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Reaction of *p*-Toluenesulfonylamide and $\mathrm{M(NMe_2)_4}$ (M = Ti, V): Generation of Electron-Deficient Imido Complexes of Early Transition Metals

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p-Toluenesulfonamide (*p*-$\mathrm{TsNH_2}$) was succesfully employed as an imido ligand precursor in the synthesis of highly air- and moisture-sensitive titanium(IV) and vanadium(IV) complexes. Reaction of $\mathrm{M(NMe_2)_4}$ (M = Ti, V) with $\mathrm{TsNH_2}$ in toluene afforded $[\mathrm{M}(\mu\text{-NTs})(\mathrm{NMe_2})_2]_2$ dimer complexes (M = Ti (**1**), V (**2**)). By contrast, the reaction carried out in dichloromethane led to $[\mathrm{Ti}\{\mu\text{-}N,O\text{-NTs}\}\mathrm{Cl}(\mathrm{NMe_2})(\mathrm{NHMe_2})_2]_2$ (**3**) and $[\mathrm{Ti}\{\mu\text{-}N,O\text{-NTs}\}\mathrm{Cl_2}(\mathrm{NHMe_2})_2]_n$ (**4**) through solvent activation. The same reaction of $\mathrm{M(NMe_2)_4/TsNH_2}$ conducted in the presence of an excess of trimethylchlorosilane produced $[\mathrm{V({=}NTs)Cl_2(NHMe_2)_2}]$ (**5**) and $[(\mathrm{Me_2HN})\mathrm{Cl_2Ti}(\mu_2\text{-}N\text{-NTs-}\kappa^2 N,O)_2\mathrm{TiCl_2}(\mathrm{NHMe_2})_2]$ (**6**). Alternatively, compound **6** has also been prepared from $\mathrm{TiCl_2(NMe_2)_2}$ and $\mathrm{TsNH_2}$. **1** was reacted with trimethylchlorosilane to afford the amide complex $[\mathrm{Ti}\{\mu\text{-}N,O'\text{-N(SiMe_3)Ts-}\kappa^3 N,O,O'\}\mathrm{Cl_2}(\mathrm{NMe_2})]_2$ (**7**) in which the tosylimide bond has been silylated. Compounds **1**–**6** represents the first examples of sulfonylimido complexes for titanium and vanadium.

Introduction

The chemistry of *N*-organoimido complexes continues to be an attractive focus.[1−7] Compounds containing the dianionic π-donor terminal imido ligand $[\mathrm{NR}]^{2-}$ (R = alkyl or aryl) have found applications in a variety of stoichiometric or catalytic transformations. Selected examples include alkene[8] and imine[9−13] metathesis, olefin polymerization,[3,14−23] C−H activation,[24−28] reactions with unsaturated C−C[29−35] or C−X bonds,[36−39] alkyne or alkene hydroamination (for

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some examples of hydroamination using imido catalysts, see refs 40−45, and for selected recent examples of hydroamination using group 4 precatalyst, see refs 46−51, carboamination reaction,[52−54] and strained heterocycle opening.[27,55]

Among early transition metal imido complexes, terminal imido compounds of general formula $[M(=N-R)Cl_2L_n]$ ($M = Ti, V$; $L_n = (NHMe_2)_2$, Py_2, Py_3, TMEDA)[16,17,56−61] have proven to be very useful "synthons" for the preparation of many other imido derivatives[43,57,60−64] that have found direct applications in olefin polymerization[16−19,21−23] and alkyne hydroamination[40−44] and have been used for the synthesis of TiN thin films.[56,65,66] In this regard, we have recently reported a very simple and direct synthesis of $[M(=N-R)Cl_2(NHMe_2)_2]$ complexes ($M = Ti$,[60] V)[16,61] on the basis of a very convenient one-pot reaction of $M(NMe_2)_4$ with RNH_2 in the presence of an excess of Me_3SiCl. This procedure appears to be applicable to a wide range of primary amines, including functional amines, enantiomerically pure amines (giving chiral imido functions), and diamines (giving diimido complexes).

Variation of the steric and electronic properties of the imido group allows the fine-tuning of catalysts containing imido spectator ligands. Among the strongest electron-withdrawing substituents known are sulfonyl groups ($-SO_2R$), and therefore, the donor capability of an aryl/alkyl sulfonylimido ligand $[NSO_2R]^{2-}$ should be lower than that of an oxo ligand.[67,68] Indeed, such (sulfonylimido)metal species are often implicated as active intermediates in nitrene group transfer (olefin aziridination,[69−77] alkane tosylamidation,[69,73,78,79] and imido transfer to phosphine).[68,80,81] Well-characterized $M{=}NSO_2R$ complexes remain sparse, including a few group 6 and 8 metal compounds (Mo,[67,68,81−83] W,[80,84,85] Ru,[69,86−89]

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Os)[90,91] and the only two reported early transition metal tosylimide $[Cp_2Zr(\mu\text{-}NSO_2Ar)]_2$ (Ar = 4-Br$-C_6H_4$)[92] and triflimide $[Nb(=NSO_2CF_3)\{N(R)Ar'\}_3]$ (R = $C(CD_3)_2CH_3$; Ar′ = 4,5-$Me_2C_6H_3$).[93]

In this paper, we report on the synthesis and structural characterization of the first members of a new family of electron-deficient titanium(IV) and vanadium(IV) complexes that possess a tosylimido function [tosyl = *p*-toluenesulfonyl (Ts)].

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon and collected by distillation. NMR spectra were recorded on Bruker AM200, AM250, ARX250, DPX300, and Avance500 spectrometers and referenced internally to residual protio-solvent (^1H) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{29}Si NMR (99.4 MHz) and ^{51}V NMR (131.60 MHz) spectra were recorded on Bruker Avance500 spectrometer. Chemical shifts are quoted in δ (ppm). Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). EPR spectra were recorded on a Bruker ESP300E spectrometer. Elemental analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France) (C, H, N) or by the Service Central de Microanalyses du CNRS at Vernaison, France (C, H, N, Cl).

The $Ti(NMe_2)_4$ used in this study was prepared by a modification of a literature procedure[94] or purchased from commercial sources (Aldrich, Acros, 99.999%). $V(NMe_2)_4$ was prepared by a modification of a literature procedure.[95] Trimethylchlorosilane was distilled and stored over 4 Å molecular sieves under argon before use. *p*-$TsNH_2$ (Aldrich, ≥99%) was recrystallized from anhydrous ethanol and dried under vacuum.

Crystal Structure Determinations. The structures of nine compounds were determined. Crystal data collection and processing parameters are given in Table 2. Crystals of **1** (yellow-orange plates), **2** (dark-red sticks), **3** (red-orange parallelepipeds), **4** (yellow blocks), **5** (orange-brown needles), **6** (yellow sticks), **7** (light green blocks), $[VCl_3Py_3]$ (green blocks), and $[V_2OCl_4Py_6]$ (dark-purple plates) were obtained. The selected crystals, sensitive to air and moisture, were mounted on a glass fiber using perfluoropolyether oil and cooled rapidly to 180 K in a stream of cold N_2. For all the structures data were collected at low temperature ($T = 180$ K) on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems Cryostream cooler device or an Oxford Diffraction Kappa CCD Excalibur diffractometer equipped with a cryojet from Oxford Instrument and using a graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections. The crystals were monitored for decay during data collection by measuring the intensities of 200 check reflections, but no significant fluctuation of intensities was observed. Structures have been solved by means of direct methods using the program SIR92[96] and subsequent difference Fourier maps; models were refined by least-squares procedures on a F^2 by using SHELXL-97[97] integrated in the package WINGX version 1.64,[98] and empirical absorption corrections were applied on all data sets.[99] For coordination polymer **4**, the structure appeared to be in monoclinic system, and the systematic absences suggested two space groups *C*2/*c* or *Cc*, with a better CFOM for *C*2/*c*. The *E*-statistics suggested a centrosymmetric structure. We then solved and refined in *C*2/*c*, and we obtained a clean and stable final refinement (a trial in *Cc* led to unsatisfactory results with a poor checkcif detecting a center of symmetry and suggesting a new space group: *C*2/*c*). The S3 atom is located on a symmetry axis. When the whole molecule was generated by applying the symmetries, S3 has either two nitrogen or two oxygen atoms on each side. From a chemical point of view, these sequences N−S−N or O−S−O are unacceptable, and therefore, the whole sequence −Ti−N−S−O− was treated as a statistic disorder. Details of the structure solution and refinements are given in the Supporting Information (CIF file). A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all structures have been deposited at the Cambridge Crystallographic Data Centre.

