The *N,N′*-bis(trimethylsilyl)pentafluorobenzamidinate ligand: enhanced ethene oligomerisation with a neutral V(III) bis(benzamidinate) alkyl catalyst†‡

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The pentafluorobenzamidinate ligand $[C_6F_5C(NSiMe_3)_2]^-$ is reported, together with its bis(benzamidinate) vanadium(III) methyl derivative; the latter is considerably more active in catalytic ethene oligomerisation than its non-fluorinated analogue.

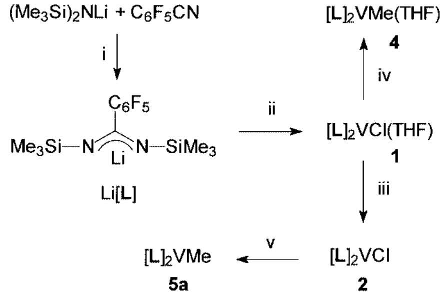
Fluorination of ancillary ligands attched to catalytically active transition-metal centres leads in many cases to a significant improvement in catalytic properties relative to the non-fluorinated analogues. Examples of this can be found in the metathesis catalysts $[(CF_3)_nMe_{3-n}CO]_2W(CHCMe_3)(NAr)$ (n = 0, 1 2; Ar = 2,6-diisopropylphenyl)[1] and in the olefin polymerisation catalysts based on [2-pyridyl–$C(CF_3)_2O]_2Zr(CH_2Ph)_2$.[2] The electron withdrawing properties of the fluorinated ligand renders the metal centre more electrophilic and, for many reaction types, more reactive. In this contribution we present the synthesis of a new fluorinated derivative of a well known ancillary ligand, *N,N′*-bis(trimethylsilyl)benzamidinate, and show that this leads to a significant improvement in the catalytic performance of an ethene oligomerisation catalyst, bis(benzamidinate)vanadium alkyl.

The *N,N′*-bis(trimethylsilyl)benzamidinate monoanionic ancillary ligand, $[PhC(NSiMe_3)_2]^-$, is widely used in transition-metal chemistry and catalysis,[3] for example in the olefin polymerisation catalysts $[PhC(NSiMe_3)_2]_2MCl_2$/MAO (M = Ti, Zr, Hf; MAO = methylaluminoxane)[4] and $Cp^*M[PhC(NSiMe_3)_2]Cl_2$/MAO (M = Ti, Zr, Hf).[5] We recently reported the neutral paramagnetic (S = 1) 12-electron bis(benzamidinate)-vanadium(III) alkyls $[PhC(NSiMe_3)_2]_2VR$ (R = Me, Et).[6] This neutral alkyl system catalyses the oligomerisation of ethene to linear alkenes without the need for added cocatalysts. The productivity of the catalyst system is modest, which is likely to be due to the relatively low electrophilicity of the metal centre. We therefore sought to increase this electrophilicity by preparing a benzamidinate with a more electron-withdrawing aryl group, pentafluorophenyl, on the ligand backbone.

Lithium *N,N′*-bis(trimethylsilyl)benzamidinate is readily prepared by reacting benzonitrile with the bis(trimethylsilyl)amide $LiN(SiMe_3)_2$.[7] The reaction of pentafluorobenzonitrile with $LiN(SiMe_3)_2$ in THF was recently reported to lead to C–F activation of the nitrile rather than to formation of the pentafluorobenzamidinate $[C_6F_5C(NSiMe_3)_2]Li$.[8] We observed that changing the solvent from THF to diethyl ether suppresses this tendency towards C–F activation. Thus, addition of 1 equivalent of C_6F_5CN to a suspension of $Li[N(SiMe_3)_2]$ in diethyl ether at −40 °C and gradual warming to ambient temperature yields a clear, pale yellow solution of the desired pentafluorobenzamidinate that is ready for further use (Scheme 1). For spectroscopic analysis, small solid samples were obtained by simply evaporating the solvent from an aliquot of the solution. NMR spectroscopy (^1H, ^{13}C and ^{19}F)[9] showed clean formation of a single product with apparent composition $[C_6F_5C(NSiMe_3)_2]Li\cdot 0.5Et_2O$ and IR spectroscopy showed no residual nitrile bands.

Reaction of 2 equivalents of $[C_6F_5C(NSiMe_3)_2]Li$ with $VCl_3(THF)_3$ in THF resulted in formation of the green bis(amidinate) complex $[C_6F_5C(NSiMe_3)_2]_2VCl(THF)$ **1** (Scheme 1), which was isolated in 58% yield. Removal of THF by heating solid **1** *in vacuo* at 120 °C for 5 h yields the orange base-free chloride $[C_6F_5C(NSiMe_3)_2]_2VCl$ **2**. The ^{19}F NMR spectrum of paramagnetic **2** shows a strong downfield shift of the *o*-F resonance (δ −106.8, $\Delta\nu_{1/2}$ 380 Hz), and less pronounced shifts for the *p*-F (δ −144.1, $\Delta\nu_{1/2}$ 85 Hz) and *m*-F (δ −155.3, $\Delta\nu_{1/2}$ 45 Hz) resonances.

