

An Amidinate Ligand with a Pendant Amine Functionality; Synthesis of a Vanadium(III) Complex and Ethene Polymerization Catalysis^[†]

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A new type of amidinate ancillary ligand has been prepared, which incorporates a pendant tertiary amine functionality. The crystal structure of a vanadium(III) derivative, $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]\text{VCl}_2(\text{THF})$ (**1**), shows that the ligand can adopt a facial geometry, with an unusual

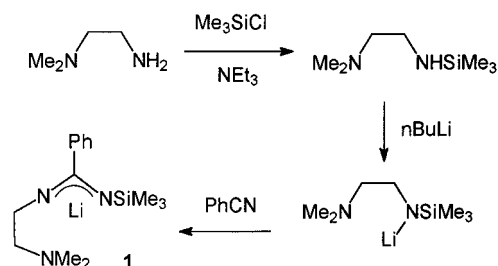
distortion of the amidinate nitrogen bearing the pendant functionality. With AlEt_2Cl cocatalyst the compound **1** produces a single-site catalytic system for the polymerization of ethene.

Amidines $[\text{RC}(\text{NR}')_2]^-$ are extensively being used as ligands for transition metals, lanthanides as well as main group elements, in which they act most frequently as bidentate 4-electron monoanionic ligands.^[1] Various routes are available to prepare amidines with a range of substitution patterns, and steric and electronic features of these ligands are readily varied.^[2] For Group 4 transition metals, amidines have been used as ancillary ligands in olefin polymerization catalysts.^[3] The applicability of these ligands could be enhanced considerably with the ability to introduce additional functionalities as pendant groups on the amidinate ligand framework. In this contribution we describe the synthesis of such a functionalized amidinate, $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]^-$, which has a pendant (dimethylamino)ethyl group attached to one of the amidinate nitrogens. A *facial* coordination mode of this ligand is illustrated by the structure of a vanadium(III) derivative, $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]\text{VCl}_2(\text{THF})$ (**1**), indicating that the new ligand may be compared with other, well-known face-capping monoanionic ligands like tris(pyrazolyl)borate and cyclopentadienyl. Compound **1** is active in the polymerization of ethene when activated by AlEt_2Cl co-catalyst.

The synthesis of the (dimethylamino)ethyl-functionalized benzamidinate $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]^-$ is based on the well-known reaction of lithium trimethylsilylamides with benzonitrile to give lithium *N*-(trimethylsilyl)benzamidines.^[2a] A suitable silylamide, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NHSiMe}_3$ was prepared by reaction of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ with Me_3SiCl and NEt_3 as base (in a preparation similar to that of $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N(Me)SiMe}_3$ ^[4a]), and isolated by vacuum distillation. Lithiation with *n*BuLi yields the lithium amide $\text{Me}_2\text{NCH}_2\text{CH}_2\text{N(Li)SiMe}_3$ which was obtained

as a crystalline solid.^[4b] This lithium amide readily reacts with benzonitrile in THF solvent to give the functionalized lithium benzamidinate $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]\text{Li}$ (Scheme 1). The route appears to be quite versatile, and this methodology should be applicable to a range of *N*-mono-functionalized, *N'*-trimethylsilyl benzamidines.