$[Ti(NTs)(NMe_2)_2]_2$ (1). To a toluene solution (5 mL) of 250 mg of $Ti(NMe_2)_4$ (1.115 mmol) was added by portions 1 equiv of *p*-$TsNH_2$ (191 mg, 1.115 mmol) at room temperature. The resulting red solution was stirred for 6 h at RT (room temperature). The volatiles were pumped off, and the orange solid was washed with pentane (2 × 10 mL) and dried under vacuum to give analytically and spectroscopically pure material. Single crystals of **1**, suitable for X-ray diffraction studies, were obtained by recrystallization from toluene solution of **1** layered with pentane. Yield: 220 mg (64%) (orange). ^1H NMR (250 MHz, C_6D_6): δ 7.95 (d, $^3J = 6.5$ Hz, 4H, C_6H_4), 6.79 (d, $^3J = 6.5$ Hz, 4H, C_6H_4), 3.26 (s, 24H, NMe_2), 1.90 (s, 6H, Me_{Ts}). $^{13}C\{^1H\}$ NMR (125.81 MHz, C_6D_6): δ 142.3, 141.6, 129.2, 126.3 (C_6H_4), 45.4 (NMe_2), 20.9 (Me_{Ts}). IR: 2861 (m), 2817 (w), 2775 (m), 1595 (m, $\nu_{C=C}$), 1496 (w), 1445 (m), 1413 (m), 1253 (vs), 1117 (vs), 1085 (s), 1021 (m), 980 (s), 935 (s), 819 (s), 684 (s), 643 (m), 629 (m), 598 (m), 582 (m), 554 (s), 512 (w), 465 (m). Anal. Calcd for $C_{22}H_{38}N_6O_4S_2Ti_2$ ($M_r = 610.44$): C, 43.29; H, 6.27; N, 13.77. Found: C, 43.34; H, 6.33; N, 13.33.

$[V(NTs)(NMe_2)_2]_2$ (2). To a toluene solution (10 mL) of 200 mg of $V(NMe_2)_4$ (0.880 mmol) was added by portions 1 equiv of *p*-$TsNH_2$ (150 mg, 1.115 mmol) at room temperature. The resulting brown solution was left at RT for 2 days. A first crop of crystals (suitable for X-ray diffraction studies) was collected (110 mg), and the solution was layered with pentane to afford a second crop of crystals (50 mg). The dark brown crystals were washed with pentane (2 × 5 mL) and dried under vacuum. Yield: 160 mg (59%) (dark brown). ^1H NMR (250 MHz, CD_2Cl_2): δ 7.58 (d, $^3J = 8.0$ Hz, 4H, C_6H_4), 7.18 (d, $^3J = 7.9$ Hz, 4H, C_6H_4), 3.11 (br s, 24H, NMe_2),

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Table 1. Comparison of Average Interatomic Distances (Å) and Angles (deg) in Complexes **1**−**6**

param	**1**	**2**	**3**	**4**[a]	**5**[b]	**6**
$M-N_{imido}$	2.106(4) [Ti1−N1] 1.974(4) [Ti1−N1]	1.9183(14)	1.8391(16)	1.945	1.672(3)	2.0707(19) [Ti1−N1] 1.931(2) [Ti2−N1]
$N_{imido}-S$	1.542(4)	1.6000(14)	1.5344(16)	1.519	1.612(3)	1.563(2)
$M-NMe_2$	1.866(4) [Ti1−N2] 1.889(4) [Ti1−N3]	1.8107(15) [V1−N2] 1.8349(15) [V1−N3]	1.9148(16)			
M−Cl			2.4530(6)	2.347	2.2603(12) [V1−Cl1] 2.2855(12) [V1−Cl2]	2.3417(5) [Ti1−Cl1] 2.3197(8) [Ti2−Cl2]
S═O	1.438(3) [S1−O1]	1.4409(13) [S1−O1] 1.4379(13) [S1−O2]	1.4622(14) [S1−O1]	1.430	1.436(3) [S1−O1] 1.435(3) [S1−O2]	1.4264(18) [S1−O2]
S−O	1.507(3) [S1−O2]		1.4791(14) [S1−O2]	1.515		1.4917(18) [S1−O1]
Ti−O (or V···O)	2.125(4) [Ti1−O2]	(3.435, 3.691)	2.1780(13) [Ti1−O2]	1.958	(3.904; 4.094)	2.1509(18) [Ti1−O1]
$M-N_{NHMe_2}$			2.2366(16) [Ti1−N3] 2.2572(17) [Ti1−N4]	2.204	2.144(3) [V1−N2] 2.141(3) [V1−N3]	2.296(4) [Ti1−N2] 2.244(2) [Ti2−N3]
S1−C1	1.759(5)	1.7678(18)	1.7718(19)	1.785	1.755(4)	1.755(2)
M···S	2.7128(16) [Ti1···S1]					2.7450(6) [Ti1···S1]
M···M	3.1297(19)	2.6027(6)	5.279	5.45		3.1637(8)
$M-N_{imido}-S$	94.8(2) [Ti1−N1−S1] 145.6(2) [Ti1−N1−S1]	138.37(9) [V1−N1−S1] 134.79(9) [V1−N1−S1]	149.46(11)		167.71(2)	97.15(9) [Ti1−N1−S1] 158.40(13) [Ti2−N1−S1]
$M-N_{imido}-M$	100.14(18)	86.69(6)				104.44(9) [Ti1−N1−Ti2]
$N_{imido}-M-N_{imido}$	79.86(18)	93.31(6)				72.45(11) [N1−Ti1−N1] 78.66(12) [N1−Ti2−N1]
Cl−M−Cl				177.87	135.48(5)	170.81(4) [Cl1−Ti1−Cl1] 93.26(5) [Cl1−Ti2−Cl1]
$N_{NHMe_2}-M-N_{NHMe_2}$			167.31(6)	178.59	163.21(12)	179.96(12) [N3−Ti2−N3]
$N_{imido}-M-N_{NHMe_2}$			98.16(7) 88.44(7)	89.63	99.14(13) [N1−V1−N3] 99.59(14) [N1−V1−N2]	151.44(10) [N1−Ti1−N2][c] 135.28(8) [N1−Ti1−N2][c] 88.61(8) [N1−Ti2−N3] 91.42(8) [N1−Ti2−N3]
$N_{imido}-M-Cl$			167.54(5)	89.90	112.43(11) [N1−V1−Cl2] 112.09(11) [N1−V1−Cl1]	170.81 [Cl1−Ti1−Cl1] 93.26 [Cl2−Ti2−Cl2]
N−S═O	118.6(2) [N1−S1−O1]	110.42(8); 109.60(8)	113.34(9) [N1−S1−O1]	114.1	109.47(17); 108.13(17)	114.88(11) [N1−S1−O2]
N−S−O	101.9(2) [N1−S1−O2]		113.28(8) [N1−S1−O2]	108.3		99.63(10) [N1−S1−O1]
Ti−O−S	95.13(18)		137.87(8)	153.4		96.11(9) [Ti1−O1−S1]
O···H−N (dist, angle)			2.07, 159.2 [O1···H4−N 4]		2.12, 154.1 [O3···H2A−N2] 2.16, 141.4 [O1···H5A−N5] 2.22, 152.3 [O2···H6A−N6] 2.24, 138.3 [O4···H3A−N3]	
other	113.1(2) [01−S1−O2] 110.2(2) [N1−S1−C1]	116.96(8) [01−S1−O2] 103.97(7) [N1−S1−C1]	111.98(9) [01−S1−O2] 107.67(9) [N1−S1−C1]		117.14(18) [01−S1−O2] 103.88(17) [N1−S1−C1]	116.35(11) [01−S1−O2] 109.79(11) [N1−S1−C1]

[a] Average values. [b] Geometric parameters are given for molecule A. [c] Two values for the two positions of the disordered $NHMe_2$.

2.36 (s, 6H, *Me*$_{Ts}$). $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2): δ 142.0, 140.9, 129.1, 126.4 (C_6H_4), 43.1 (N*Me*$_2$), 21.1 (*Me*$_{Ts}$). ^{51}V NMR (131.60 MHz, CD_2Cl_2): δ +15.6 ($w_{1/2}$ = 150 Hz). IR: 2861 (m), 2777 (w), 1597 (m, $\nu_{C=C}$), 1494 (w), 1453 (m), 1423 (m), 1414 (m), 1274 (vs), 1158 (m), 1142 (vs), 1079 (vs), 1021 (w), 956 (s), 919 (m), 812 (m), 714 (s), 706 (s), 659 (m), 622 (w), 592 (m), 553 (m). Anal. Calcd for $C_{22}H_{38}N_6O_4S_2V_2$ (M_r = 612.60): C, 42.85; H, 6.21; N, 13.63. Found: C, 42.79; H, 6.25; N, 13.36.

