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Synthesis and Structure of a Series of New d^1-Aryl Imido–Vanadium(IV) Complexes Stabilized by N-Donor Ligands

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A family of new coordination vanadium(IV) compounds supported by a terminal or bridged aryl imido ligand are reported. Reaction of $V(NMe_2)_4$ with anilines $ArNH_2$, where Ar = 2,6-*i*-Pr_2-C_6H_3, 2,6-Me_2-C_6H_3, Ph, 2,6-Cl_2-C_6H_3, and C_6F_5, afforded the diamagnetic imido-bridged complexes $[V(NAr)(NMe_2)_2]_2$ (**1a**–**e**). Chlorination of **1a**–**e** with trimethylchlorosilane afforded complexes **2a**–**e** formulated as $[V({=}NAr)Cl_2(NHMe_2)_x]_n$. One-pot reaction of $V(NMe_2)_4$ with $ArNH_2$ in the presence of an excess of trimethylchlorosilane gave the five-coordinate compound $[V({=}NAr)Cl_2(NHMe_2)_2]$ (**3a**–**e**). Reaction of **3a**–**e** with pyridine, bipyridine (bipy), or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) gave respectively the six-coordinate tris- or bis(pyridine) adducts $[V({=}NAr)Cl_2(Py)_3]$ (**4a**–**e**) or $[V({=}NAr)Cl_2(Py)_2(NHMe_2)]$ (**5a**), bipyridine complexes $[V({=}NAr)Cl_2(bipy)(NHMe_2)]$ (**5a**–**e**) and $[V({=}NAr)Cl_2(bipy)(Py)]$ (**9a**), and tmeda adduct $[V({=}NAr)Cl_2(tmeda)(NHMe_2)]$ (**10a**). Moreover, five-coordinate complexes free of $NHMe_2$ ligands, such as $[V({=}NAr)Cl_2(Py)_2]$ (**5a**), $[V({=}NAr)Cl_2(bipy)]$ (**8a**), and $[V({=}NAr)Cl_2(tmeda)]$ (**11a**), were directly prepared starting from precursors **2a**–**e**. All compounds were totally characterized by spectroscopic methods (IR, ^{1}H NMR for diamagnetic complexes, and EPR for paramagnetic complexes), elemental analysis, magnetism, and single-crystal X-ray diffraction studies for **1b**, **3a**, **3d**, **4b**, **4d**, **7c**, **10a**, and **11a**.

Introduction

The last two decades have witnessed a strong interest in the coordination chemistry of transition metal complexes containing imido ligands $[NR]^{2-}$ (R = alkyl or aryl).[1,2] The dianionic π-donor terminal imido functional group is involved in a rich chemistry that can be subdivided into two types: the first concerns reactions in which the imido group acts as a spectator ligand,[1,2] the $[NR]^{2-}$ moiety being isolobal with $[C_5H_5]^{-}$ [3] (e.g. in alkene methathesis[4] or olefin polymerization[5−7]), but the M═NR linkage itself can also be involved in a variety of transformations such as imine metathesis,[8] oxo-imido exchange,[9] C−H activation,[10] reactions with unsatured C−C[11] or C−X bonds,[12]...

As part of an ongoing study of vanadium alkoxide,[13] diamide,[14] poly-yne,[15] or iminoacyl[16] complexes, we recently described the synthesis and molecular structure of the new terminal imido complex $[V(N{=}Ar)Cl_2(NHMe_2)_2]$ (Ar = 2,6-*i*-Pr_2-C_6H_3),[7] one of the very few Cp-free vanadium(IV)

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terminal imido compounds that have been structurally characterized.[17−20]

In this paper we report on the synthesis of a series of new aryl imido derivatives of vanadium(IV) prepared by an extremely convenient one-pot reaction, together with some aspects of their coordination chemistry toward neutral N-donor ligands: pyridine (Py), bipyridine (bipy), and *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmeda).

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, and DPX300 spectrometers and referenced internally to residual protio-solvent (^{1}H) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). ^{19}F NMR (188 MHz) spectra were recorded on a Brucker AM200 spectrometer (reference CF_3CO_2H). Chemical shifts are quoted in δ (ppm). Infrared spectra were prepared as KBr pelets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumber (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). Magnetic susceptibility data were collected on powdered samples of the different compounds with use of a homemade Faraday-type automatic magnetometer with mercury tetra(thiocyanato)cobaltate (susceptibility at 20°, 16.44×10^{-6} cm^3 mol^{-1}). Diamagnetic corrections were applied by using Pascal's constants.[21] Although each compound was characterized by IR spectroscopy, only the data corresponding to ν_{NH} are given in the experimental part; for full IR spectroscopy data see the Supporting Information.

$V(NMe_2)_4$ was prepared by a modification of a literature procedure.[22] Liquid anilines $ArNH_2$ (Ar = 2,6-*i*-Pr_2-C_6H_3, 2,6-Me_2-C_6H_3, Ph) were dried over KOH, refluxed, distilled, and stored over 4 Å molecular sieves under argon before use. Trimethylchlorosilane was distilled and stored over 4 Å molecular sieves under argon before use.

Crystal Structure Determination of 1b, 3d, 4b, 4d, 7c, 10a, and 11a. Reference is made to the numerical designation of complexes in Chart 1. The structures of the seven compounds in Table 1 were determined: crystals of **1b** (dark-red blocks), **3d** (orange blocks), **4b** (red blocks), **4d** (dark-red blocks), **7c** (red blocks), **10a** (red plates), and **11a** (dark-green blocks). For the seven 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 and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and the crystal decay was monitored during data collection by measuring 200 reflections by image; no significant fluctuation of intensities has been observed. Structures have been solved by means of Direct Methods with the program SIR92,[23] and subsequent difference Fourier maps and models were refined by least-squares procedures on F^2 by using SHELXL-97[24] integrated in the package WINGX version 1.64,[25] and empirical absorption corrections were applied to the data.[26] All hydrogen atoms have been located on differences Fourier maps and introduced in the refinement in idealized positions by using rigid groups with an isotropic thermal parameter fixed at 20% higher than those of carbon atoms with which they are connected, except for few specific hydrogen atoms which have been isotropically refined (those on $NHMe_2$ groups). For the seven structures all non-hydrogen atoms were anisotropically refined: in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

Chart 1. Designation of Vanadium−Imido Complexes[a]

$[V^{IV}(NAr)(NMe_2)_2]_2$	**1a-e**	$[V^{IV}(=NAr)Cl_2(bipy)(NHMe_2)]$	**7a-e**
$[V^{IV}(NAr)Cl_2]_n$	**2a-e**	$[V^{IV}(=NAr)Cl_2(bipy)]$	**8a**
$[V^{IV}(=NAr)Cl_2(NHMe_2)_2]$	**3a-e**	$[V^{IV}(=NAr)Cl_2(bipy)(Py)]$	**9a**
$[V^{IV}(=NAr)Cl_2(Py)_3]$	**4a-e**	$[V^{IV}(=NAr)Cl_2(tmeda)(NHMe_2)]$	**10a**
$[V^{IV}(=NAr)Cl_2(Py)_2]$	**5a**	$[V^{IV}(=NAr)Cl_2(tmeda)]$	**11a**
$[V^{IV}(=NAr)Cl_2(Py)_2(NHMe_2)]$	**6a**		

[a] Ar = 2,6-*i*-Pr_2-C_6H_3 (a), 2,6-Me_2-C_6H_3 (b), Ph (c), 2,6-Cl_2-C_6H_3 (d), and C_6F_5 (e).

Synthesis of Complexes $[V(NAr)(NMe_2)_2]_2$ (1a−e): General Procedure (See Supporting Information for Full Details). A toluene solution (4 g) of 1.00 g of $V(NMe_2)_4$ (4.40 mmol) and $ArNH_2$ (4.40 mmol) was heated at 100 °C for 1 day giving a dark-red solution. Removal of the volatiles under vacuum gave a purple oil that was triturated several times with 5 mL of pentane and dried under vacuum for a prolonged period of time to afford a sticky solid. Analytically pure samples were obtained after two successive recrystallizations in cold pentane.

(a) $[V(N\text{-}2,6\text{-}C_6H_3\textit{i}Pr_2)(NMe_2)_2]_2$ (1a): Yield 51% (red purple solid). ^{1}H NMR (C_6D_6) 7.28 (d, 2H, *m*-C_6H_3), 7.00 (t, 1H, *p*-C_6H_3), 4.35 (sept, 2H, C*H*Me_2), 3.00 (s, 12H, N*Me*$_2$), 1.24 (d, 12H, CH*Me*$_2$). $\mu_{eff}(20\ °C) = 0\ \mu_B$. Anal. Calcd for $C_{16}H_{29}N_3V$: C, 61.13; H, 9.30; N, 13.37. Found: C, 60.91; H, 9.42; N, 13.62.