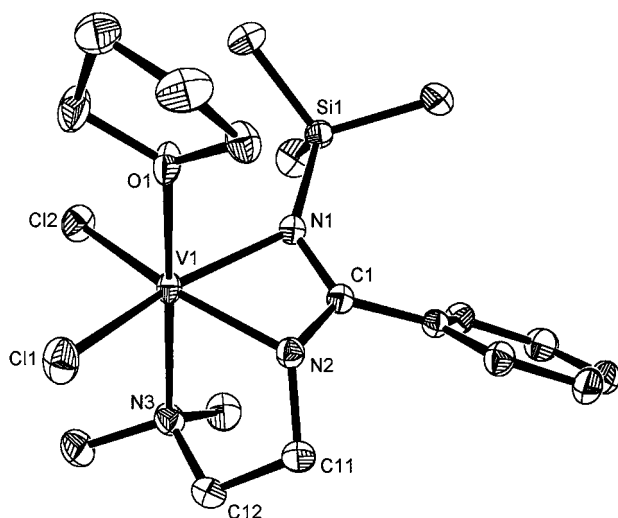
Scheme 1



Reaction of one equivalent of $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]\text{Li}$ with $\text{VCl}_3(\text{THF})_3$ in THF produces the highly air sensitive, paramagnetic (by ^1H NMR), green V(III) mono(amidinate) dichloride complex^[5] $[\text{SiMe}_3\text{NC(Ph)NCH}_2\text{CH}_2\text{NMe}_2]\text{VCl}_2(\text{THF})$ (**1**), which was obtained as crystals suitable for X-ray diffraction by diffusion of pentane vapor into a THF solution of the compound. The structure of **1** (Figure 1) shows a distorted octahedral coordination of the metal, with the functionalized amidinate ligand adopting a facial geometry. The amidinate nitrogen bearing the (dimethylamino)ethyl functionality, N(2), is distinctly non-planar, the sum of the angles around N(2) being 336.4° as compared to 359.9° for N(1). This is unusual for metal amidines, and may suggest that the ligand has partial amido-imine character. Indeed, the V–N(2) distance is 0.1 \AA shorter than V–N(1), but the C(1)–N distances in the amidinate backbone differ only slightly (if significantly), with C(1)–N(1) being 0.017 \AA

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Figure 1. ORTEP diagram of the molecular structure of **1**. Hydrogen atoms are omitted for clarity. The unlabeled atoms are carbon^[a]



^[a] Selected interatomic distances [Å] and angles [°]: V–Cl(1) = 2.3477(5), V–Cl(2) = 2.3153(4), V–O = 2.103(1), V–N(1) = 2.124(1), V–N(2) = 2.016(1), V–N(3) = 2.230(1), C(1)–N(1) = 1.322(2), C(1)–N(2) = 1.339(2), Cl(1)–V–Cl(2) = 106.47(2), O–V–N(3) = 172.50(5), N(1)–V–N(2) = 64.10(4), N(1)–V–N(3) = 100.62(5), N(2)–V–N(3) = 74.91(5), N(1)–V–Cl(1) = 156.44(3), N(2)–V–Cl(2) = 151.99(4), V–N(2)–C(1) = 93.77(8), V–N(2)–C(11) = 121.41(9), C(11)–N(2)–C(1) = 121.21(9), N(1)–C(1)–N(2) = 111.4(1).

(8σ) shorter than C(1)–N(2). A highly asymmetrically bound amidinate was also observed in [MeC(N*i*Pr)₂]₂Ge (with a relatively small nonplanarity of one of the amidinate nitrogen atoms), but this only showed similarly small differences in the C–N distances of the amidinate backbone.^[6]

The geometry around the metal center in **1** is significantly more distorted than in other octahedral vanadium(III) complexes with monoanionic tridentate ligands such as Tp*VCl₂L (Tp* = (3,5-dimethyl-1-pyrazolyl)borate; L = DMF,^[7] 4-methylpyridine^[8]). In the latter complexes, the N–V–N angles and V–N distances involving the tridentate ligand are all rather similar (around 86° and 2.12 Å respectively), whereas in **1** both features vary over a considerable range [from 64.10(4)° to 100.62(5)° and from 2.016(1) Å to 2.230(1) Å respectively].

When activated with AlEt₂Cl (20 mol per mol V), **1** catalyzes the polymerization of ethene in toluene. Table 1 shows activity and GPC data for 30 minutes ethene polymerization runs at three different temperatures (30, 50, and

80°C). The catalyst is most active at 30°C, with a productivity of 447 kg mol^{−1} h^{−1} bar^{−1}, and the product molecular weight distribution is characteristic for the presence of a single active site. At 50°C the overall productivity drops substantially, indicating a limited thermal stability of the catalyst. At 80°C catalyst decomposition is rapid, and the molecular weight distribution of the polyethene formed is bimodal. For comparison, polymerization runs with a vanadium catalyst with an unfunctionalized amidinate ligand, {[PhC(NSiMe₃)₂]VCl₂(THF)}₂ (**2**), are given in Table 1 as well. At 30°C this system has a substantially lower activity than 1/AlEt₂Cl, and forms polyethene with a significantly higher molecular weight. The catalyst activity is higher at 50°C but this is accompanied by a broadening of the polymer molecular weight distribution. Again, this system suffers from catalyst degradation at 80°C accompanied by formation of a bimodal distribution of the PE product. Thus the introduction of a pendant Lewis-base functionality on the benzamidinate ligand significantly increases the polymerization activity of the homogeneous V^{III} amidinate catalyst system at temperatures close to ambient, but does not improve the thermal stability of the catalytic species.