[Ti{μ-*N,O*-NTs}Cl(NMe$_2$)(NHMe$_2$)$_2$]$_2$ (3). This compound was crystallized from a complex mixture of products obtained using a procedure similar to the synthesis of **1** but using dichloromethane as solvent and a reaction time of 24 h. The crystals were of good quality for X-ray diffraction studies, but the amount of **3** was not enough for full characterization. A ^1H NMR spectrum of the mixture of products obtained is given as Supporting Information.

[Ti{μ-*N,O*-NTs}Cl$_2$(NHMe$_2$)$_2$]$_n$ (4). This compound was prepared using the procedure described for **3** by allowing to stand at room temperature for 3 days a dichloromethane solution (3 mL) composed of 125 mg of $Ti(NMe_2)_4$ and 95 mg of $TsNH_2$. Removal of the volatiles gave a yellow solid that was washed with some pentane (yield: 175 mg). Complex **4** was obtained as yellow crystals from a dichloromethane solution layered with toluene and pentane. Due to its polymeric nature, the low solubility of **4** in CD_2Cl_2 precluded NMR studies. In addition, the ^1H NMR spectrum of a suspension of **4** in CD_2Cl_2 rapidly evolves to show signals attributed to compound **6** and decomposition products. IR: 3211 (br, s, NH), 2924 (s), 1597 (m, $\nu_{C=C}$), 1465 (s), 1250 (s), 1118 (vs), 1094 (vs), 1035 (vs), 1015 (vs), 896 (m), 813 (m), 682 (s), 559 (s), 461 (w). Anal. Calcd for $C_{11}H_{21}Cl_2N_3O_2S_1Ti_1$ (M_r = 378.14): C, 34.94; H, 5.60; N, 11.11. Found: C, 34.95; H, 5.77; N, 10.78.

[V(═NTs)Cl$_2$(NHMe$_2$)$_2$] (5). To a toluene solution (15 mL) of 250 mg of $V(NMe_2)_4$ (1.100 mmol) was added by portions 1 equiv of *p*-$TsNH_2$ (188 mg, 1.100 mmol), and subsequently 1.2 g of Me_3SiCl was slowly added at room temperature. The resulting solution was stirred for 12 h at RT. Filtration (to remove about 60 mg of a brown solid residue) afforded a yellow solution. Addition of pentane (1 mL) to this solution afforded upon standing at −20 °C orange needles of **5** that were washed with pentane (2 × 5 mL) and dried under vacuum. Yield: 110 mg (26%) (orange). EPR (CH_2Cl_2, RT): g = 1.983, $A(^{51}V)$ = 87.0 G. ^{51}V NMR (131.60 MHz, CD_2Cl_2): δ −402.6 ($w_{1/2}$ = 200 Hz). IR: 3144 (s, br, NH), 2969 (w), 1597 (w, C═C), 1466 (s), 1250 (s), 1154 (s), 1094 (s), 1019 (s), 850 (s), 818 (m), 678 (m), 555 (m). Anal. Calcd for $C_{11}H_{21}Cl_2N_3O_2SV$ (M_r = 381.22): C, 34.66; H, 5.55; N, 11.02. Found: C, 34.56; H, 5.52; N, 10.95.

[(Me$_2$HN)Cl$_2$Ti(μ_2-*N*-NTs-κ^2*N,O*)$_2$TiCl$_2$(NHMe$_2$)$_2$] (6). Method 1 (One-Pot Synthesis from TiN(Me$_2$)$_4$/TsNH$_2$/Me$_3$SiCl). The procedure was similar to the one described for **5**, starting with $T(NMe_2)_4$ (250 mg), *p*-$TsNH_2$ (188 mg), and 1.0 g of Me_3SiCl. A total of 200 mg of **6** was obtained, contaminated with unknown products. Selective recrystallizations from toluene/pentane solutions afforded low amounts of pure **6** (30 mg). ^1H NMR (250 MHz, C_6D_6): two isomers (A and B) in a ratio A:B = 2:1. Isomer A (**6a**): δ 8.44 (d, ^3J = 8.3 Hz, 4H, *m*-C_6H_4), 6.81 (d, ^3J = 8.2 Hz,

Table 2. Crystallographic Data, Data Collection, and Refinement Parameters for Compounds **1**−**7**

param	**1**	**2**	**3**	**4**	**5**	**6**
chem formula	$C_{22}H_{38}N_6O_4S_2Ti_2$	$C_{22}H_{38}N_6O_4S_2V_2$	$C_{26}H_{54}Cl_2N_2O_4S_2Ti_2$	$C_{110}H_{210}Cl_{20}N_{31}O_{19}S_{10}Ti_{10}$	$C_{11}H_{21}Cl_2N_3O_2SV$	$C_{20}H_{35}Cl_4N_5O_4S_2Ti_2$
fw	610.50	616.60	773.55	3779.69	381.22	711.27
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/n$	$C2/c$
a, Å	8.0903(10)	8.0142(5)	9.6076(7)	35.005(2)	9.9919(8)	22.652(2)
b, Å	21.086(2)	8.8093(8)	12.2159(9)	12.4083(8)	18.2905(13)	11.4504(8)
c, Å	9.5039(12)	20.0954(14)	15.8021(12)	25.2366(17)	19.6658(16)	15.357(1)
α, deg	90.0	90.0	90.0	90.0	90.0	90.0
β, deg	114.395(13	94.020(8)	97.555(6)	128.269(8)	101.128(7)	128.659(5)
γ, deg	90.0	90.0	90.0	90.0	90.0	90.0
V, Å^3	1476.5(3)	1415.23(18)	1838.5(2)	8606.1(13)	3526.5(5)	3110.5(4)
Z	2	2	2	2	8	4
D_{calc}, g cm^{-3}	1.373	1.447	1.397	1.459	1.436	1.52
μ(Mo Kα), mm^{-1}	0.719	0.846	0.735	0.932	0.987	1.026
F(000)	640	644	816	3918	1576	1464
θ range (deg)	2.54−26.12	3.08−25.97	2.71−32.10	2.94−25.68	2.74−26.37	3−32
measd reflcns	14 536	12 049	18 768	29 219	25 499	31 117
unique reflcns/R_{int}	2908/0.2115	2749/0.0308	6092/0.0340	8135/0.0420	7210/0.0779	5123/0.02
params/restraints	168/0	168/0	206/ 0	470/6	371/0	174/0
final R indices [$I > 2\sigma(I)$]	R1 = 0.0549 wR2 = 0.0758	R1 = 0.0272 wR2 = 0.0738	R1 = 0.0359 wR2 = 0.0948	R1 = 0.0700 wR2 = 0.01522	R1 = 0.0411 wR2 = 0.0852	R1 = 0.0317 wR2 = 0.0380
final R indices all data	R1 = 0.1627 wR2 = 0.1001	R1 = 0.0335 wR2 = 0.075	R1 = 0.0599 wR2 = 0.1143	R1 = 0.0938 wR2 = 0.1625	R1 = 0.1073 wR2 = 0.1026	
goodness of fit	0.859	1.036	1.022	1.074	0.883	1.080
$\Delta\rho_{max}$, $\Delta\rho_{min}$	0.469 and −0.616	0.309 and −0.327	0.537 and −0.972	1.072 and −1.005	0.288 and −0.336	0.57 and −0.88

4H, *o*-C_6H_4), 3.95 (br m, 2H, N*H*Me$_2$), 3.37 (m, 1H, N*H*Me$_2$), 2.57 (d, ^3J = 6.2 Hz, 6H, NH*Me$_2$*), 2.44 (d or s depending on the concentration, ^3J = 5.7 Hz, 6H, NH*Me$_2$*), 2.14 (d or s depending on the concentration, ^3J = 5.8 Hz, 6H, NH*Me$_2$*), 1.83 (s, 6H, Me_{Ts}). Isomer B (**6b**): δ 8.39 (d, ^3J = 8.3 Hz, 4H, *m*-C_6H_4), 6.74 (d, ^3J = 8.1 Hz, 4H, *o*-C_6H_4), 3.95 (br m, 2H, N*H*Me$_2$), 3.37 (m, 1H, N*H*Me$_2$), 2.97 (br s, 6H, NH*Me$_2$*), 2.57 (d, ^3J = 6.2 Hz, 6H, NH*Me$_2$*), 1.78 (s, 6H, Me_{Ts}), 2.59 (br s, 6H, NH*Me$_2$*). $^{13}C\{^1H\}$ NMR (125.81 MHz, C_6D_6): isomer A (**6a**), δ 144.58, 137.42, 129.38, 128.70 (*C*$_6$H$_4$), 44.27 (N*Me$_2$*), 44.22 (N*Me$_2$*), 42.62 (N*Me$_2$*), 21.02 (Me_{Ts}); isomer B (**6b**), δ 144.29, 137.73, 129.38, 128.70 (*C*$_6$H$_4$), 45.64 (N*Me$_2$*), 42.77 (N*Me$_2$*), 41.90 (N*Me$_2$*), 21.02 (Me_{Ts}). IR: 3222 (m, NH), 3192 (m, NH), 1596 (w, $\nu_{C=C}$), 1466 (m), 1276 (m), 1255 (m), 1148 (m), 1113 (s), 1093 (s), 1075 (s), 1036 (vs), 1023 (s), 1011 (vs), 981 (s), 896 (s), 813 (m), 705 (m), 682 (vs), 595 (m), 554 (s), 496 (w), 458 (w), 420 (w), 415 (w). Anal. Calcd for $C_{20}H_{35}Cl_4N_5O_4S_2Ti_2$ (M_r = 711.20): C, 33.78; H, 4.96; N, 9.85. Found: C, 35.89; H, 5.16; N, 9.38. We were unable to obtain a satisfactory elemental analysis for this compound, probably because of its high moisture sensitivity (similar problems were reported for related (sulfonamido)titanium complexes).[100]