(b) $[V(N\text{-}2,6\text{-}C_6H_3Me_2)(NMe_2)_2]_2$ (1b): Yield 70% (red purple solid). ^{1}H NMR (C_6D_6) 7.19 (d, 2H, *m*-C_6H_3), 6.98 (t, 1H, *p*-C_6H_3), 2.99 (s, 12H, N*Me*$_2$), 2.07 (s, 6H, Me_{Ar}). $\mu_{eff} = 0\ \mu_B$ (300 K). Anal. Calcd for $C_{12}H_{21}N_3V$: C, 55.81; H, 8.20; N, 16.27. Found: C, 54.98; H, 8.29; N, 15.08.

(c) $[V(NPh)(NMe_2)_2]_2$ (1c): Yield 80% (dark-purple solid). ^{1}H NMR (C_6D_6) 7.51 (dd, 2H, *m*-C_6H_5), 7.41 (d, 2H, *o*-C_6H_5), 6.98 (t,

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Table 1. Crystallographic Data, Data Collection, and Refinement Parameters for Compounds **1b**, **3d**, **4b**, **4d**, **7c**, **10a**, and **11a**

	1b	**3d**	**4b**	**4d**	**7c**	**10a**	**11a**
chem formula	$C_{24}H_{42}N_6V_2$	$C_{10}H_{17}Cl_4N_3V$	$C_{51}H_{48}Cl_4N_9V_2$	$C_{21}H_{18}Cl_4N_4V$	$C_{19}H_{22}Cl_4N_4V$	$C_{20}H_{40}Cl_2N_4V$	$C_{18}H_{33}Cl_2N_3V$
fw	516.52	372.01	1030.66	519.13	499.15	458.40	413.31
cryst system	monoclinic	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P\bar{1}$	$I2/a$	$P2_1/n$
a, Å	10.2676(8)	9.879(5)	33.724(5)	10.355(2)	9.916(5)	14.431(3)	11.147(5)
b, Å	14.6499(11	10.247(5)	9.941(5)	9.966(2)	11.723(5)	13.298(3)	19.357(5)
c, Å	18.1559(14)	10.334(5)	16.617(5)	22.725(5)	12.082(5)	28.605(6)	10.003(5)
α, deg	90.0	109.261(5)	90.0	90.0	110.152(5)	90.0	90.0
β, deg	97.638(9)°	100.005(5)	102.497(5)	98.84(3)	112.847(5)	94.40(3)	94.763(5)
γ, deg	90.0	117.271(5)	90.0	90.0	96.685(5)	90.0	90.0
V, Å^3	2706.8(4)	809.3(7)	5439(3)	2317.3(8)	1163.1(9)	5473(2)	2150.9(15)
Z	4	2	4	4	2	8	4
D_{calcd}, g cm^{-3}	1.267	1.527	1.259	1.488	1.425	1.113	1.276
μ(Mo Kα), mm^{-1}	0.712	1.259	0.581	0.905	0.898	0.568	0.715
F(000)	1096	378	2124	1052	510	1960	876
2θ range (deg)	4.52−52.34	4.52−46.50	4.82−44.92	5.46−41.62	4.66−52.24	4.94−46.52	4.60−52.16
measured reflcns	19956	5927	13448	3740	11148	14292	16529
unique reflcns/R_{int}	5039/0.0518	2175/0.0578	3514/0.0325	1719/0.1560	4130/0.0364	3898/0.0421	4103/0.0481
parameters/restraints	301/0	173/1	162/365	272/0	259/0	262/25	225/0
final R indices [$I > \sigma 2(I)$]							
R1	0.0363	0.0586	0.0455	0.1227	0.0349,	0.0403,	0.0298
wR2	0.0813	0.1504	0.1214	0.3470	0.0918	0.1052	0.0781
final R indices all data							
R1	0.0597	0.0683	0.0509	0.1384	0.0374	0.0504	0.0342
wR2	0.0901	0.1587	0.1269	0.3597	0.0938	0.1100	0.0807
goodness of fit	0.970	1.062	1.045	1.130	1.043	1.047	1.039
$\Delta\rho_{max} - \Delta\rho_{min}$	0.329 and −0.326	0.832 and −0.511	1.076 and −0.436	0.704 and −0.775	0.597 and −0.669	0.289 and −0.315	0.387 and −0.245

1H, p-C_6H_5), 3.04 (s, 12H, NMe_2). $\mu_{eff} = 0\ \mu_B$ (300 K). Anal. Calcd for $C_{10}H_{17}N_3V$: C, 52.17; H, 7.44; N, 18.25. Found: C, 51.33; H, 7.62; N, 17.27.

(d) [V(N-2,6-$C_6H_3Cl_2$)(NMe_2)$_2$]$_2$ (1d): Yield 70% (brown solid). ^{1}H NMR (C_6D_6) 6.80 (d, 2H, m-C_6H_3), 6.50 (t, 1H, p-C_6H_3), 3.25 (s, 12H, NMe_2). $\mu_{eff} = 0\ \mu_B$ (300 K). Anal. Calcd for $C_{10}H_{15}Cl_2N_3V$: C, 40.16; H, 5.05; N, 14.05. Found: C, 39.12; H, 4.36; N, 11.25.

(e) [V(NC_6F_5)(NMe_2)$_2$]$_2$ (1e): Yield 68% (dark red-purple solid). ^{1}H NMR (C_6D_6) 3.08 (s, 12H, NMe_2). ^{19}F NMR (C_6D_6) −78.60 (d, 2F, o-C_6F_5), −89.80 (t, 2F, m-C_6F_5), −92.65 (t, 1F, o-C_6F_5). $\mu_{eff} = 0\ \mu_B$ (300 K). Anal. Calcd for $C_{10}H_{12}F_5N_3V$: C, 37.52; H, 3.78; N, 13.12. Found: C, 38.06; H, 3.72; N, 12.33.

EPR Monitoring of the Formation of 1a−e. A stock solution of V(NMe_2)$_4$ (10^{-2} M) in toluene was prepared and used as reference for EPR and to perform a calibration curve of the EPR spectra at different concentrations. One equivalent of the anilines $ArNH_2$ was added to 1 mL of V(NMe_2)$_4$ solution and the evolution of the reaction (formation of the bridged imido complex) was monitored by EPR spectroscopy at room temperature and 100 °C. The vanadium(IV) signal was integrated and compared to the signal of the reference solution of V(NMe_2)$_4$ and its calibration curve. In all cases, when present, the EPR signal observed after reaction with the aniline integrated less than 5% of the initial integration of the vanadium(IV) before adding the aniline.

Attemps to Prepare [V(NAr)Cl_2]$_n$: Synthesis of Compounds 2a−e. A toluene solution (2 g) of 250 mg of V(NMe_2)$_4$ (1.10 mmol) and 1 equiv of aniline $ArNH_2$ (1.10 mmol) was heated at 100 °C for 1 day giving a dark-red solution. After removal of the volatiles, toluene (2 g) and excess Me_3SiCl (1.20 g) were added and the solution was stirred for 2 days at 100 °C. Removal of the volatiles under vaccum and washing with pentane afforded dark red-purple (**2a**, **2c**, **2e**) or brown (**2b**, **2d**) solids (240−300 mg). EPR ($PhCH_3$, 20 °C): **2a**, $g = 1.989$, $A(^{51}V) = 92.5$ G; **2b**, $g = 1.989$, $A(^{51}V) = 93.1$ G; **2d**, $g = 1.988$, $A(^{51}V) = 90.5$ G; **2e**, $g = 1.989$, $A(^{51}V) = 89.4$ G. Satisfactory and reproducible elemental analyses (C, H, N) have not been obtained for this series of compounds, with data corresponding to compounds having analyses between those expected for **2a−e** and **3a−e** (see Results and Discussion).

Synthesis of Complexes [V(═NAr)Cl_2($NHMe_2$)$_2$] (3a−e): General Procedure (See Supporting Information for Full Details). To a toluene solution (5 mL) of 1.00 g of V(NMe_2)$_4$ (4.40 mmol) was added the aniline $ArNH_2$ (4.40 mmol) at room temperature. Then, to this solution was slowly added 4.00 g of Me_3SiCl at room temperature. The resulting solution was placed in a 25 mL screw cap vial and heated at 100 °C for 20 h. The volatiles were pumped off, and the yellow-orange microcrystalline solid was washed with pentane (2 × 10 mL) and dried under vacuum.