It proved to be difficult to obtain single crystals of **2** that were suitable for X-ray diffraction. For structural characterisation the benzonitrile adduct $[C_6F_5C(NSiMe_3)_2]_2VCl(NCPh)$ **3a** was prepared by addition of benzonitrile to a pentane solution of **2** followed by recrystallisation from diethyl ether. Its molecular structure§ is shown in Fig. 1. For comparison a structure determination of the non-fluorinated analogue **3b** was also performed.§ This compound is essentially isostructural, and its



Scheme 1 *Reagents and conditions*: i, Et_2O, −40 to 20 °C, 16 h; ii, $VCl_3(THF)_3$ (0.5 equiv.), THF, −78 to 20 °C, 16 h; iii, 120 °C, vacuum, 5 h; iv, MeMgCl, THF, −78 to 20 °C, 1 h; v, MeLi, Et_2O, −78 to 20 °C, 1 h.

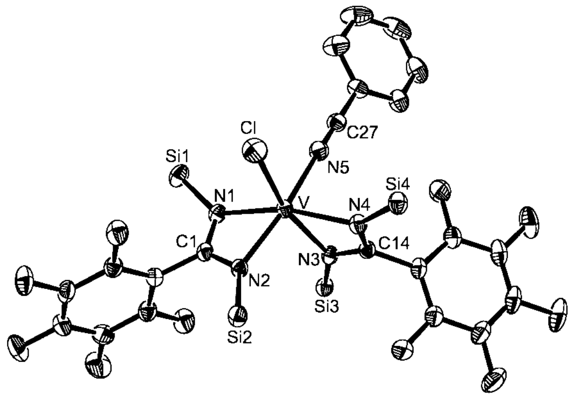


Fig. 1 Molecular structure of **3a** ($SiMe_3$ methyl groups omitted for clarity). Selected interatomic distances (Å) and angles (°): V–Cl 2.3060(9), V–N(1) 2.082(2), V–N(2) 2.067(2), V–N(3) 2.104(2), V–N(4) 2.121(2), V–N(5) 2.153(2), N(1)–C(1) 1.326(3), N(2)–C(1) 1.317(2), N(5)–C(27) 1.139(3); Cl–V–N(5) 91.33(5), N(1)–V–N(2) 65.59(6), V–N(5)–C(27) 177.5(2).

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† Electronic supplementary information (ESI) available. Synthetic and spectroscopic details and ethene oligomerisation experiments. See http://www.rsc.org/suppdata/cc/b0/b000397m

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molecular structure is not shown here. The metal centre in **3a** has a distorted octahedral geometry, with two bidentate amidinate ligands and with the chloride and benzonitrile ligands being *cis* relative to each other. The pentafluorobenzamidinate exhibits a normal bidentate coordination mode, and the aryl substituent is perpendicular to the ligand NCN plane. In this respect it does not differ significantly from the non-fluorinated ligand in **3b**. The largest differences between the structures of the two complexes are found in the V–Cl distance and the Cl–V–N(5) and N(1)–V–N(4) angles [2.306(1) Å, 91.33(3) and 164.63(7)°, respectively, in **3a**; 2.350(1) Å, 86.01(8) and 168.6(1)° in non-fluorinated **3b**].

Unlike with the non-fluorinated analogue,[6] reaction of **1** with MeMgCl in THF followed by crystallisation from pentane yields a stable THF adduct of the methyl complex, $[C_6F_5C(NSiMe_3)_2]_2VMe(THF)$ **4** (Scheme 1). The stability of this adduct is an indication of the enhanced electrophilicity of the metal centre in the fluorinated benzamidinate complexes. Reaction of the base-free chloride **2** with MeLi in diethyl ether, followed by extraction with and crystallisation from pentane, affords the orange 12-electron methyl complex $[C_6F_5C(NSiMe_3)_2]_2VMe$ **5a** in 52% isolated yield. NMR spectra indicate that this alkyl compound (without β hydrogens) is thermally robust in benzene solution at 80 °C (no noticeable decomposition after 18 h).