Method 2 (from $TiCl_2(NMe_2)_2$ and $TsNH_2$). Solid $TsNH_2$ (82 mg) was added to a toluene solution (5 mL) of $TiCl_2(NMe_2)_2$ (0.4833 mM). The resulting red solution was stirred for 1 day and then concentrated to 1 mL. Pentane (10 mL) was slowly added to this concentrate, which induced the formation of yellow crystals. The crystals were washed with pentane (2 × 5 mL) and dried under vacuum (yield: 150 mg, 87%). Analytical and spectroscopic data were similar to those obtained by method 1.

[Ti{μ-*N*,*O*′-N(SiMe$_3$)Ts-κ^3*N*,*O*,*O*′}Cl$_2$(NMe$_2$)]$_2$ (7). Method 1. Me_3SiCl (142 mg, 0.6553 mM) was slowly added to a 3 mL dichloromethane solution of **1** (50 mg, 0.08191 mM). The solution turned red and was stirred for 1 day at RT. Volatiles were removed under vacuum, and the green solid was washed with pentane (3 × 3 mL) and dried under vacuum. Yield: 40 mg (60%). ^1H NMR (250 MHz, C_6D_6): δ 7.88 (d, ^3J = 8.2 Hz, 4H, C_6H_4), 6.57 (d, ^3J = 8.2 Hz, 4H, C_6H_4), 3.40 (s, 12H, N*Me$_2$*), 1.74 (s, 6H, Me_{Ts}), 0.27 (s, 18H, Si*Me$_3$*). $^{13}C\{^1H\}$ NMR (125.81 MHz, C_6D_6): δ 414.40, 137.26, 129.88, 127.69, (*C*$_6$H$_4$), 49.41 (NH*Me$_2$*), 20.84 (Me_{Ts}), 1.13 (Si*Me$_3$*). ^{29}Si NMR (99.4 MHz, C_6D_6): δ 10.43. IR: 2959 (w), 1597 (w, $\nu_{C=C}$), 1459 (w), 1254 (s), 1223 (s), 1157 (vs), 1117 (m), 1127 (s), 1095 (s), 1021(m), 999 (m), 933 (m), 852 (vs), 815 (m), 782 (m), 743 (m), 579 (m), 541 (m), 458 (m). Anal. Calcd for $C_{24}H_{44}Cl_4N_4O_4S_2Si_2Ti_2$ (M_r = 810.48): C, 35.57; H, 5.47; N, 6.91. Found: C, 35.43; H, 5.51; N, 6.83.

Method 2 (from $Ti(NMe_2)_4$, without Isolating 1). To a toluene solution (5 mL) of 250 mg of $Ti(NMe_2)_4$ (1.115 mmol) was added by portions 1 equiv of *p*-$TsNH_2$ (191 mg, 1.115 mmol) at room temperature. The resulting solution was stirred for 12 h at RT. The volatiles were pumped off, to afford an orange solid. To be sure that no dimethylamine was retained, 4 mL of toluene was added to this solid, and the solvent was removed under vacuum, followed by addition of 5 mL of pentane, trituration of the solid, and removal of the solvent under vacuum (twice). The solid was solubilized in 5 mL of dichloromethane, and 1.0 g of Me_3SiCl was slowly added to give a red solution that was left overnight at RT. This step has also been performed in toluene at RT for 12 h, or 80 °C for 1 h without noticeable difference, but heating the solution at 110 °C for longer period of time led to decomposition products. The solution was concentrated to 2 mL, followed by addition of 3 mL of toluene and layering with a solution of pentane, affording after 5 days green crystals that were collected and washed with pentane. Yield: 215 mg (48%) (green). Analytical and spectroscopic data were similar to those obtained by method 1.

Results and Discussion

The synthesis and proposed structures of the tosylimido complexes of titanium(IV) and vanadium(IV) are summarized in Schemes 1−3. Structures of nine complexes are set out in Figures 1−8 or are given as Supporting Information; selected metric data are collected in Table 1.

1. Synthesis and Characterization of the Bridged Imido Complexes [M(NTs)(NMe$_2$)$_2$]$_2$ (M = Ti, V). In previous studies,[40,61] we described the synthesis of diamagnetic arylimido vanadium complexes [V(NAr)(NMe$_2$)$_2$]$_2$, from the

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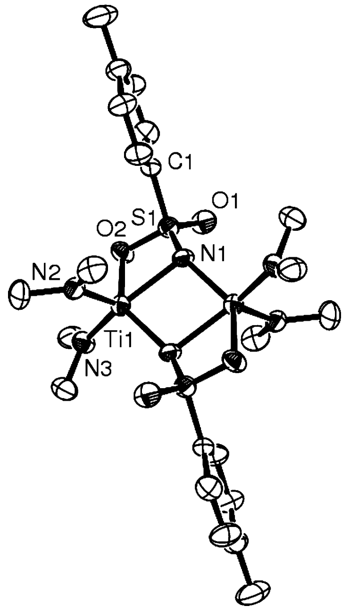
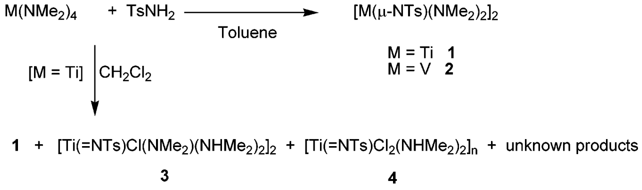


Figure 1. Molecular structure of **1**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

Scheme 1. Synthesis of Tosylimido-Bridged Dimer Complexes **1** and **2** and Terminal Tosylimido Complexes **3** and **4**



reaction of an aniline $ArNH_2$ with $V(NMe_2)_4$ in toluene. Titanium analog alkylimido dimers have also been prepared from $Ti(NMe_2)_4$.[101,102] Inspired by these results, we attempted the synthesis of related titanium– and vanadium–tosylimido analog complexes (tosyl = *p*-toluenesulfonyl).

As shown in Scheme 1, treatment of $Ti(NMe_2)_4$ with 1 equiv of tosylamine $TsNH_2$ in toluene rapidly produced the imido-bridged compound $[Ti(NTs)(NMe_2)_2]_2$ (**1**) as an orange solid with good yields. A similar reaction starting with $V(NMe_2)_4$ and 1 equiv of $TsNH_2$ in toluene gave the vanadium congener $[V(NTs)(NMe_2)_2]_2$ (**2**) as dark brown crystals in 59% yields. This formulation for **1** and **2** follows from NMR spectroscopic studies, IR, and microanalysis and has been confirmed unequivocally through a crystal structure determination. Single crystals of both complexes **1** and **2** were obtained (see Experimental Section) and were suitable for structural characterization by X-ray crystallography. Thermal ellipsoid plots are presented in Figures 1 and 2. Metric parameters for **1** and **2** are summarized in Table 1 to facilitate comparison between them.