(a) [V(═N-2,6-C_6H_3*i*Pr_2)Cl_2($NHMe_2$)$_2$] (3a): Yield 88%. EPR ($PhCH_3$, 20 °C) $g = 1.990$, $A(^{51}V) = 92.3$ G. IR 3274 (m, ν_{NH}), 3263 (m, ν_{NH}). $\mu_{eff} = 1.80\ \mu_B$ (300 K). Anal. Calcd for $C_{16}H_{31}Cl_2N_3V$: C, 49.62; H, 8.07; N, 10.85; Cl, 18.31. Found: C, 49.34; H, 8.00; N, 10.63; Cl, 18.25.

(b) [V(═N-2,6-$C_6H_3Me_2$)Cl_2($NHMe_2$)$_2$] (3b): Yield 79%. EPR (CH_2Cl_2, 20 °C) $g = 1.990$, $A(^{51}V) = 92.9$ G. IR 3247 (s, ν_{NH}). $\mu_{eff} = 1.92\ \mu_B$ (300 K). Anal. Calcd for $C_{12}H_{23}Cl_2N_3V$: C, 43.52; H, 7.00; N, 12.69. Found: C, 42.78; H, 6.96; N, 12.50.

(c) [V(═NPh)Cl_2($NHMe_2$)$_2$] (3c): Yield 80%. EPR ($PhCH_3$, 20 °C) $g = 1.990$, $A(^{51}V) = 92.2$ G. IR 3232 (s, ν_{NH}). $\mu_{eff} = 1.90\ \mu_B$ (300 K). Anal. Calcd for $C_{10}H_{19}Cl_2N_3V$: C, 39.62; H, 6.32; N, 13.86; Cl, 23.39. Found: C, 39.50; H, 6.21; N, 13.66; Cl, 22.72.

(d) [V(═N-2,6-$C_6H_3Cl_2$)Cl_2($NHMe_2$)$_2$] (3d): Yield 96%. EPR ($PhCH_3$, 20 °C) $g = 1.988$, $A(^{51}V) = 92.4$ G. IR 3255 (s, ν_{NH}). Anal. Calcd for $C_{10}H_{17}Cl_4N_3V$: C, 32.29; H, 4.61; N, 11.30; Cl, 38.12. Found: C, 32.26; H, 4.73; N, 11.07; Cl, 37.53.

(e) [V(═NC_6F_5)Cl_2($NHMe_2$)$_2$] (3e): Yield 73%. EPR ($PhCH_3$, 20 °C) $g = 1.992$, $A(^{51}V) = 87.7$ G. IR 3252 (s, ν_{NH}). Anal. Calcd for $C_{10}H_{14}Cl_2F_5N_3V$: C, 30.56; H, 3.59; N, 10.69. Found: C, 30.05; H, 3.75; N, 10.67.

Preparation of 2a from 3a. A 100-mg sample of orange complex **3a** was heated at 160 °C under a dynamic vacuum of 0.005−0.001 mbar for 2 h. The color of the solid turned red-purple. Yield 70 mg. Analytically pure sample was obtained after extraction with toluene (to remove trace of impurities due to decomposition).

EPR (CH_2Cl_2, 20 °C) $g = 1.990$, $A(^{51}V) = 92.9$ G. Anal. Calcd for $C_{12}H_{17}Cl_2NV$: C, 48.51; H, 5.77; N, 4.71. Found: C; 48.35; H, 5.95; N, 5.44.

Synthesis of Complexes [V(=NAr)Cl$_2$(Py)$_3$] (4a−e): General Procedure (See Supporting Information for Full Details). (a) [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(Py)$_3$] (4a): A 250-mg sample (0.6465 mM) of **3a** were dissolved in 2 mL of pyridine. The resulting red solution was stirred overnight. Volatiles were removed under vacuum to afford a red solid that was washed with pentane (yield 330 mg, 95%). EPR ($PhCH_3$, 20 °C) $g = 1.990$, $A(^{51}V) = 92.9$ G. $\mu_{eff} = 1.90\ \mu_B$ (300 K). Anal. Calcd for $C_{27}H_{32}Cl_2N_4V$: C, 60.68; H, 6.04; N, 10.48. Found: C, 60.16; H, 6.13; N, 10.55. Alternatively, **4a** was prepared by the same procedure but starting with **2a** (instead of **3a**), giving **4a** in quantitative yield.

(b) [V(=N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(Py)$_3$] (4b): Compound **4b** crystallized as a pyridine solvate. Yield 36%. EPR ($PhCH_3$, 20 °C) $g = 1.991$, $A(^{51}V) = 93.5$ G. $\mu_{eff} = 1.84\ \mu_B$ (300 K). Anal. Calcd for $C_{23}H_{24}Cl_2N_4V.C_5H_5N$: C, 60.63; H, 5.24; N, 12.56. Found: C, 59.94; H, 5.30; N, 12.36.

(c) [V(=NPh)Cl$_2$(Py)$_3$] (4c): Yield 86%. EPR ($PhCH_3$, 20 °C) $g = 1.993$, $A(^{51}V) = 92.1$ G. $\mu_{eff} = 1.98\ \mu_B$ (300 K). Anal. Calcd for $C_{21}H_{20}Cl_2N_4V$: C, 56.02; H, 4.48; N, 12.44. Found: C, 55.94; H, 4.98; N, 12.19.

(d) [V(=N-2,6-C$_6$H$_3$Cl$_2$)Cl$_2$(Py)$_3$] (4d): Yield 83%. EPR (pyridine, 20 °C) $g = 1.991$, $A(^{51}V) = 91.5$ G. $\mu_{eff} = 1.82\ \mu_B$ (300 K). Anal. Calcd for $C_{21}H_{18}Cl_4N_4V$: C, 48.58; H, 3.49; N, 10.79. Found: C, 48.41; H, 3.45; N, 10.69.

(e) [V(=NC$_6$F$_5$)Cl$_2$(Py)$_3$] (4e): Yield 90%. EPR (CH_2Cl_2, 20 °C) $g = 1.992$, $A(^{51}V) = 92.1$ G. Anal. Calcd for $C_{21}H_{15}Cl_2F_5N_4V$: C, 46.69; H, 2.80; N, 10.37. Found: C, 47.00; H, 3.45; N, 10.17.

Preparation of [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(Py)$_2$] (5a). Method 1: A 100-mg sample of complex **4a** was heated at 105 °C for 1 h under a dynamic vacuum (0.005−0.001 mbar) giving **5a** as a brown-red powder (80 mg). Anal. Calcd for $C_{22}H_{27}Cl_2N_3V$: C, 58.03; H, 5.98; N, 9.23. Found: C, 56.84; H, 5.73; N, 8.87.

Method 2: An 80-mg sample of pyridine (1.001 mM) was added to a dichloromethane solution (2 mL) of compound **2a** (150 mg, 0.5049 mM). The resulting red solution was layered with pentane giving red crystals of **5a** (110 mg, 55%). EPR ($PhCH_3$, 20 °C) $g = 1.993$, $A(^{51}V) = 91.4$ G. Anal. Calcd for $C_{22}H_{27}Cl_2N_3V$: C, 58.03; H, 5.98; N, 9.23. Found: C, 58.69; H, 5.72; N, 10.07.

Synthesis of [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(NHMe$_2$)(Py)$_2$] (6a). A 55-mg sample of pyridine (0.6939 mM) was added to a toluene solution (3 mL) of **3a** (125 mg, 0.3304 mM) with stirring for 7 h. The solution was filtered through a bed of Celite, and the solvent of the filtrate was removed under vacuum to afford an orange solid (110 mg, 67%). EPR ($PhCH_3$, 20 °C) $g = 1.990$, $A(^{51}V) = 93.6$ G. IR 3274 (ν_{NH}, w), 3266 (ν_{NH}, w). Anal. Calcd for $C_{24}H_{34}Cl_2N_4V$: C, 57.61; H, 6.85; N, 11.20. Found: C, 57.00; H, 6.67; N, 10.63.

Synthesis of Complexes [V(=NAr)Cl$_2$(bipy)(NHMe$_2$)] (7a−e): General Procedure (See Supporting Information for Full Details). (a) [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(bipy)(NHMe$_2$)] (7a): To a dichloromethane solution (2 mL) of complex **3a** (125 mg, 0.3304 mM) was added by portions 1 equiv of bipyridine (50 mg). The resulting red-orange solution was left at room temperature without stirring for 1 day, and then pentane (4 mL) was carefully layered on this solution and the system was allowed to equilibrate for 3 days. The solvent was decanted, and the deep red crystals of **7a** were collected, washed with pentane, and vaccum dried (150 mg, 78%). **7a** crystallized with one molecule of dichloromethane. EPR (CH_2Cl_2, 20 °C) $g = 1.992$, $A(^{51}V) = 90.5$ G. IR 3290 (m, ν_{NH}), 3270(m, ν_{NH}). $\mu_{eff} = 1.94\ \mu_B$ (300 K). Anal. Calcd for $C_{24}H_{32}Cl_2N_4V{\cdot}CH_2Cl_2$: C, 51.48; H, 5.88; N, 9.60. Found: C, 51.56; H, 5.86; N, 9.98.