In conclusion, we have developed a convenient route to a new amidinate ligand with a tethered dialkylamine functionality. A vanadium(III) complex with this ligand was prepared and structurally characterized, revealing the possibility of this ligand to adopt a facial coordination mode. As such, this ligand is complementary to the familiar, more symmetrical facial monoanionic 6-electron tridentate ligands such as tris(pyrazolyl)borate and cyclopentadienyl. We are presently pursuing the scope of this synthesis method for the attachment of other functionalities to the benzamidinate framework and the use of these ligands with a variety of transition metals.

This investigation was carried out in connection with NIOK, the Netherlands Institute for Catalysis Research, and supported by the Department of Economic Affairs of the Netherlands.

Experimental Section

General: All experiments were performed under nitrogen atmosphere using standard Schlenk and glove-box techniques unless mentioned otherwise. Deuterated solvents (Aldrich) were dried over Na/K alloy and vacuum transferred before use. Other solvents were distilled from Na/K alloy or Na (toluene) before use. For the polymerization experiments toluene (Aldrich, 99.8%) was percolated over molecular sieves (3 Å) before use, ethene (AGA polymer

Table 1. Ethene polymerization catalyzed by **1** and **2** with AlEt₂Cl cocatalyst^[a]

Catalyst	<i>T</i> [°C]	PE yield [g]	activity [kg mol ^{−1} h ^{−1} bar ^{−1}]	<i>M_w</i> (× 10 ^{−6})	<i>M_w</i> / <i>M_n</i>
1	30	13.40	447	0.76	2.1
1	50	7.25	242	0.54	2.1
1	80	1.38	46	0.22	4.5 ^[b]
2	30	3.87	129	1.60	2.4
2	50	11.18	373	1.37	3.8
2	80	8.38	279	1.46	10.0 ^[b]

^[a] Toluene solvent, 6 bar ethene, 10 μmol V, V:Al = 1:20, 30 min run time. — ^[b] Bimodal distribution.

grade) was passed over a supported copper scavenger (BASF R 3-11) and molecular sieves (3 Å) before being passed to the reactor. – NMR spectra were run on Varian Gemini 200 and VXR 300 spectrometers. – IR spectra were recorded from Nujol mulls between KBr disks on a Mattson-4020 Galaxy FT-IR spectrophotometer. – GPC analyses were performed on solutions of the polymers in distilled 1,2,4-trichlorobenzene on a PL-GPC210 instrument of Polymer Laboratories. – Elemental analyses were carried out at the Micro-Analytical Department of the University of Groningen.

Preparation of (*N,N*-dimethyl-*N'*-trimethylsilyl)ethylene Diamine: To a solution of (*N,N*-dimethyl)ethylenediamine (35.4 g, 0.4 mol) and an excess of triethylamine (1.28 mol) in 200 mL of 1,4-dioxane, trimethylsilylchloride (66.6 mL, 0.44 mol) was added dropwise in 20 minutes. A white precipitate (triethylamine hydrochloride) formed, and the mixture was stirred for 16 h. The mixture was filtered and the residual salts extracted with 3×50 mL of diethyl ether. The combined filtrates were concentrated under reduced pressure, and pentane was added to precipitate any remaining salts. The mixture was filtered, the filtrate concentrated again and distilled under reduced pressure. The fraction boiling at 73.5–74.0 °C (45 mmHg) consisted of the title compound (36.06 g, 0.22 mol, 50%). – ^1H NMR ($[\text{D}_6]$ benzene): δ = 0.00 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 0.98 (s, 1 H, NH), 2.17 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 2.24 (t, $^3J_{\text{HH}}$ = 6.5, 2 H, CH_2), 2.74 (t, $^3J_{\text{HH}}$ = 5.3, 2 H, CH_2).