The X-ray structure analysis confirmed that the Ti complex **1** is a centrosymmetric dimer (monoclinic, $P2_1/n$), composed of two $(Me_2N)_2Ti$ moieties bridged by two tosylimido ligands. Both Ti atoms are pentacoordinated because one sulfonyl oxygen of each monomeric unit is bonded to the other metal center in this dimeric complex. The coordination geometry of titanium is distorted square pyramidal ($\tau = 0.14$);[103] the Ti atom is 1.43(4) Å out of the mean plane through N3O2N1N1′ [mean deviation 0.063(2) Å]. The Ti_2N_2 core is planar (torsion angle = 0°) and is characterized by a short Ti$\cdots$Ti distance common in imido dimers[60,101,104,105] [Ti1$\cdots$Ti1′ = 3.1297(19) Å] and two Ti–N_{imido} bond distances of 2.106(4) and 1.974(4) Å. These Ti–N_{imido} distances are longer by ca. 0.2 Å than in the terminal tosylimido complex **3** (vide infra) and are, as expected, in the range observed for sulfonamido complexes of titanium(IV).[106–109] The $(Me_2N)_2Ti$ moiety is normal[101] and displays expected Ti–N bond distances and angles [Ti–N_{amido} 1.866(4) and 1.889(4) Å]. Coordination of the sulfonyl oxygen to titanium results in a lengthening of the S–O bond distance of about 0.06 Å and in a decrease of the N–S–O bond angle by ca. 8° with respect to N–S–O bond parameters of uncoordinated sulfonyl oxygen (e.g., in complexes **2** and **5**). The Ti–O distance of 2.125(4) Å is much shorter than the sum of the van der Waals radii, and the difference in the S1–O1 and S1–O2 distances confirms that this is a single bond.

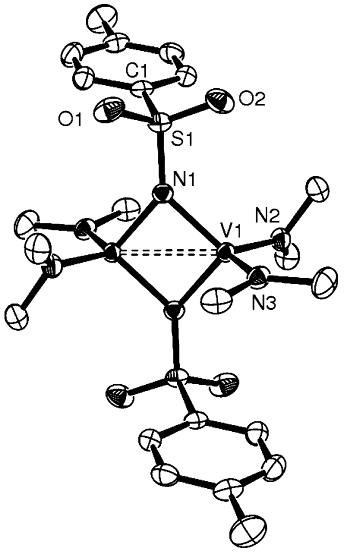


Figure 2. Molecular structure of **2**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

The molecular structure of **2** is shown in Figure 2, and selected bond distances and angles are reported in Table 1. The complex is a dimer $[V(NTs)(NMe_2)_2]_2$ with two imido ligands bridging two $(Me_2N)_2V$ moieties. The main differ-

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ence observed in the structure of **2** vs **1** is a coordination geometry around the vanadium centers that is distorted tetrahedral with no additional coordination of a sulfonyl oxygen atom. The V_2N_2 core is planar (torsion angle 0°) with a short V···V distance of 2.6027(6) Å. Such a short distance has been found in other dinuclear complexes of vanadium and may be indicative of a V−V bond.[110−116] For comparison it is longer by ca. 0.1 Å than one of the shortest distances found in related arylimido dimers $[V(NAr)(NMe_2)_2]_2$.[40,61] The angle formed by the bridging nitrogen atoms with the two vanadium atoms [V1−N1−V2 = 86.69(6)°] deviates significantly from that expected for an sp^2 nitrogen atom. The $V-N_{imido}$ distance of 1.9183(14) Å is slightly longer than the one found in related arylimido dimers $[V(NAr)(NMe_2)_2]_2$ (typically in the range 1.84−1.87 Å),[40,61] which reflects of the higher electron-withdrawing nature of the tosyl substituent. The $V-N_{amido}$ bond distances are in the normal range [1.8107(15) and 1.8349(15) Å] but are shorter by ca. 0.06 Å than the one reported for **1**.

Complexes **1** and **2** could later be characterized by ^{1}H and ^{13}C NMR spectroscopy (the sharpness of the peaks of the well-solved ^{1}H NMR spectrum of **2** indicates that the dinuclear structure is retained in CD_2Cl_2 solution), IR, elemental analysis, and the absence of magnetic moment for **2**. The diamagnetism of **2** indicates a strong electronic coupling between the two metal centers, either through the nitrogen atoms of the imido bridges or as a result of the short V−V distance.

2. Reaction of $Ti(NMe_2)_4$ and *p*-$TsNH_2$ in Dichloromethane. Interestingly, using dichloromethane as solvent in the room-temperature reactions between $Ti(NMe_2)_4$ and $TsNH_2$ gave less clear-cut observations, since a complex mixture of compounds arose with several unassigned signals observed in the ^{1}H NMR spectrum. Moreover the composition of these mixtures was dependent on the reaction time[117] and, therefore, will not be discussed further here, except for complexes **3** and **4** which crystallized directly from the solution and thereby permitted X-ray structural analysis. Thermal ellipsoid plots of the structures of **3** and **4** are presented in Figures 3 and 4, and Table 1 gives a comparison of their structural parameters.

In the solid state, compound **3** is a dimer formulated as $[Ti\{\mu\text{-}N,O\text{-}NTs\}Cl(NMe_2)(NHMe_2)_2]_2$ with two six-coordinated titanium centers linked by two bridging (*N*,*O*)-coordinated terminal tosylimido ligands thus forming an 8-membered cycle. The additional ligands on each metal center are one dimethylamido ligand (Ti−N = 1.9148(16) Å), one chloro ligand (Ti−Cl = 2.4530(6) Å) cis to the $-NMe_2$ group, and two trans dimethylamino groups (Ti−N = average 2.25 Å). The presence of a Ti−Cl bond is explained by chloride abstraction from dichloromethane solvent. Compound **3** represents the first group 4 metal complex with a *terminal* tosylimido group, and therefore the geometric parameters associated with the tosylimido ligand deserves some comment. The titanium−nitrogen bond distance of the imido fragment of 1.8391(16) Å is shorter by ca. 0.2 Å than the $Ti-N_{imido}$ bond distance in the bridged-

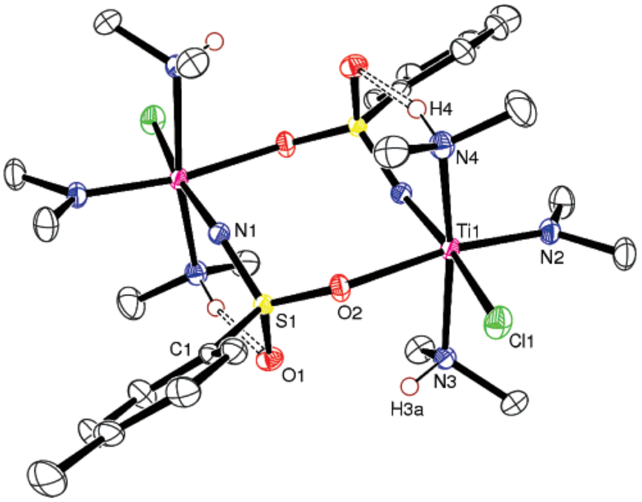

Figure 3. Molecular structure of **3**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

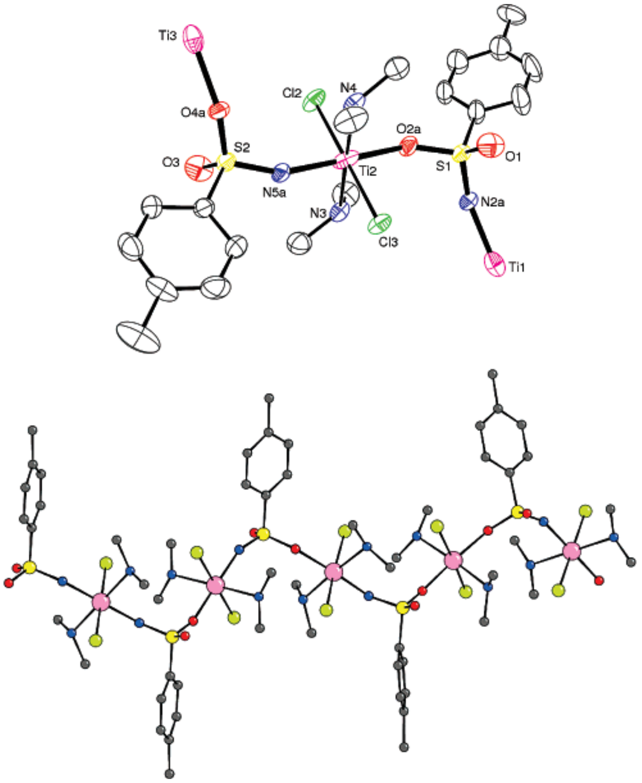

Figure 4. Molecular structure of the asymmetric unit of **4** (top) and part of the infinite chain (bottom), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

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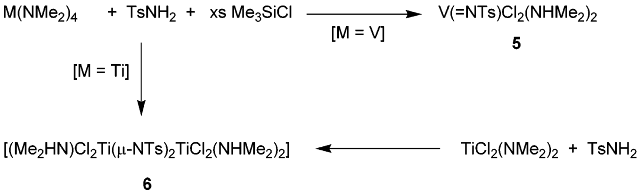
(117) Composition vs time of a dichloromethane solution containing equimolar amounts of $Ti(NMe_2)_4$ and $TsNH_2$: After 5 h the major compound is **1**. After 1 day we noted the presence of several species (or isomers) including **3**. After 3 days the major compound is **4**.

tosylimido complex **1**. However, such a value (1.8391(16) Å) for a terminal Ti−N imido bond is slightly above the upper limit[118] found in structurally established terminal alkyl- and (arylimido)titanium(IV) complexes.[119] A comparison with the normal V═NTs bond in compound **5** (vide infra) would suggest that the long Ti═NTs in **3** is indeed because of the (N,O)-bridging nature of the tosylimido linkage. The imido fragment is further characterized by a Ti−N−S angle of 149.46(11)° that deviates significantly from linearity. The reason for that is unclear, and we cannot compare with other complexes as **3** is the only example of group 4 metal complex with a terminal M═NTs function. A possible explanation would be the delocalization of the nitrogen lone pair on the sulfonyl fragment but could also be due to strong intramolecular hydrogen bonding between the sulfonyl oxygen and the hydrogen atom of one dimethylamine ligand (O1⋯H4 = 2.069 Å, O1−H4−N4 = 159.2°).