(b) [V(=N-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(bipy)(NHMe$_2$)] (7b): Yield 90%. EPR (CH_2Cl_2, 20 °C) $g = 1.993$, $A(^{51}V) = 91.5$ G. IR 3279 (w, ν_{NH}). Anal. Calcd for $C_{20}H_{24}Cl_2N_4V$: C, 54.31; H, 5.47; N, 12.67. Found: C, 53.97; H, 5.42; N, 12.36.

(c) [V(=NPh)Cl$_2$(bipy)(NHMe$_2$)] (7c): Yield 73%. This compound crystallized with one molecule of dichloromethane as shown by an X-ray analysis (vide infra). EPR (CH_2Cl_2, 20 °C) $g = 1.991$, $A(^{51}V) = 92.8$ G. IR 3220 (m, ν_{NH}). Anal. Calcd for $C_{18}H_{20}Cl_2N_4V.CH_2Cl_2$: C, 45.72; H, 4.44; N, 11.22. Found: C, 45.70; H, 4.48; N, 11.20.

(d) [V(=N-2,6-C$_6$H$_3$Cl$_2$)Cl$_2$(bipy)(NHMe$_2$)] (7d): Yield 80%. EPR (CH_2Cl_2, 20 °C) $g = 1.990$, $A(^{51}V) = 90.8$ G. IR 3250 (m, ν_{NH}). Anal. Calcd for $C_{18}H_{18}Cl_4N_4V$: C, 44.75; H, 3.76; N, 11.60. Found: C, 43.80; H, 3.77; N, 10.97.

(e) [V(=NC$_6$F$_5$)Cl$_2$(bipy)(NHMe$_2$)] (7e): Yield, 75%. EPR (CH_2Cl_2, 20 °C) $g = 1.991$, $A(^{51}V) = 89.2$ G. IR 3245 (m, ν_{NH}). Anal. Calcd for $C_{18}H_{15}Cl_2F_5N_4V$: C, 42.88; H, 3.00; N, 11.11. Found: C, 42.84; H, 3.32; N, 11.40.

Synthesis of [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(bipy)] (8a). Method 1: A 79-mg sample of bipyridine was added to a dichloromethane (4 mL) of compound **2a** (150 mg, 0.5049 mM). After a few hours, crystallization started to occur, and pentane was slowly layered to the dark red solution. Red crystals were collected by decantation and dried under vacuum (190 mg, 83%). EPR (CH_2Cl_2, 20 °C) $g = 1.993$, $A(^{51}V) = 88.7$ G. Anal. Calcd for $C_{22}H_{25}Cl_2N_3V$: C, 58.29; H, 5.56; N, 9.27. Found: C, 57.84; H, 5.03; N, 9.58.

Method 2: A 74-mg sample of compound **7a** was heated at 140 °C under a dynamic vacuum of 0.05 mbar for 1 h (60 mg, 63%). Anal. Calcd for $C_{22}H_{25}Cl_2N_3V$: C, 58.29; H, 5.56; N, 9.27. Found: C, 56.70; H, 5.18; N, 9.20.

Synthesis of [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(bipy)(Py)] (9a). To a dichloromethane solution (2 mL) of complex **3a** (125 mg, 0.3304 mM) was added in portions 1 equiv of bipyridine (50 mg). The resulting red-orange solution was left at room temperature with stirring for 2 h, and then 118 mg of pyridine was added. After 16 h, pentane was slowly added on the top of this solution. The red-orange solid was collected after decantation of the solution and dried under vacuum (170 mg, 96%). EPR (CH_2Cl_2, 20 °C) $g = 1.992$, $A(^{51}V) = 92.1$ G. Anal. Calcd for $C_{27}H_{30}Cl_2N_4V$: C, 60.91; H, 5.68; N, 10.52. Found: C, 59.50; H, 5.78; N, 10.55.

Synthesis of [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(tmeda)(NHMe$_2$)] (10a). A 355-mg sample of tmeda was added with stirring to a toluene solution (3 mL) of complex **3a** (0.6455 mM). After 18 h, the volatiles were removed under vacuum, to give 290 mg of orange crystals (yield 97%). EPR (CH_2Cl_2, 20 °C) $g = 1.990$, $A(^{51}V) = 92.9$ G. IR 3282 (w, ν_{NH}). $\mu_{eff} = 1.80\ \mu_B$ (300 K). Anal. Calcd for $C_{20}H_{40}Cl_2N_4V$: C, 52.40; H, 8.80; N, 12.22. Found: C, 52.35; H, 9.03; N, 11.37.

Synthesis of [V(=N-2,6-C$_6$H$_3$*i*Pr$_2$)Cl$_2$(tmeda)] (11a). Complex **11a** was prepared according to the same preparation as for complex **10a**, but starting with 250 mg of **2a** (yield 160 mg, 46%). EPR ($PhCH_3$, 20 °C) $g = 1.990$, $A(^{51}V) = 92.5$ G. $\mu_{eff} = 1.76\ \mu_B$ (300 K). Anal. Calcd for $C_{18}H_{33}Cl_2N_3V$: C, 52.31; H, 8.05; N, 10.17. Found: C, 51.99; H, 8.32; N, 11.09.

Results and Discussion

This work constitutes the first systematic investigation of the synthetic and structural chemistry of aryl imido−vanadium(IV) complexes of any type. The synthesis and proposed structures of the new aryl imido complexes of vanadium(IV) are summarized in Schemes 1−3. Structures of eight complexes are set out in Figures 1−8; selected metric data are collected in Table 2.

1. Synthesis of the Imido Precursors. In our preliminary paper,[7] we described the synthesis of $[V(=N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)Cl_2(NHMe_2)_2]$, in a two-step synthesis: reaction of the aniline $2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3\text{-}NH_2$ with $V(NMe_2)_4$ in toluene at 100 °C for 1 day afforded a dark red arylimido complex **A** that we initially formulated as being "$[V(=NAr)(NMe_2)_2(NHMe_2)_2]$". A subsequent reaction with an excess of trimethylchlorosilane at room temperature in toluene for 2 days afforded a purple solid from which we could crystallized a complex formulated as $[V(=NAr)Cl_2(NHMe_2)_2]$ based on its X-ray determination. Keeping in mind that we are dealing with d^1-V(IV) paramagnetic species, and despite an elementary analysis for **A** in accordance with a dimethylamine-free compound of the type $[V(=NAr)(NMe_2)_2]$, we concluded there must be a bis-dimethylamine adduct **A** to explain the presence of two $NHMe_2$ in **3a** (revealed by the crystal structure determination of **3a**).

Since then, we reexamined the first step of the reaction between $V(NMe_2)_4$ and different anilines $ArNH_2$ (Ar = $2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3$, $2,6\text{-}Me_2\text{-}C_6H_3$, Ph, $2,6\text{-}Cl_2\text{-}C_6H_3$, C_6F_5), in both pentane and toluene as solvent, in particular by following the course of the reaction by EPR spectroscopy. In toluene, at room temperature and 100 °C, the EPR spectra of a solution containing an equimolar amount of $V(NMe_2)_4$ and $ArNH_2$ show the disappearance of more than 95% of the strong eight-line characteristic signal of paramagnetic d^1-V(IV) species (due to hyperfine interaction between the vanadium nucleus ($I = {}^7/_2$) and the unpaired electron), which suggest the formation of diamagnetic compounds. From the reaction of $V(NMe_2)_4$ and $ArNH_2$ in toluene at 100 °C, we isolated dark red to brown often sticky solids (Scheme 1), but fortunately we were able to obtain crystals of one of these complexes with Ar = $2,6\text{-}Me_2\text{-}C_6H_3$ by cooling a saturated pentane solution of **1b** to −20 °C, which allowed us to determine its molecular structure.

The molecular structure of **1b** is shown in Figure 1, with selected bond distances and angles: the complex is a dimer $[V(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(NMe_2)_2]_2$ with two imido ligands bridging two $(Me_2N)_2V$ moieties. The molecule is a centrosymmetric dimer (monoclinic, $P21/n$), and the coordination geometry of vanadium is distorted tetrahedral. The V_2N_2 core is almost planar (torsion angle V1−N1−V2−N2 = 10.93(8)°) and is characterized by a short V···V distance [V1···V2 = 2.4955(6) Å]; although this is one of the shortest distances ever found among dinuclear complexes of vanadium, such a short V···V distance is not unusual.[27] The angle formed by the bridging nitrogen atoms with the two vanadium atoms [V1−N1−V2 = 83.70(8)°] deviates significantly from that expected for an sp^2 nitrogen atom. The $V-N_{imido}$ distances being comprised between 1.864 and 1.878 Å are longer by ca. 0.2 Å than in terminal imido complexes (vide infra). The $(Me_2N)_2V$ moiety is normal[14] with the expected V−N bond distances and angles [$V-N_{amido}$ ranging from 1.842 to 1.866 Å].