Preparation of *N'*-lithio(*N,N*-dimethyl-*N'*-trimethylsilyl)ethylene Diamine: In 30 minutes, 30 mL of a 2.5 M *n*BuLi/hexane solution was added to a solution of 12.07 g (75 mmol) of (*N,N*-dimethyl-*N'*-trimethylsilyl)ethylene diamine in 200 mL of ether at –50 °C. The mixture was allowed to warm to room temperature after which the volatiles were removed in vacuo. This yielded 11.0 g (66 mmol, 88%) of the title compound as a white solid. – ^1H NMR ($[\text{D}_8]$ toluene/ $[\text{D}_8]$ THF): δ = 0.19 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 2.06 [s, 6 H, $\text{N}(\text{CH}_3)_2$], 2.38 (br, 2 H, CH_2), 3.23 (t, $^3J_{\text{HH}}$ = 5.3, 2 H, CH_2). – ^{13}C NMR ($[\text{D}_8]$ toluene/ $[\text{D}_8]$ THF): δ = 62.51 (CNLi), 45.70, 45.21 (Me_2NCH_2 , NCH_3), –2.15 ($\text{Si}(\text{CH}_3)_3$). – $\text{C}_7\text{H}_{19}\text{LiN}_2\text{Si}$ (166.27): calcd. C 50.57, H 11.52, N 16.85; found C 50.22, H 11.37, N 15.94.

Preparation of $[\text{Me}_3\text{SiNC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2]\text{Li}$: To a solution of 0.98 g (5.88 mmol) of *N'*-lithio(*N,N*-dimethyl-*N'*-trimethylsilyl)ethylene diamine in 20 mL of THF, 0.60 mL of benzonitrile was added at –40 °C. After 30 minutes the solvent was removed in vacuo and the residue stripped of remaining THF by repeatedly stirring with portions of pentane which were then pumped off. This yields the title compound as a pale yellow powder. Yield: 1.29 g (4.76 mmol, 81%). – ^1H NMR ($[\text{D}_6]$ benzene): δ = 0.01 [s, 9 H, $\text{Si}(\text{CH}_3)_3$], 1.96 [s, 6 H, $\text{N}(\text{CH}_3)_2$], 2.10 (t, $^3J_{\text{HH}}$ = 5.3, 2 H, CH_2), 2.82 (t, $^3J_{\text{HH}}$ = 5.3, 2 H, CH_2), 7.2–7.1 (5 H, Ph). – ^{13}C NMR (C_6D_6): δ = 178.13 (NCN), 143.59 (Ph *ipso*-C), 128.31, 126.75, 126.43 (Ph CH), 58.38 (NCH_2), 41.70, 41.21 (Me_2NCH_2 , NCH_3), –1.86 [$\text{Si}(\text{CH}_3)_3$].

Preparation of $[\text{SiMe}_3\text{NC}(\text{Ph})\text{NCH}_2\text{CH}_2\text{NMe}_2]\text{VCl}_2(\text{THF})$ (1): For this synthesis the lithium salt of the ligand was conveniently generated in situ. To a solution of 1.43 g (8.58 mmol) of *N'*-lithio(*N,N*-dimethyl-*N'*-trimethylsilyl)ethylene diamine in 90 mL of THF 0.88 mL (8.62 mmol) of benzonitrile was added at –40 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. Subsequently, the mixture was cooled to –50 °C and 3.32 g (8.88 mmol) of $\text{VCl}_3(\text{THF})_3$ was added. The mixture was allowed to warm to room temperature and was stirred overnight, giving a dark brown solution. The solvent was removed in vacuo

and the residue was extracted with 50 mL of diethyl ether. The solvent was removed from the extract in vacuo, and the residue dissolved in 5 mL of THF. Slow diffusion of pentane vapor into the solution resulted in formation of green crystals of **1** (2.78 g, 6.1 mmol, 58%). – ^1H NMR ($[\text{D}_6]$ benzene): δ = 12.68 ($\Delta\nu_{1/2}$ = 150 Hz), 2.02 ($\Delta\nu_{1/2}$ = 150 Hz), –0.94 ($\Delta\nu_{1/2}$ = 250 Hz). – IR (Nujol, KBr): $\tilde{\nu}$ = 1503 (m), 1400 (m), 1240 (m), 1190 (w), 1086 (w), 1044 (m), 1022 (s), 943 (m), 912 (m), 866 (s), 839 (s), 797 (m), 756 (w), 721 (m), 691 (w), 517 (m), 496 (w), 478 (w) cm^{-1} . – $\text{C}_{18}\text{H}_{32}\text{Cl}_2\text{N}_3\text{OSiV}$ (456.40): calcd. C 47.37, H 7.07, N 9.21; found C 47.49, H 7.10, N 9.24.