Complex **4** was obtained as the only characterizable product when the previous reaction was left for a longer period of time (3 days). As revealed by an X-ray structure determination illustrated in Figure 4, **4** is a coordination polymer composed of infinite O−Ti−N−S− chains with repetitive $[Ti({=}NTs)Cl_2(NHMe_2)_2]_n$ units. The compound crystallized in the monoclinic space group $C2/c$, with an asymmetric unit containing 2.5 of the $[Ti({=}NTs)Cl_2(NHMe_2)_2]$ structural motifs. The sulfur atom S3 lies in a general position and is therefore necessarily disordered about the C_2 axis, with 50% occupancy at each position. The O−Ti−N−S− sequence as a whole is described by this crystallographically imposed disorder. As a consequence of the high degree of uncertainty, the metric parameters in **4** have limited value for comparison (Table 1). Each $[Ti({=}NTs)Cl_2(NHMe_2)_2]$ unit contains an octahedral Ti center surrounded by two chlorine atoms with trans configuration, two trans-oriented $NHMe_2$ ligands, and one nitrogen atom of the imido group that is in a position trans to the sulfonyl oxygen atom. Each of the two titanium centers is connected to neighboring titanium centers through (N,O)-tosylimido bridges and forms an infinite polymeric network as shown in Figure 4 (bottom). The nonbonding Ti⋯Ti separation amounts to 5.45 Å. Unfortunately, but not surprisingly for an inorganic polymer, **4** is insoluble in most common noncoordinating solvents, except in dichloromethane, a solvent in which it seems to be slightly soluble. Nevertheless, ^1H NMR studies of a suspension of **4** in CD_2Cl_2 suggests its rapid evolution into complex **6** (i.e., resulting from the loss of a $NHMe_2$ ligand; vide infra) accompanied by signals attributed to decomposition products.

3. One-Pot Reaction of $M(NMe_2)_4$/p-$TsNH_2$/Me_3SiCl [M = Ti, V]. Previously, we have reported the direct synthesis of terminal imido complexes of titanium and vanadium of general formula $M({=}NR)Cl_2(NHMe_2)_2$ [M = Ti,[60] V][16,22,61] on the basis of a very convenient single step and one-pot reaction of $M(NMe_2)_4$ with RNH_2 in the presence of an excess of trimethylchlorosilane. In this reaction Me_3SiCl acts as a chlorinating agent.[120] In an attempt to prepare the elusive tosylimido congeners $M({=}NTs)Cl_2(NHMe_2)_2$, we initially reacted $M(NMe_2)_4$ with p-$TsNH_2$ in the presence of an excess of Me_3SiCl.

Scheme 2. Synthesis of Terminal Tosylimido Complex **5** and Dinuclear Tosylimido-Bridged Complex **6**



A toluene solution of $V(NMe_2)_4$, when reacted at RT with 1 equiv of p-$TsNH_2$ in the presence of an excess of Me_3SiCl (8 equiv), afforded a yellow solution from which orange needles (suitable for X-ray study; vide infra) of complex **5** separated upon addition of pentane and slow cooling (Scheme 2).

The well-resolved electron paramagnetic resonance (EPR) spectrum of **5** at room temperature in dichloromethane solution revealed a resonance at $g = 1.985$ with the characteristic octet pattern ($A_{iso}(^{51}V) = 87.0$ G) expected for the interaction of an unpaired electron of V^{IV} with the ^{51}V nucleus ($I = 7/2$). In agreement, the magnetic moment is consistent with a d^1 electronic configuration ($\mu_{eff} = 1.71\ \mu_B$).

The solid-state structure determination revealed the structure of the desired vanadium complex $V({=}NTs)Cl_2(NHMe_2)_2$. Two independent molecules are present in the asymmetric unit cell. Figure 5 shows the structure of one of these molecules (molecule A), and selected bond distances and angles are given in Table 1 (only for molecule A; metric parameters for the second molecule are almost the same) for a comparison of their structural parameters. In the solid state, the molecular structure of **5** lies between square pyramidal and trigonal bipyramidal ($\tau = 0.46$ and 0.38 respectively for molecules A and B) with no coordination of the sulfinyl oxygen atoms to the metal center. The distances and angles associated with the vanadium center and the ligands are broadly comparable to those found in other $M({=}NR)Cl_2(NHMe_2)_2$ complexes [M = Ti,[60,63] V].[16,61] **5** exhibits a short $V-N_{imido}$ bond distance of 1.672(3) Å. Although shorter by ca. 0.25 Å than in the bridged tosylimido V complex **2** described in this study, this value is in the range of those found in related terminal arylimides $V({=}NAr)Cl_2(NHMe_2)_2$ (1.65−1.70 Å).[16,61] One would have expected a longer V−N bond distance (as in titanium compound **3**) due to the highly electron-withdrawing nature of the tosyl substituent, but examination of the $M-N_{imido}$ bond distance

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[118] Ti−N bond distances in structurally characterized terminal imido complexes usually range 1.66−1.76 Å (Cambridge Crystallographic Database).

[119] For representative examples of Ti═N bond distances, see refs 17, 57, 60, 63, and the following: Roesky, H. W.; Voelker, H.; Witt, M.; Noltemeyer, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 669−670.

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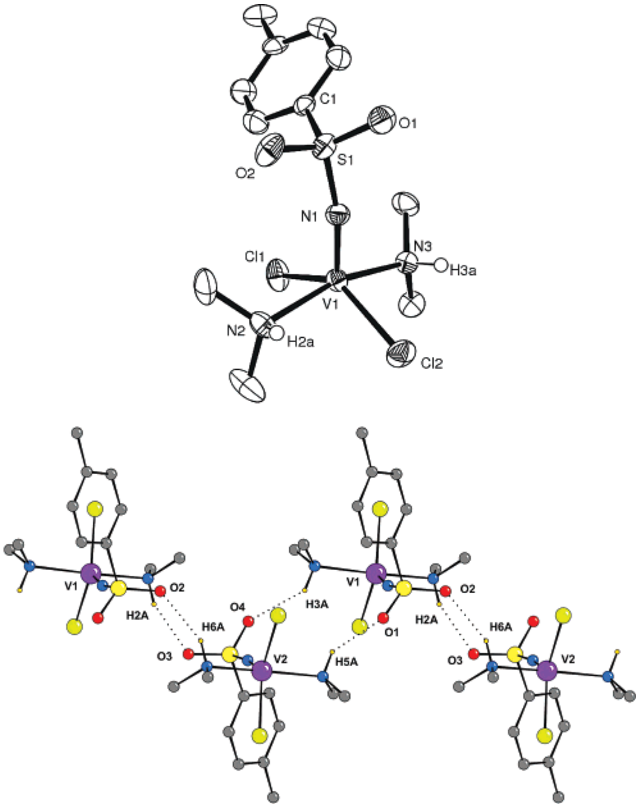

Figure 5. Molecular structure of one of the two independent molecules of **5** (molecule A, top), showing 50% probability ellipsoids and partial atom-labeling schemes, and hydrogen bond networks (bottom). Hydrogen atoms are omitted for clarity.

in molybdenum complexes $Mo(NR)_2(Et_2dtc)_2$ reveals little or no difference between R = Ts and Ar. The imido linkage is almost linear [$V-N_{imido}-S$ angle = 167.7(2) and 172.8(2)° respectively for molecules A and B], which, together with the short $V-N_{imido}$ bond, is consistent with the lone pair on nitrogen being donated to an acceptor orbital on vanadium. As a consequence, the imido V−N bond in **5** can be considered as a triple bond with the imido acting as a six-electron donor ligand. The two trans dimethylamino ligands have mean $V-N_{NHMe_2}$ bond distances of ca. 2.14 Å. Most interestingly, some authors have used the metal−chlorine bond lengths as a probe for comparison of molybdenum Lewis acidity in a series of structurally characterized bis(imido) complexes.[82] In **5**, the two vanadium−chlorine bond distances of 2.2603(12) and 2.2855(12) Å are shorter than those measured in related arylimides $V(=NAr)Cl_2(NHMe_2)_2$ (2.32−2.33 Å),[16,61] which reflects the higher electron-withdrawing nature of the tosyl substituent. Moreover, this value is even shorter than the V−Cl bond distances found in the oxo analog complex $V(=O)Cl_2(NHMe_2)_2$ (V−Cl = 2.3085(11) Å).[121]

The supramolecular structure is dominated by strong hydrogen bonding between the sulfonyl oxygen atoms and the hydrogen atoms of a dimethylamine ligand of a neighboring molecule in the asymmetric unit (with O···H bond distances in the range 2.12−2.24 Å and associated angles O−H−N of 138−154°). Figure 5 (bottom) illustrates the extended packing in **5** with each molecule donating two N−H···O hydrogen bonds and accepting two hydrogen bonds and thus consisting of infinite bilayers (with the second infinite chains based on molecule B) running parallel to the crystallographic axis *a*.