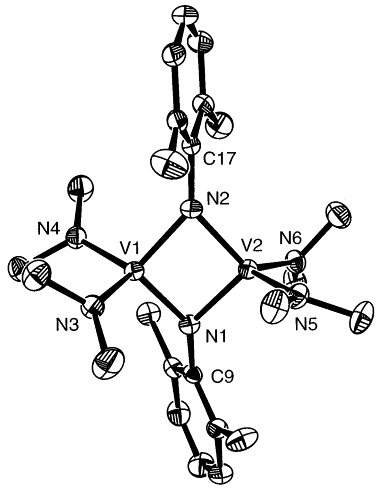

Figure 1. Molecular structure of **1b** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. V1···V2 2.4955(6), V1−N1 1.864(2), V1−N2 1.873(2), V1−N3 1.862(2), V1−N4 1.864(2), V2−N1 1.877(2), V2−N2 1.878(2), V2−N5 1.866(2), V2−N6 1.842(2), N1−C9 1.408(3), N2−C17 1.408(3); V1−N1−V2 83.70(8), V1−N2−V2 83.40(8), N1−V1−N2 95.73(9), N1−V2−N2 95.11(9).

Diamagnetic complexes **1a**−**e** could later be characterized by their ^1H NMR spectroscopy (the sharpness of the peaks of the well-solved ^1H NMR spectrum of **1a**−**e** indicate that the dinuclear structure is retained in C_6D_6 solution), elemental analysis, and the absence of magnetic moment. The diamagnetism of **1a**−**e** indicates a strong electronic coupling between the two metal centers, either through the nitrogen

Scheme 1. Synthesis of Aryl Imido−Vanadium(IV) Complexes **1**−**3**

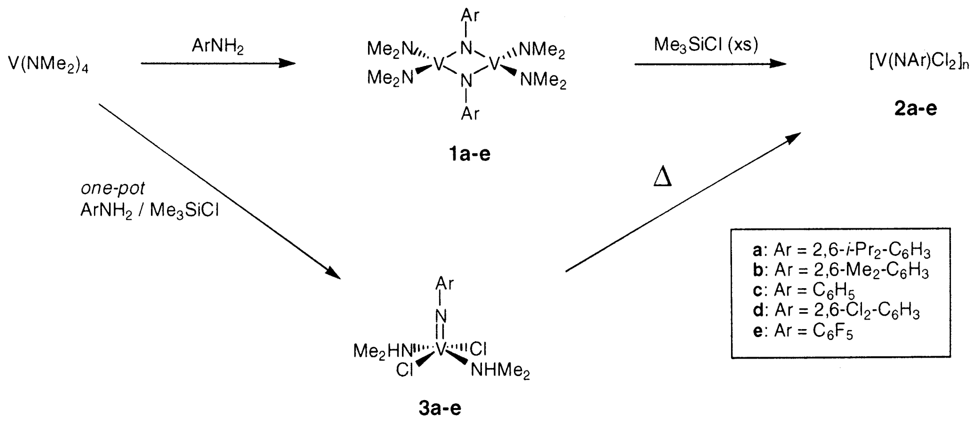

Table 2. Comparison of Average Interatomic Distances (Å) and Angles (deg)

	1b	3a[a]	3d	4b	4d	7c	10a	11a
V−N_{imido}	1.872(3)[b]	1.654(3)	1.656(4)	1.709(3)	1.671(14)	1.6754(16)	1.676(2)	1.6674(13)
N_{imido}-C_{ipso}	1.483(3)[b]	1.380(5)	1.388(6)	1.395(4)	1.38(2)	1.373(2)	1.389(4)	1.3936(18)
V−N_{imido}−C_{ipso}		178.4(3)	176.0(3)	171.4(2)	170.0(14)	171.74(14)	177.59(19)	164.48(10)
V−Cl1		2.3199(14)	2.3216(18)	2.4724(10)	2.390(6)	2.3866(12)	2.3573(10)	2.3078(8)
V−Cl2		2.3268(12)	2.3185(16)	2.4676(9)	2.394(5)	2.4075(10)	2.3748(11)	2.3231(8)
Cl1−V−Cl2		136.48(5)	135.69(6)	168.44(3)	168.0(2)	93.73(3)	154.67(3)	91.06(3)
V−N_{NHMe2}		2.095(5)[b]	2.148(4)[b]			2.1947(19)	2.16(3)	
V−N_{Py}(trans)				2.363(3)	2.298(14)			
V−N_{Py}(cis)				2.208(3)[b]	2.161(16)[b]			
V−N_{bipy}						cis 2.1255(17) trans 2.2363(16)		
V−N_{tmeda}							cis 2.224(2) trans 2.820(3)	2.199(2)[b]

[a] See ref 7. [b] Mean distance.

atoms of the imido bridges or resulting from the short V−V distance. In pentane, the room temperature reactions between $V(NMe_2)_4$ and $ArNH_2$ give less clear-cut observations, since mixtures of two or three compounds are often formed and will not be discussed further here.

In a second step (Scheme 1), when **1a**−**e** is reacted with an excess of Me_3SiCl in toluene at 100 °C,[28] dimethylamido ligands are exchanged for chlorine atoms, giving red-purple or brown compounds **2a**−**e**. We believe these compounds have a general formula of variable composition $[V(NAr)Cl_2(NHMe_2)_x]_n$, x being between 0 and 2, based on three pieces of evidence: (1) the color of **2a**−**e** differs from yellow-orange $[V({=}NAr)Cl_2(NHMe_2)_2]$ (**3a**−**e**) (fully characterized, vide infra), (2) very weak ν_{NH} bands may be observed in the 3250 cm^{-1} region in **2a**−**e** infrared spectra, and (3) the elemental analysis of **2a**−**e** is consistent with such formulation for **2** (presence of $NHMe_2$). The amount of coordinated dimethylamine present in these materials is probably dependent on the aryl group and on the length of time complexes **1a**−**e** were dried under vacuum in the preceding step. The presence of $NHMe_2$ in compounds **2a**−**e** may arise from the difficulty of removing it totally from oily or sticky **1a**−**e**, and may explain why we originally crystallized a bis-amino adduct **3a** from these red-purple or brown solutions. The paramagnetic properties of these materials precluded further spectroscopic investigations, and compounds **2a**−**e** rather could imply a mixture of compounds in solution. While the available experimental data do not establish a solution structure, we propose **2a**−**e** consist of an equilibrium mixture of oligomeric $[V(NAr)Cl_2]_n$, Me_2NH, and the monomeric imido complex **3a**−**e**. A similar equilibrium has already been suggested in titanium imido chemistry.[29a] In the solid state, compounds **2a**−**e** may have an oligomeric structure such as that in $[Ti(Nt\text{-}Bu)(NH_2t\text{-}Bu)_2]_3$,[29a] $[(Me_3SiN)TiCl_2]_8$,[29b] or $[t\text{-}BuNH_3]_2[V_7(t\text{-}BuN)_7(\mu\text{-}Cl)_{14}Cl_2]$[17] but with additional Me_2NH co-ligands.

Taking into account this fact, we discovered a much more convenient path to complexes of the type $[V({=}NAr)Cl_2(NHMe_2)_2]$, **3a**−**e**. When a toluene solution of $V(NMe_2)_4$ is reacted in a one-pot reaction with 1 equiv of $ArNH_2$ and an excess of trimethylchlorosilane in a screw-cap vial at 100 °C overnight, yellow-orange **3a**−**e** compounds are formed exclusively and often separate by crystallization on cooling to room temperature as large yellow-orange needles or crystals with good yields (73−96%) (see Scheme 1). **3a**−**e** have been characterized by their infrared spectrum (with strong ν_{NH} absorptions around 3250 cm^{-1} consistent with NH···Cl−V intermolecular hydrogen bonding weak interactions), room temperature EPR spectrum ($A(^{51}V)$ ca. 88−93 G and $g = 1.990$), elemental analysis, and magnetism studies in agreement with d^1-paramagnetic species (μ_{eff} = ca. 1.7−1.9 μ_B).