Crystal Structure Analysis of 1: Enraf-Nonius CAD4-F diffractometer, Mo- K_α radiation (λ = 0.71073 Å), T = 130 K; triclinic, $P\bar{1}$, a = 10.286(1), b = 10.461(1), c = 10.710(1) Å, α = 93.648(5), β = 100.075(5), γ = 98.924(5)°, V = 1114.1(2) Å³, Z = 2, D_x = 1.361 g cm^{-3} , μ = 7.5 cm^{-1} . The structure was solved by Patterson methods and extended by direct methods applied to difference structure factors. A final refinement on F^2 converged at $wR(F^2)$ = 0.0766 for 4849 reflections with $F_o^2 \geq 0$ and $R(F)$ = 0.0274 for 4524 reflections with $F_o \geq 4.0 \sigma(F_o)$ and 363 parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102816. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of $\{[\text{PhC}(\text{NSiMe}_3)_2]\text{VCl}_2(\text{THF})\}_2$ (2): To a suspension of $\text{VCl}_3(\text{THF})_3$ (5.28 g, 14.1 mmol) in 80 mL of THF, cooled to –78 °C, was added 4.80 g (14.0 mmol) of $[\text{PhC}(\text{NSiMe}_3)_2]\text{Li}(\text{THF})$. The mixture was allowed to warm to room temperature while stirring, and the resulting brown-green solution was stirred for 4 h. Subsequently, the volatiles were removed in vacuo and the residue was stirred with 20 mL of pentane which was subsequently pumped off. Extraction with diethyl ether and cooling the extract to –30 °C yielded a mixture of brown **2** and green $[\text{PhC}(\text{NSiMe}_3)_2]\text{VCl}_2(\text{THF})_2^{[\text{sc}]}$ which was dissolved in 50 mL of toluene and warmed to 50 °C for 10 min after which the solvent was pumped off. Recrystallization from diethyl ether at –30 °C yielded 3.50 g (3.83 mmol, 55% yield on amidinate) of brown crystalline **2**. – ^1H NMR ($[\text{D}_6]$ benzene): δ 11.24–7.36 ($\Delta\nu_{1/2}$ = 70–380 Hz, 5 H, Ph), 3.64 ($\Delta\nu_{1/2}$ = 90 Hz, 4 H, α -THF), 1.47 ($\Delta\nu_{1/2}$ = 120 Hz, 4 H, β -THF), –0.51 ($\Delta\nu_{1/2}$ = 120 Hz, 18 H, SiMe_3). – IR (Nujol mull, KBr, cm^{-1}): $\tilde{\nu}$ = 1503(w), 1445(s), 1361(s), 1261(m), 1248(s), 1175(w), 1074(w), 1047(w), 1030(w), 1001(m), 988(s), 922(w), 841(s), 785(m), 764(m), 743(w), 704(m), 690(m), 530(m), 446(w). – $\text{C}_{17}\text{H}_{31}\text{Cl}_2\text{N}_2\text{OSi}_2\text{V}$ (457.46): calcd. C 44.63, H 6.83, Cl 15.50, N 6.12, V 11.14; found C 44.34, H 6.61, Cl 15.78, N 6.58, V 10.91.

Ethene Polymerization Experiments: Polymerizations were carried out in a fully temperature and pressure controlled Medimex 1 L stainless steel autoclave. The autoclave was charged with 250 mL of toluene containing 0.10 mmol of AlEt_2Cl , brought to the desired temperature and saturated with ethene (6 bar). Subsequently, a solution of the catalyst precursor (10 μmol of vanadium) with 0.10 mmol of AlEt_2Cl in 5 mL of toluene (mixed 15 min prior to injection) was injected into the reactor. During the reaction the monomer was fed continuously to the reactor. After 30 min the reaction was quenched by injection of 10 mL of methanol. The contents of the reactor were stirred in 100 mL of acidified methanol for 1 h. The precipitated polymer was rinsed repeatedly with ethanol and dried at 60 °C for 2 d.

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