Although it is a generally clean transformation in related arylimido complexes $V(NAr)Cl_2(NHMe_2)_2$, attempted displacement of $NHMe_2$ ligands in **5** by pyridines in dichloromethane failed, with formation of the known, reduced, vanadium(III) complexes VCl_3Py_3[122] and $V_2OCl_4Py_6$.[123] It is conceivable that these vanadium(III) complexes are formed along with other uncharacterized—organic and/or inorganic—products via ligands redistribution or redox reactions that are common features in vanadium chemistry.[124] Nevertheless, we were unable to isolate other species out of the reaction, but this unexpected reactivity is currently under further examination in our group. Both vanadium(III) compounds were characterized by X-ray diffraction analyses that are given as Supporting Information, as they crystallized in space groups different from those previously reported.[125]

If we turn now to titanium, the one-pot reaction of $Ti(NMe_2)_4$ with 1 equiv of *p*-$TsNH_2$ in the presence of an excess of Me_3SiCl (8 equiv) appeared more complicated, as it gave mixtures of products or isomers (as we will see below).[126,127] However, we have been able to crystallize selectively one of these compounds (compound **6**) and to determine its molecular structure by an X-ray crystallographic analysis.[128] The molecular structure of **6** is shown in Figure 6, and selected bond distances and angles are reported in Table 1. This study revealed the structure of an unexpected dinuclear titanium complex formulated as $[(Me_2HN)Cl_2Ti(\mu_2\text{-}N\text{-}NTs\text{-}\kappa^2 N,O)_2TiCl_2(NHMe_2)_2]$, composed of two titanium centers (one six- and one seven-coordinate metal atom)

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(121) Lorber, C. Unpublished result. The synthesis and crystal structure of $V(=O)Cl_2(NHMe_2)_2$ will be described elsewhere.

(122) Fowles, G. W.; Greene, P. T. *J. Chem. Soc. A* **1967**, 1869−1874.

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(125) (a) We crystallized VCl_3Py_3 both in $P2_1/n$ (as reported by the following: Sorensen, K. L.; Ziller, J. W.; Doherty, N. M. *Acta Crystallogr.* **1994**, *C50*, 407−409) and in $P2_1/c$ (a = 13.2975(10), b = 8.5345(8), and c = 15.5771(14) ?, and β = 98.878(10)°; see Supporting Information). (b) $V_2OCl_4Py_6$ crystallized in $P\bar{1}$ with cell parameters a = 15.306(3), b = 15.806(3), and c = 16.916(3) ? and α = 98.44(3), β = 96.79(3), and γ = 98.97(3)° (see Supporting Information). This compound was already reported to crystallize in two different space groups ($C2/c$ and $P2_1/c$): Zhang, Y.; Holm, R. H. *Inorg. Chem.* **1990**, *29*, 911−917. Rambo, J. R. Castro, S. L.; Folting, K.; Bartley, S. L.; Heintz, R. A.; Christou, G. *Inorg. Chem.* **1996**, *35*, 6844−6852.

(126) The composition of these mixtures (the amount of unknown byproducts) is also dependent on the experimental conditions and, in particular, on the time between the addition of $TsNH_2$ to $Ti(NMe_2)_4$ and the addition of Me_3SiCl. The optimum conditions for maximum yield in **6** were not optimized.

(127) At this point, we do not know the exact nature of the byproducts, but we suggest that they result from electrophylic attack of the trimethylchlorosilane on either $Ti-N_{amido}$ or $Ti-N_{imido}$ of $Ti(NMe_2)_4$ or preformed **1** or **6**.

(128) Complex **5** has also been obtained as yellow plates that crystallized in the triclinic space group $P\bar{1}$ (a = 12.866(3), b = 15.240(3), c = 17.991(4) ?; β = 102.37(3)°). Bond distances and angles in the two diamorphs are very similar, but two independent molecules are present in the cell of the triclinic diamorph and the overall structure differs by the respective position of the N−H bonds of the trans $NHMe_2$ ligands in one of these molecules (*syn* vs *anti*).

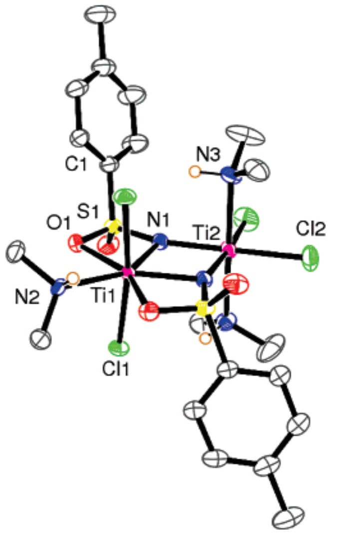
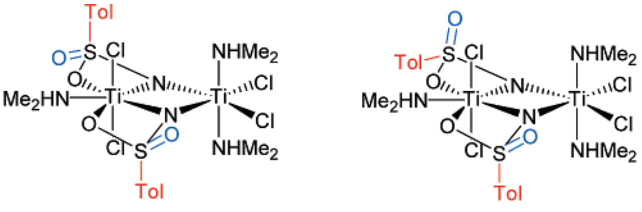


Figure 6. Molecular structure of **6**, showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity.

separated by 3.16 Å and linked by two μ-*N*-tosylimido groups. The striking difference in **6**, as compared to the expected $Ti(=NTs)Cl_2(NHMe_2)_2$ complex which is analogous to the vanadium compound **5**, is the loss of one dimethylamine ligand—as a result of the coordination of a sulfinyl oxygen atom of each bridging tosylimido moiety to the same metal center (Ti1). Loss of $NHMe_2$ ligands has already been observed in dimethylamine adducts $Ti(=NR)Cl_2(NHMe_2)_2$.[60] The six-coordinate titanium center (Ti2) has an approximately octahedral geometry, with two trans dimethylamine ligands, two cis chloride ligands, and two cis bridging tosylimido groups, whereas the seven-coordinate titanium (Ti1) possesses two trans chloride ligands, one dimethylamine group in the plane of the two coordinated oxygen atoms of the sulfynyl groups, and the two nitrogen atoms of the bridging imido ligands. The $Ti-N_{imido}$ bond distances of 2.0707(19) and 1.931(2) Å are comparable with those found in the bridging tosylimido complex **1**. All other bond distances are in the expected range. The Ti−Cl [Ti1−Cl1 2.3417(5) Å, Ti2−Cl2 2.33197(8) Å] and $Ti-N_{imido}$ [Ti1−N1 2.0707(19) Å, Ti2−N1 1.931(2) Å] distances for Ti1 are longer than those for Ti2, consistent with the higher coordination number of Ti1. Coordination of the sulfonyl oxygen atom to the titanium center (Ti1−O1 bond distance of 2.1509(18) Å) results in a lengthening of the S−O bond distance of about 0.05 Å and in a decrease of the N−S−O bond angle by ca. 11° with respect to N−S−O bond parameters of uncoordinated sulfonyl oxygen (e.g., in complexes **2** and **5**), as already noted in titanium complex **3**.

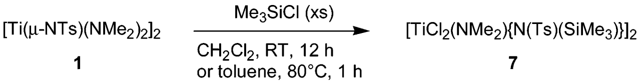
It is noteworthy that the ^1H NMR (C_6D_6 solution, 287 K) spectrum of a *single crystal* of **6** appears more complex than expected. The spectrum exhibits two sets of signals in a ratio 2:1 for each of the three types of protons (*o*-H, *m*-H, and Me) of the tosyl ligand and magnetically inequivalent methyl groups in the $NHMe_2$ ligands. This is likely due to the presence of two isomers in solution at RT (in a ratio 2:1) and to hindered rotation of some $NHMe_2$ groups. In accordance with the NOESY and VTP NMR experiments, we suggest these two isomers to be the species **6a**,**b** presented in Figure 7, which differ from each other by the respective position of the sulfonyl oxygen atom and tolyl substituent of the two bridging tosylimide ligands. The major isomer (**6a**) would have the two S═O bonds (or the two tolyl substituents) in *anti* position, as suggested by the NOESY studies, an arrangement that corresponds to the solid-state structure determination of the material that crystallized from the solution (Figure 6). Under strictly anhydrous conditions, **6** is stable in benzene solution for hours and in the solid state for several months. However, its high reactivity is reflected by the pronounced sensitivity toward hydrolysis.