Single crystals of two of these complexes, **3a** and **3d**, suitable for X-ray diffraction studies were obtained from cold toluene−pentane (**3a**)[30] or toluene (**3d**) solutions. A thermal ellipsoid plot is presented in Figures 2 and 3 along with selected bond lengths and angles, and Table 2 shows a comparison of their structural parameters. Both molecular structures are best described as distorted square-pyramid with an axial aryl imido that exhibits a short vanadium−nitrogen distance of 1.654(3) Å for **3a** and 1.656(4) Å for **3d**. The imido linkage being almost linear [V1−N1−C1 angle = 178.4(3)° in **3a** and 176.0(3)° in **3d**] is consistent with the lone pair on nitrogen being donated to an acceptor orbital on vanadium. Hence the imido V−N bond can be considered as a triple bond. The two chlorine atoms are mutually trans with a Cl1−V−Cl2 angle of 136.48(5)° (**3a**) and 135.69(6) Å (**3d**). V−Cl bonds are normal with mean V−Cl 2.323 Å (**3a**) and 2.320 Å (**3d**). The two trans dimethylamino ligands

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(28) Although generally sufficient, it is nevertheless necessary in some cases to perform the reaction at 100 °C to afford total and/or rapid chlorination of the two dimethylamido ligands.

(29) (a) Lewkebandara, T. S.; Sheridan, P. H.; Heeg, M. J.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1994**, *33*, 5879−5889. (b) Bettenhausen, R.; Milius, W.; Schnick, W. *Chem. Eur. J.* **1997**, *3*, 1337−1341.

(30) The molecular structure of **3a** was presented in a preliminary communication (see ref 7). This complex was recently crystallized (pentane, −20 °C) in a different crystallographic group: orthorhombic *Pbnm*, a = 10.4066(9) Å, b = 16.6909(11) Å, c = 10.7051(7) Å, V = 2193.6(3) Å^3.

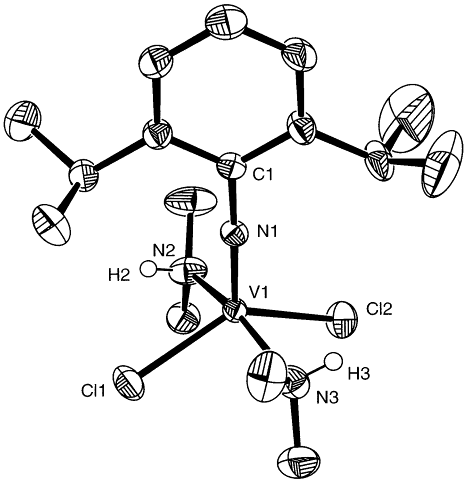

Figure 2. Molecular structure of **3a** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity, except those on nitrogen amino groups. V1−N1 1.654(3), V1−N2 2.018(5), V1−N3 2.171(4), V1−Cl1 2.3202(14), V1−Cl2 2.3257(12), N1−C1 1.388(5); C1−N1−V1 178.4(3), Cl1−V1−Cl2 136.48(5), N2−V1−N3 165.23(16).

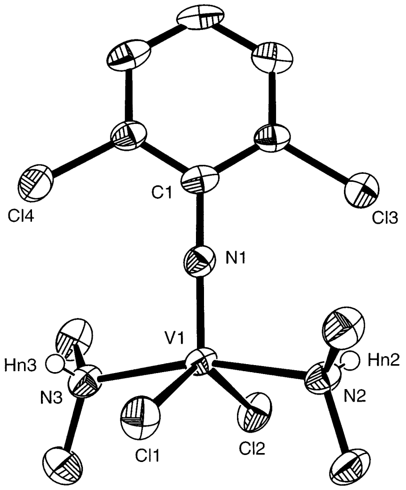

Figure 3. Molecular structure of **3d** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity, except those on nitrogen amino groups. V1−N1 1.656(4), V1−N2 2.151(4), V1−N3 2.146(4), V1−Cl1 2.3216(18), V1−Cl2 2.3185(16), N1−C1 1.388(6), N2−HN2 0.69(5), N3−HN3 0.69(5); C1−N1−V1 176.0(3), Cl1−V1−Cl2 135.69(6), N2−V1−N3 163.96(17).

form the base of the square pyramid with the two chlorine atoms, and have $V-N_{amine}$ bonds of 2.018(5) and 2.171(4) Å in **3a** and 2.151(4) and 2.146(4) Å in **3d**, with an $N_{amine}-V-N_{amine}$ angle of 165.23(16)° in **3a** and 163.96(17)° in **3d**.

The hydrogen bonds between the N−H groups of $NHMe_2$ ligands and V−Cl on neighboring vanadium complexes may be considered as “intermediate” according to Brammer and Orpen’s classification[31] with $V-Cl\cdots H-N$ contacts of 2.987 (**3a**) and 2.848 Å (**3d**) with associated angles of 127.9° and 154.6°, respectively.

Heating yellow-orange **3a** at 160 °C for 2 h under vacuum (0.001 mbar) gives a red-purple solid with little decomposition. This compound having almost no ν_{NH} in its IR spectrum (in comparison to the strong ν_{NH} in **3a**) suggests the loss of $NHMe_2$ ligands, with formation of a complex that may certainly be similar to that of **2a**.

Terminal imido compounds **3a**−**e** obviously may be key starting materials in a whole new coordination chemistry of vanadium, and we have started to explore this new chemistry.

2. Reactivity toward Pyridine. When dissolved in pyridine, complexes **3a**−**e** (and **2a**−**e**) instantly give dark red solutions at room temperature. Slow addition of toluene followed by layering these solutions with pentane affords red crystals characterized as being the tris-pyridine adduct *trans,mer*-$[V(=NAr)Cl_2(Py)_3]$, **4a**−**e**. Compounds **4a**−**e** are formed from **3a**−**e** by an amine elimination reaction with good yields (83−95%) (Scheme 2). Crystals suitable for an X-ray analysis have been obtained for complexes **4b** and **4d** and an ORTEP view is presented in Figures 4 and 5.[32] Compound **4b** crystallizes with one molecule of pyridine. Both complexes have a pseudooctahedral geometry with mutually trans chloride and pyridine ligands, the third pyridine ligand being trans to the imido group. The aryl rings are rotated out of the $VCl(1)Cl(2)N_{imido}N_{Py-\mathit{trans}}$ plane by ca. 53.8(1)° and 61.5(4)° respectively for **4b** and **4d**, and so may interact to some extent with both of the imido nitrogen $p\pi$ orbitals (although the presence of *o*-aryl substituents may contribute to that feature). Bond lengths and angles are unexceptional, and are very similar to those of titanium analogues:[33] the vanadium−nitrogen bond distances of the imido fragments were 1.709(2) and 1.700(14) Å respectively for **4b** and **4d**, $V-N_{imido}-C_{ipso}$ of 171.4(2)° and 170.0(14)° respectively for **4b** and **4d**, and average V−Cl of 2.470(10) and 2.392(6) Å respectively for **4b** and **4d**. The trans V−N(Py) of 2.363(3) and 2.398(14) Å respectively for **4b** and **4d** are significantly longer than average cis V−N(Py) bond distances of 2.208(3) and 2.161(16) Å respectively for **4b** and **4d**, suggesting that the *trans*-pyridine ligand is less tighly bound then those bonded cis reflecting the trans-labilizing ability of the imido ligand. Indeed, heating a sample of **5a** at 105 °C under a dynamic vacuum (0.005−0.001 mbar) gave almost quantitative conversion to the corresponding five-coordinate bis-pyridine complex $[V(=NAr)Cl_2Py_2]$ (**5a**: Ar = 2,6-iPr$_2$-C_6H_3), as a brownish powder, reflecting the trans-labilizing ability of the imido group in **5a**.

5a could also be prepared by addition of only 2 equiv of pyridine to complex **2a**, affording a crystalline sample of **5a**. Although we do not have a crystal structure of this compound, we suggest it has a similar structure to that of the titanium analogue,[33] with the pyridine ligands trans of the base of a square pyramid.

However, when the tris-amino complex **3a** was reacted with only 2 equiv of pyridine in toluene, an orange complex **6a** was obtained (Scheme 2). This compound possesses two ν_{NH} bands in its infrared spectrum and its elemental analysis

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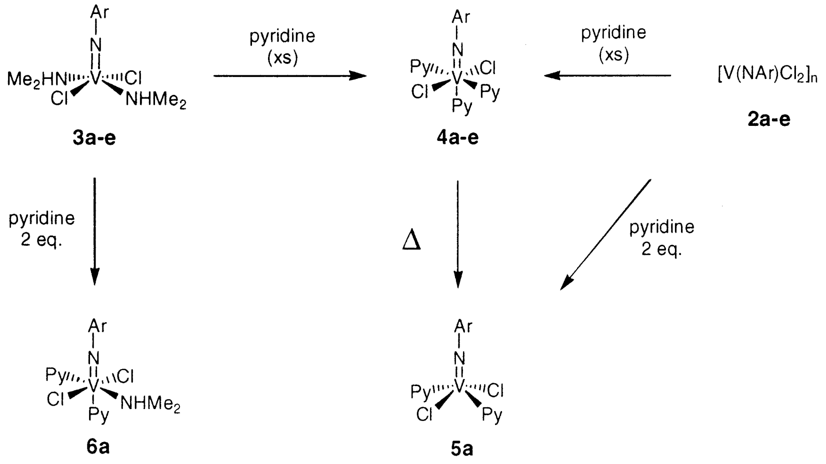
[31] Aullon, G.; Bellamy, D.; Brammer, L.; Bruton, E. A.; Orpen, A. G. *Chem. Commun.* **1998**, 653−654.