To illustrate the effect of the fluorination of the amidinate ligand on the reactivity of the metal complexes, we compared the catalytic conversion of ethene by the neutral alkyl **5a** and its non-fluorinated analogue **5b**. Reactions on NMR tube scale had already shown that at 80 °C **5b** converts ethene to linear alkenes.[6] Initially, linear alk-1-enes are formed which are isomerised to internal alkenes when the system is starved of ethene. Autoclave experiments (80 °C, toluene, 4 or 8 bar ethene pressure) were performed using **5a** and **5b** as catalysts. Under these conditions, **5b** produces a Flory–Schultz distribution of linear alk-1-enes ($>99\%$ by GC) with $[C_{n+2}]/[C_n] = 0.87(2)$ over the range C_8–C_{32}, that is practically invariant with ethene pressure. The catalyst productivity for **5b** (as determined from isolated material precipitated with methanol) at 8 bar ethene (4 h run time) is 1.5 kg (mol V)$^{-1}$ h^{-1} of a material with $M_n = 850$ (by NMR). Under the same conditions, the fluorinated catalyst **5a** shows a productivity that is more than five times higher, 8.1 kg (mol V)$^{-1}$ h^{-1} giving a material with higher molecular weight ($M_n = 1780$, $M_w/M_n = 2.3$ by GPC).

A series of experiments with **5a** at 4 bar ethene pressure and run times of 2, 4 and 16 h shows that catalyst deactivation occurs, as the observed overall productivity drops from 7.4 to 4.5 and 1.3 kg (mol V)$^{-1}$ h^{-1}, respectively. As vanadium-based polymerisation catalysts are generally considered to deactivate through reduction of the metal centre to V(II),[10] it is likely that the electron-withdrawing nature of the fluorinated ligand accellerates this process.

In conclusion, we have prepared the new *N,N′*-bis(trimethylsilyl)pentafluorobenzamidinate ligand in a convenient manner, and have shown that the fluorination of the aryl substituent has a significant effect in the reactive properties of the metal centre in complexes with this ligand. Presently we are extending the chemistry of this ligand to other catalytically active metal centres. We are also using the synthesis route to prepare pentafluoro-derivatives of other trimethylsilylbenzamidinates (such as the amidinate–amine ligands reported recently by us[11]).

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Notes and references

§ *Crystallographic data*: for **3a**: $C_{33}H_{41}ClF_{10}N_5Si_4V$, $M = 896.44$, triclinic, space group $P\bar{1}$, $a = 10.206(2)$, $b = 13.176(2)$, $c = 17.992(3)$ Å, $\alpha = 86.41(1)$, $\beta = 74.73(1)$, $\gamma = 67.63(1)°$, $U = 2148.1(7)$ Å, $T = 130$ K, $Z = 2$, $D_c = 1.386$ g cm^{-3}, $\mu = 4.8$ cm^{-1}, Enraf Nonius CAD4-F diffractometer, λ(Mo-Kα) = 0.71073 Å, 8144 unique reflections, final residuals $wR(F^2) = 0.0986$, $R(F) = 0.0356$ for 7274 reflections with $F_o > 4\sigma(F_o)$ and 650 parameters. For **3b**: $C_{33}H_{51}ClN_5Si_4V$, $M = 716.54$, orthorhombic, space group *Pbca*, $a = 20.778(1)$, $b = 17.918(1)$, $c = 21.623(1)$ Å, $U = 8050.2(7)$ Å, $T = 130$ K, $Z = 8$, $D_c = 1.182$ g cm^{-3}, $\mu = 4.6$ cm^{-1}, Enraf Nonius CAD4-F diffractometer, λ(Mo-Kα) = 0.71073 Å, 6975 unique reflections, final residuals $wR(F^2) = 0.109$, $R(F) = 0.051$ for 5016 reflections with $F_o > 4\sigma(F_o)$ and 601 parameters. CCDC 182/1548. See http://www.rsc.org/suppdata/cc/b0/b000397m/ for crystallographic files in .cif format.

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9 $[C_6F_5C(NSiMe_3)_2]Li\cdot 0.5Et_2O$: ^1H NMR (200 MHz, C_6D_6) δ 3.20 (q, 2H, *J* 7.1, OCH_2), 0.98 (t, 3H, *J* 7.1, ether Me), −0.02 (s, 18H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6) δ 162.2 (NCN), 142.2 (d, J_{CF} 243.4, *m*-CF), 140.7 (d, J_{CF} 253.0, *p*-CF), 138.0 (d, J_{CF} 253.0, *o*-CF), 119.6 (br, C *ipso*), 65.7 (OCH_2), 14.4 (ether Me), 1.1 ($SiMe_3$). ^{19}F NMR (188 MHz, C_6D_6) δ −144.6 (dd, 2F, *J* 24.8, 7.9, *o*-F), −160.9 (t, 1F, *J* 24.8, *p*-F), −164.6 (td, 2F, *J* 24.8, 7.9, *m*-F).

10 See for example: Y. Ma, D. Reardon, S. Gambarotta, G. Yap, H. Zahalka and C. Lemay, *Organometallics*, 1999, **18**, 2773 and references therein.

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