6a **6b**

Figure 7. Possible Structures for isomers A and B (**6a**,**b**).

Scheme 3. Silylation Reaction of **1** Leading to Amido Complex **7**



In summary, the one-pot procedure that consisted of reacting $Ti(NMe_2)_4/TsNH_2/Me_3SiCl$ gave unsatisfactory results: **6** was formed in low yields after necessary recrystallization steps to separate it from byproducts that, most certainly, arose from side reactions involving Me_3SiCl (vide infra).[127] To avoid the problem of possible competing reactions with chlorosilane, we attempted to generate **6** from alternative methods. First, we reacted the imido precursor $Ti(=NBu^t)Cl_2(NHMe_2)_2$ with $TsNH_2$ but we did not observe the transamination reaction. Then we used $TiCl_2(NMe_2)_2$ as starting material; $TiCl_2(NMe_2)_2$ is known to generate $Ti(=NR)Cl_2(NHMe_2)_2$ complexes in presence of RNH_2.[63] The reaction of $TiCl_2(NMe_2)_2$ with 1 equiv of $TsNH_2$ proceeded smoothly in toluene and afforded yellow crystals as in the previous reaction with $Ti(NMe_2)_4/Me_3SiCl$. Spectroscopic studies (IR, NMR), elemental analysis, and X-ray studies (cell parameters determination) confirmed these yellow crystals to be complex **6**. As judged by ^1H NMR spectroscopic studies, the reaction that uses $TiCl_2(NMe_2)_2$ appeared very clean (no byproduct) and in C_6D_6 solution the same ratio of isomers **6a**:**6b** was observed (2:1). Therefore, this synthetic route is preferable as it gives higher yields of pure **6**.

4. Reaction of Tosylimido Bonds with Me_3SiCl. To verify the foregoing suggested hypothesis concerning the reactivity of the titanium−tosylimide bond vs Si−Cl, we reacted selected Ti and V complexes reported above with an excess of Me_3SiCl.

The NMR tube reaction of vanadium compound **2** with an excess of trimethylchlorosilane in CD_2Cl_2 at room temperature suggested a complete transformation with precipitation of a black solid. The low solubility and probable paramagnetism of this material precluded further studies.

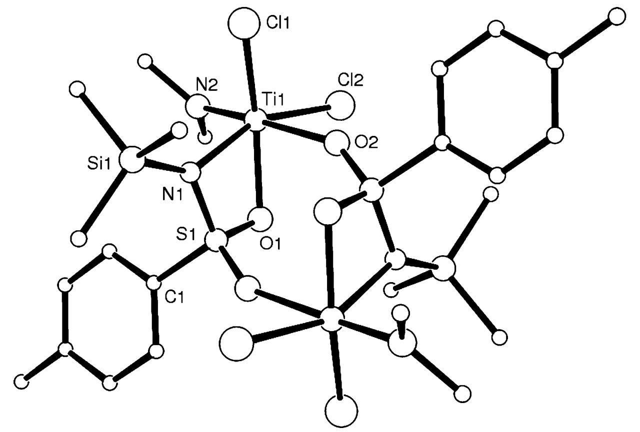


Figure 8. Molecular structure of one of the two independent molecules of **7**, with partial atom-labeling schemes. Atoms are drawn as spheres of arbitrary radius, and hydrogen atoms are omitted for clarity.

A yellow-orange solution of **1** treated with excess trimethylchlorosilane turned deep red, in dichloromethane for 12 h or in toluene at 80 °C for 1 h,[129] and afforded after suitable workup green crystals of **7** (Scheme 3).[130] Multinuclear NMR experiments (^{1}H, ^{13}C, ^{29}Si) showed the presence of signals typical of $-SiMe_3$ and $-NMe_2$, as well as Ts groups, and indicated a ligand $SiMe_3/NMe_2/Ts$ ratio of 1:1:1. A X-ray structure determination analysis (see Supporting Information) on a single crystal of **7** identified this compound as the dimer $\{TiCl_2(NMe_2)[\mu_2\text{-}N,O'\text{-}N(Ts)(SiMe_3)\text{-}\kappa^3N,O,O']\}_2$, illustrated in Figure 8. The poor quality of the crystals of **7** prevents discussion of its structural details but confirms the silylation of the tosylimide group with formation of an $-N(Ts)(SiMe_3)$ amide ligand. The structure is composed of two six-coordinate titanium centers that are bridged by two $-N(Ts)(SiMe_3)$ amide ligands, thus forming an 8-member cyclic system. The $-N(Ts)(SiMe_3)$ ligand is coordinated to one Ti atom via the nitrogen atom and one sulfonyl oxygen atom and to the other Ti center via the second sulfonyl oxygen atom. The coordination sphere around the metal center is completed by two chlorine atoms (in a cis configuration) and one dimethylamide group in a position trans to the oxygen atom of the symmetry related tosylamide ligand.

Therefore, we propose the mechanism depicted in Figure 9 for the reactivity of the $Ti-N_{tosylimido}$ bond of **1** with a $Si-Cl$ bond of Me_3SiCl. This mechanism is highly reminiscent to the reactivity of chlorosilanes with $M{=}O$ groups observed in some oxometal complexes.[131]

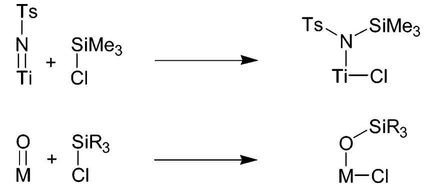


Figure 9. Mechanistic considerations for the silylation of the tosylimide function and oxo group.

Finally, the reaction of **6** with an excess of trimethylchlorosilane in CD_2Cl_2 at room temperature gave inconclusive results. A very slow evolution and formation of small amounts of an insoluble green material was noted, which could not be further characterized owing to its poor solubility.

Conclusions

We have demonstrated that use of the amine elimination method in the reaction of $TsNH_2$ and $M(NMe_2)_4$ (M = Ti, V) or $TiCl_2(NMe_2)_2$ precursors has allowed the generation of the first *p*-toluenesulfonylimide complexes of titanium(IV) and vanadium(IV). These imido complexes are unusual in that they bear strongly electron-withdrawing groups at the nitrogen atom. The structural data reveal the electron-deficient character of the tosylimido group but also display high structural diversity for the complexes bearing the tosylimide function. Currently, we are continuing to investigate in more detail the reactivity and catalytic properties of these and related early transition metal electron-poor complexes.

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Supporting Information Available: CIF files and tables of atomic coordinates, bond distances, and angles for the X-ray crystal structures of complexes **1**−**7**, VCl_3Py_3, and $V_2OCl_4Py_6$, ^{1}H NMR spectra of **6** (mixture of isomers A and B, from a diluted solution at 293 K and from a concentrated solution at 283−293 and 333 K), 2D NOESY experimental data for **6**, and an ^{1}H NMR spectrum of the mixture of products obtained from the reaction of $Ti(NMe_2)_4$ with $TsNH_2$ in CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(129) Heating a toluene solution of **1** to higher temperatures (110 °C) led to the formation of intractable products.

(130) Note that **7** could also be obtained in a two-step reaction from $Ti(NMe_2)_4$ and $TsNH_2$, without isolation of **1** but by removing under vacuum $HNMe_2$ and subsequent reaction with Me_3SiCl.

(131) For selected examples of reaction of $M{=}O$ bonds (in V, Cr, Mo, W, and Re complexes) with R_3SiCl, see the following: (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-lnterscience: New York, 1988. (b) Lorber, C.; Donahue, J. P.; Goddard, C. A.; Nordlander, E.; Holm, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 8102−8112. (c) Xiao, Z.; Gable, R. W.; Wedd, A. G.; Young, C. G. *J. Am. Chem. Soc.* **1996**, *118*, 2912−2921. (d) Huang, M.; DeKock, C. W. *Inorg. Chem.* **1993**, *32*, 2287−2291. (e) Luo, L.; Lanza, G.; Fragalà, Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 3111−3122. (f) Stavropoulos, P.; Bryson, N.; Youinou, M.-T.; Osborn, J. A. *Inorg. Chem.* **1990**, *29*, 1807−1811.