[32] A crystal structure for complex **4a** was also determined but will not be discussed here. Monoclinic $P2_1/n$, $a = 18.6863(19)$ Å, $b = 17.8866(18)$ Å, $c = 18.7909(18)$ Å, $\beta = 119.447(10)°$, $V = 5469.2(1)$ Å^3.

[33] Collier, P. E.; Dunn, S. C.; Mountford, P.; Shishkin, O. V.; Swallow, D. *J. Chem. Soc., Dalton Trans.* **1995**, 3743−3745.

Scheme 2. Synthesis of Aryl Imido−Vanadium(IV) Complexes **4**−**6**



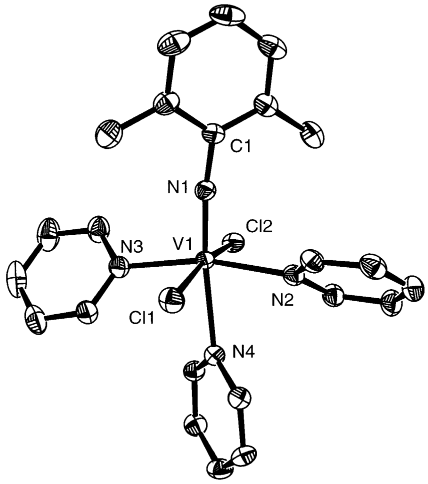


Figure 4. Molecular structure of **4b** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. V1−N1 1.709(3), V1−N2 2.215(3), V1−N3 2.201(3), V1−N4 2.363(3), V1−Cl1 2.4724(10), V1−Cl2 2.4676(9), N1−C1 1.395(4), C1−N1−V1 171.4(2); Cl1−V1−Cl2 168.44(3), N1−V1−N4 174.03(10), N1−V1−N2 94.33(10), N1−V1−N3 99.35(11), N3−V1−N2 166.25(9).

is consistent with a dimethylamino−bis-pyridine adduct $[V(=NAr)Cl_2(NHMe_2)Py_2]$ (Ar = 2,6-*i*-Pr-C_6H_3). At this point we cannot exclude that **6a** is a mixture of isomers, i.e., the ligand trans to the imido group could either be the $NHMe_2$ group or one pyridine ligand.

3. Reaction with Bipyridine. Complexes **3a**−**e** were also reacted with 1 equiv of bipyridine at room temperature in dichloromethane (Scheme 3). The solution rapidly turned dark red, and slow addition of pentane caused the crystallization of red crystals of complexes **7a**−**e**. The structure was assigned as being $[V(NAr)Cl_2(bipy)(NHMe_2)]$ based on spectral and analytical data, and from an X-ray crystallographic structure determination. The infrared spectra of **7a**−**e** show the characteristic band for ν_{NH} around 3250 cm^{-1}. A crystal structure for one of these new derivatives (**7c**) has been obtained and is presented in Figure 6. The solid-state structure of **7c** confirms the presence of one $NHMe_2$ ligand with coordination of one bipy ligand and the pseudooctahedral nature of the complex with the imido in the axial position [$V-N_{imido}$ = 1.6754(16) Å, $V-N_{imido}-C_{ipso}$ = 171.74(14)°]. The chlorine atoms are mutually cis [V−Cl1 = 2.3866(12) Å and V−Cl2 = 2.4075(10) Å], the $NHMe_2$ ligand is trans to one chloride and cis to the other [$V-N(NHMe_2)$ = 2.195(2) Å], and the bipy ligand is trans to the imido group and to one chloride atom, with the nitrogen atom trans to the imido being significantly longer by ca. 0.11 Å [trans $V-N_{bipy}$ = 2.2363(16) Å, cis $V-N_{bipy}$ = 2.1255(17) Å].

The hydrogen bonds between the N−H group of the $NHMe_2$ ligand and V−Cl on neighboring vanadium complexes are now shorter with V−Cl···H−N contacts of 2.58 Å and an associated angle of 148.0°.

Compound **2a** possesses similar reactivity to that of **3a**, with the exception that complexes free of $NHMe_2$ are now accessible: **2a** was reacted with 1 equiv of bipyridine in dichloromethane. Dark red crystals of $[V(NAr)Cl_2(bipy)]$, **8a** (Ar = 2,6-*i*-Pr-C_6H_3), were obtained by carefully layering pentane into this solution (Scheme 3). This compound was also prepared by heating a sample of **7a** at 140 °C under a dynamic vacuum (0.05 mbar) for a prolonged time, which released the coordinated $NHMe_2$ ligand in **7a** (confirmed by the absence of the ν_{NH} band in the infrared spectrum of **8a** prepared in this way).

Seeking a complex containing both pyridine and bipyridine ligands, we first reacted complex **3a** with 1 equiv of bipyridine (with in-situ formation of **7a**) and 2 h later with 4 equiv of pyridine. Slow addition of pentane afforded crystalline red-orange complex $[V(NAr)Cl_2(bipy)(Py)]$, **9a** (Ar = 2,6-*i*-Pr-C_6H_3). Although we do not have a crystal structure of this compound yet, we propose its structure is similar to that of **7a** with one pyridine ligand instead of the dimethylamino group, but other isomers cannot be excluded (Scheme 3).

4. Reaction with tmeda. We also investigated the coordination chemistry of our imido complexes toward tmeda (Scheme 3). Addition of 6 equiv of tmeda to a toluene solution of **3a** leads to complex **10a** with 97% yield,[34] fully characterized including by an X-ray structure such as $[V(=NAr)Cl_2(tmeda)(NHMe_2)]$ (Ar = 2,6-*i*-Pr-C_6H_3). Again, the infrared spectrum shows the characteristic bands for the $NHMe_2$ ligand at 3281 cm^{-1}. The molecular structure (Figure

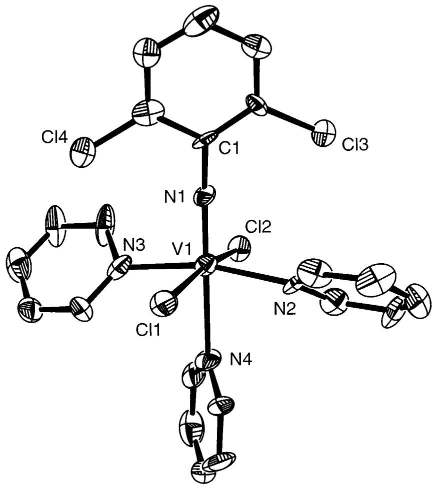


Figure 5. Molecular structure of **4d** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Pyridine solvent and hydrogen atoms are omitted for clarity. V1−N1 1.671(14), V1−N2 2.154(15), V1−N3 2.168(16), V1−N4 2.298(14), V1−Cl1 2.390(6), V1−Cl2 2.394(5), N1−C1 1.38(2); C1−N1−V1 170.0(14), Cl1−V1−Cl2 168.44(3), N1−V1−N4, N1−V1−N2 96.9(6), N1−V1−N397.0(7), N3−V1−N2 166.1(6).

