used. Table 2 gives further details of the individual structure determinations. The γ and δ carbon atoms of one of the butyl chains of $\mathbf{L}^2$V(nBu)$_2$ showed large thermal parameters, and significant electron density features were found close to these atoms. This clearly implies some kind of disorder in the chain, but no satisfactory multisite model was derived.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101413. Copies of the data can be obtained free of charge on application to CCCD, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] P. A. White, J. Calabrese, K. H. Theopold, *Organometallics* **1996**, *15*, 5473; Y. Liang, G. A. P. Yap, A. L. Rheingold, K. H. Theopold, *Organometallics* **1996**, *15*, 5284; K. H. Theopold, *Eur. J. Inorg. Chem.* **1998**, *1*, 15.

[2] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514.

[3] M. Rahim, N. J. Taylor, S. Xin, S. Collins, *Organometallics* **1998**, *17*, 1315.

[4] Theopold has very recently reported on studies of Ti$^{\mathrm{III}}$, V$^{\mathrm{III}}$, and Cr$^{\mathrm{III}}$ complexes of the $\mathbf{L}^4$ ligand: W.-K. Kim, L. MacAdams, M. Fevola, L. Liable-Sands, A. L. Rheingold, K. Theopold, 215th ACS National Meeting, Division of Inorganic Chemistry, Dallas, **1998**, *Conference Abstract* 279.

[5] G. Scheibe, *Chem. Ber.* **1923**, *56*, 1923; J. E. Parks, R. H. Holm, *Inorg. Chem.* **1968**, *7*, 1408.

[6] R. Knorr, A. Weiss, *Chem. Ber.* **1982**, *115*, 139.

[7] P. B. Hitchcock, M. F. Lappert, D.-S. Liu, *J. Chem. Soc., Chem. Commun.* **1994**, 1699 and 2637.

[8] H. van der Heijden, C. J. Schaverien, A. G. Orpen, *Organometallics* **1989**, *8*, 255.

[9] D. Drees, J. Magull, *Z. Anorg. Allg. Chem.* **1994**, *620*, 814.

[10] A. A. Danopoulos, P. G. Edwards, *Polyhedron* **1989**, *8*, 1339.

[11] A. R. Wills, P. G. Edwards, M. Harman, M. B. Hursthouse, *Polyhedron* **1989**, *8*, 1457; A. R. Wills, P. G. Edwards, *J. Chem. Soc., Dalton Trans.* **1989**, 1253.

[12] B. Hessen, J. H. Teuben, T. H. Lemmen, J. C. Huffman, K. G. Caulton, *Organometallics* **1985**, *4*, 946; B. Hessen, T. M. Lemmen, H. J. G. Luttikhedde, J. H. Teuben. J. L. Petersen, J. C. Huffman, S. Jagner, K. G. Caulton, *Organometallics* **1987**, *6*, 2354.

[13] B. Hessen, A. Meetsma, J. H. Teuben, *J. Am. Chem. Soc.* **1989**, *111*, 5977; B. Hessen, J.-K. F. Buijink, A. Meetsma, J. H. Teuben, G. Helgesson, M. Håkansson, S. Jagner, A. L. Spek, *Organometallics* **1993**, *12*, 2286.

[14] J.-K. F. Buijink, A. Meetsma, J. H. Teuben, *Organometallics* **1993**, *12*, 2004.

[15] J. R. Hagadorn, J. Arnold, *J. Am. Chem. Soc.* **1996**, *118*, 893.

[16] A. R. Johnson, W. M. Davis, C. C. Cummins, *Organometallics* **1996**, *15*, 3825.

[17] R. K. Minhas, L. Scoles, S. Wong, S. Gambarotta, *Organometallics* **1996**, *15*, 1113.

[18] L. Giannini, E. Solari, S. de Angelis, T. R. Ward, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1995**, *117*, 5801.

[19] J. D. Scollard, D. H. McConville, *J. Am. Chem. Soc.* **1996**, *118*, 10008; J. D. Scollard, D. H. McConville, N. C. Payne, J. J. Vittal, *Macromolecules* **1996**, *29*, 5241.

[20] L. E. Manzer, *Inorg. Synth.* **1982**, *21*, 135.

[21] A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245.

[22] F. Cramer, K. Baer, *Chem. Ber.* **1960**, *93*, 1231.

[23] The crystalline product is rather insoluble, but we usually found that the crude product first dissolves and only starts to crystallize after a period of a few hours or days. If, for some reason, crystallization starts *before* extraction is complete, the best way to proceed is to extract the residue with a fairly large volume of hot toluene containing a few drops of THF.

[24] G. M. Sheldrick, *SHELXTL-PLUS Rev 4.2*, Göttingen, Germany, **1990**; *SHELXL-93*, Göttingen, Germany, **1993**.

[25] T. Hahn (Ed.), *International Tables for Crystallography*, vol. A ("Space Group Symmetry"), 2nd ed., D. Reidel, Dordrecht, **1984**.

[98117]