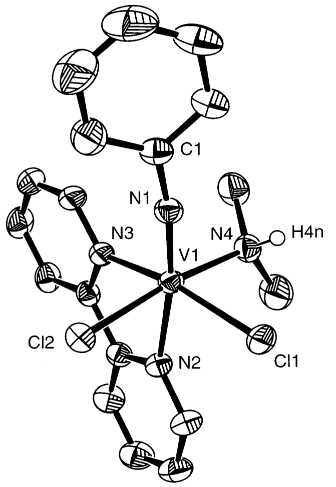
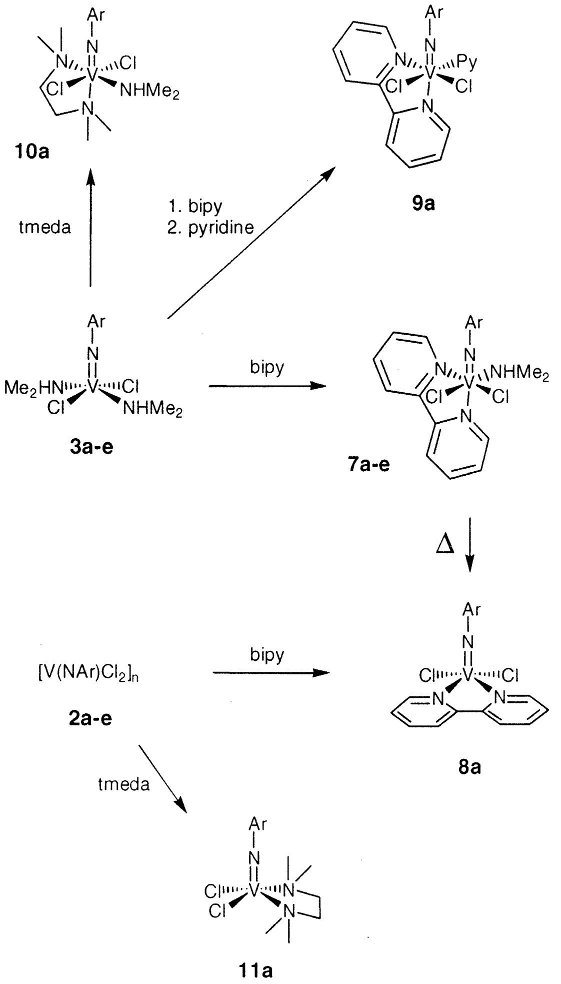


Figure 6. Molecular structure of **7c** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Dichloromethane solvent and hydrogen atoms are omitted for clarity, except the one on the nitrogen amino group. V1−N1 1.6754(16), V1−N2 2.2363(16), V1−N3 2.1255(17), V1−N4 2.1947(19), N1−C1 1.373(2), V1−Cl1 2.3866(12), V1−Cl2 2.4075(10), V−H(4N) 0.88(3); V1−N1−C1 171.74(14), Cl1−V1−Cl2 93.73(3), N1−V1−N2 169.40(7), N1−V1−N3 95.71(7), N2−V1−N3 73.79(6).

Scheme 3. Synthesis of Aryl Imido−Vanadium(IV) Complexes **7**−**11**



7) confirms the presence of one NHMe$_2$ and one tmeda ligand, with a pseudooctahedral geometry around the vanadium center. The imido fragment sits in the axial position with a vanadium−nitrogen distance of 1.676(2) Å and a V−N$_{\text{imido}}$−C$_{\text{ipso}}$ angle of 177.59(19)°. Mutually trans chlorine atoms are cis to the imido group [V−Cl1 = 2.3773(10) and V−Cl2 = 2.3448 (11) Å], and the NHMe$_2$ ligand is cis to both chlorine atoms and trans to one nitrogen atom of the tmeda ligand [V−N(NHMe$_2$) = 2.167(3) Å]. The tmeda ligand, which is located trans to the imido group and to the NHMe$_2$ ligand, has a surprising coordination mode: the nitrogen atom trans to the imido is longer by ca. 0.60 Å as compared to the one in the basal plane [trans V−N$_{\text{tmeda}}$ = 2.820(3) Å, cis V−N$_{\text{bipy}}$ = 2.224(2) Å]. This very long V−N$_{\text{tmeda}}$ bond may arise from the trans influence of the imido group. In that way, complex **10a** may be regarded as a 5-coordinate square-pyramidal complex (as in the bis-amino complexes **3a**−**e**) but with a very weak extra-coordination to the tmeda nitrogen trans to the imido moiety. This point may explain why the chlorine atoms are mutually trans in tmeda complex **10a** whereas they are cis in bipyridine complex **7a**.

Addition of tmeda to a toluene solution of **2a** afforded the NHMe$_2$-free complex [V(=NAr)Cl$_2$(tmeda)] (**11a**) (Ar = 2,6-*i*-Pr-C$_6$H$_3$), in a similar way as we already observed with bipy (complex **8a**) or with 2 equiv of pyridine (complex **6a**) (Scheme 3). The molecular structure (Figure 8) is best described as a distorted square pyramid as in compound **3a** with an axial aryl imido that exhibits a V−N distance of 1.6674(13) Å, the imido linkage being somewhat less linear than in **3a** [V1−N$_{\text{imido}}$−C$_{\text{ipso}}$ angle = 164.48(10)°]. Compared to **3a**, the major difference comes from the tmeda ligand that forces the two chlorine atoms to be cis with a Cl1−V−Cl2 angle of 91.06(3)° [V−Cl1 = 2.3078(8) Å and V−Cl2 = 2.3231(8) Å]. The two cis nitrogen atoms of the tmeda ligand form the base of the square pyramid with the

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(34) For unknown reasons, complex **3d** does not react with an excess of tmeda with replacement of the NHMe$_2$ ligands.

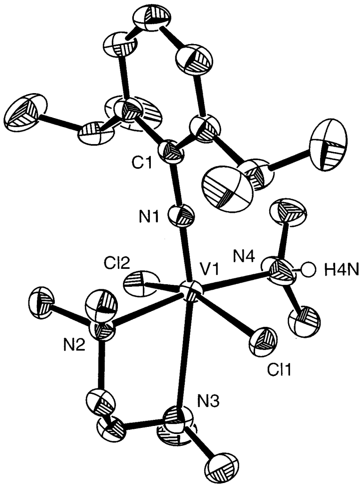

Figure 7. Molecular structure of **10a** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity, except the one on the nitrogen amino group. V1−N1 1.676(2), V1−N2 2.224(2), V1−N3 2.820(3), V1−N4 2.167(3), N1−C1 1.389(4), V1−Cl1 2.3748(11), V1−Cl2 2.3573(11); V1−N1−C1 177.59(19), Cl1−V1−Cl2 154.67(3), N1−V1−N3 166.37(9), N1−V1−N2 92.28(9), N2−V1−N3 74.45(10).

chlorine atoms, and have V−N_{tmeda} bonds of 2.1774(15) and 2.2196(14) Å, with a N_{tmeda}−V−N_{tmeda} angle of 79.39(5)°.

Conclusions

We have described simple routes to paramagnetic N-containing ligands supported aryl imido−vanadium(IV) dichloride complexes that demonstrate that such terminal imido vanadium(IV) species are now accessible. The bis(dimethylamido) aryl imido complexes **1a**−**e** have been shown to be diamagnetic dimers that can be transformed by chlorination into complexes **2a**−**e**. Although the structure of these materials was not conclusively established and remains unclear, we showed that they represent precursors for the synthesis of monomeric terminal imido complexes, free of dimethylamine co-ligands. The bis(dimethylamino) aryl imido dichloride derivatives **3a**−**e** are stable and readily obtained in a synthetically useful way, and give easy access to the corresponding complexes with pyridine, bipyridine, or tmeda adducts. We are exploring the chemistry of imido vanadium(IV) complexes with other imido groups (in particular alkyl groups) and other donor ligands (with O or P ligation) and their use in homogeneous catalysis. These results will appear in future publications.

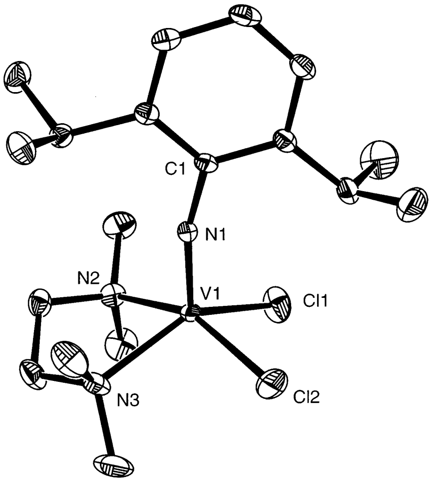

Figure 8. Molecular structure of **11a** with selected bond distances (Å) and angles (deg), showing 50% probability ellipsoids and partial atom-labeling schemes. Hydrogen atoms are omitted for clarity. V1−N1 1.6674(13), V1−N2 2.1774(15), V1−N3 2.2196(14), N1−C1 1.3936(18), V1−Cl1 2.3078(8), V1−Cl2 2.3231(8), V1−N1−C1 164.48(10), Cl1−V1−Cl2 91.06(3), N2−V1−N3 79.39(5), N1−V1−N2 100.81(5), N1−V1−N3 108.24(6).

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Supporting Information Available: Full details for experimental procedures for complexes **1a**−**e**, **3a**−**e**, **4a**−**e**, and **7a**−**e** and the complete IR spectroscopic data for all complexes; crystallographic data for compounds **1b**, **3d**, **4b**, **4d**, **7c**, **10a**, and **11a**, including ORTEP diagrams, tables of crystal data and data collection parameters, atomic coordinates, anisotropic displacement parameters, and all bond lengths and bond angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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