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Key indicators

Single-crystal X-ray study
 $T = 147$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.027
 wR factor = 0.034
Data-to-parameter ratio = 11.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Chloro(*p*-tolylimido- κN)[*N,N'*-(trimethylsilyl)ferrocene-1,1'-diaminato- $\kappa^2 N,N'$]vanadium(V)

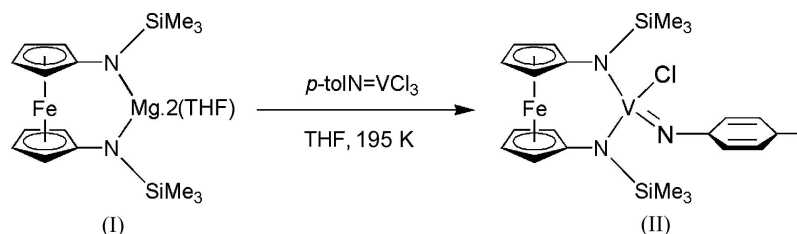
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The title compound, $[\text{VCl}(\text{C}_7\text{H}_7\text{N})\{\text{Fe}(\text{C}_8\text{H}_{13}\text{NSi})_2\}]$ or $[\text{FeV}(\text{C}_7\text{H}_7\text{N})(\text{C}_8\text{H}_{13}\text{NSi})_2\text{Cl}]$, crystallizes with the aromatic ring in the *p*-tolylimido unit parallel to the two cyclopentadienyl rings of the ferrocene moiety; the vanadium-bound chloride ion also lies in the plane occupied by the imido ligand. A mirror plane bisects the molecule through the V atom, the imido ligand and the Fe atom.

Comment

Ferrocene-containing ligands have been widely employed in coordination chemistry (Togni & Hayashi, 1995). Previous work in our laboratory has explored group 4 complexes supported by bidentate (Shafir & Arnold, 2003) and tetradentate (Shafir *et al.*, 2002) dianionic ligands derived from 1,1'-diaminoferrocene. In one notable instance, a diaminoferrocene-based ligand has been shown to stabilize a cationic titanium center *via* a remarkably short Ti–Fe interaction (Shafir & Arnold, 2001). We have more recently become interested in preparing related group 5 imido complexes, which offer excellent potential for the formation of similarly stabilized cationic species. Our attempts to prepare such complexes *via* metathesis of the magnesium salt of an *N,N'*-functionalized diaminoferrocene, (I), with tantalum imido materials of the form $\text{RN}=\text{TaCl}_3$ ($R = \textit{para}$ -tolyl or *tert*-butyl) gave intractable product mixtures. However, the salt exchange reaction with *para*-tolylimido vanadium trichloride gave the title compound, (II).



In the structure of (II) part of the molecule (Fig. 1) lies on a crystallographic mirror plane, perpendicular to the *b* axis. This mirror plane bisects the molecule through the V atom, the imido ligand and the Fe atom of the diaminoferrocene group. The diaminoferrocene core thus exhibits eclipsed cyclopentadienyl rings, in which the two amino substituents and their associated trimethylsilyl groups are also eclipsed.

The coordination geometry at vanadium is considerably distorted from tetrahedral. The $\text{N1}-\text{V1}-\text{N2}$ and $\text{N1}^i-\text{V1}-\text{N2}$ [symmetry code: (i) $x, \frac{1}{2} - y, z$] bond angles between the diaminoferrocene nitrogen donors and the imido N atom are

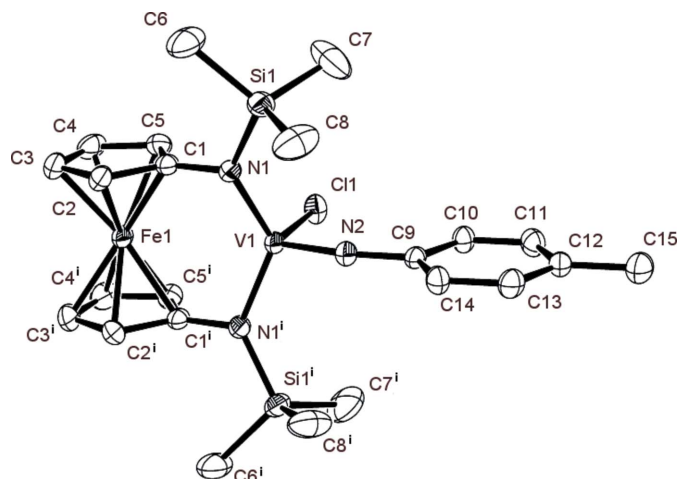


Figure 1

View of the molecular structure of (II), with displacement ellipsoids drawn at the 50% probability level; H atoms have been omitted for clarity. Symmetry operator is as in Table 1.

105.16 (7)°, slightly smaller than the tetrahedral angle of 109.47°. The N1–V1–Cl1 and N1ⁱ–V1–Cl1 angles are in almost exact accordance with the tetrahedral angle at 109.09 (6)°, while the N2–V1–Cl1 angle is significantly smaller at 100.1 (1)°. The V=N imido bond length is 1.658 (3) Å, this distance being both comparable to previously reported examples (Gambartotta *et al.*, 1984) and appreciably shorter than the 1.861 (2) Å observed for the V1–N1 and V1–N1ⁱ single bonds. These latter distances, and that of 2.257 (1) Å exhibited by the V1–Cl1 interaction are also comparable to literature values (Devore *et al.*, 1987). The Fe–C distances within the ferrocene group (Table 1) and the N–Si bond lengths between the trimethylsilyl Si atom and the N atom of the diaminoferrocene unit are in the usual range (Allen *et al.*, 1987).

Experimental

Under an inert atmosphere, a solution of *para*-tolylimido vanadium trichloride (325 mg, 1.24 mmol) in THF (15 ml) was cooled to 195 K. To this was added a solution of [*N,N'*-(trimethylsilyl)-1,1'-diaminoferrocenyl] magnesium-2(THF), (I) (700 mg, 1.24 mmol), in THF (15 ml), dropwise with stirring. The resulting black mixture was allowed to warm to room temperature and stirring was continued for 15 h. The solution was then filtered and the brown filtrate concentrated under reduced pressure. Recrystallization of this material from pentane at 233 K gave single crystals of (II) as dark-red prisms.

Crystal data

[FeV(C ₇ H ₇ N)(C ₈ H ₁₃ NSi) ₂ Cl]	Z = 4
<i>M_r</i> = 549.95	<i>D_x</i> = 1.388 Mg m ⁻³
Orthorhombic, <i>Pnma</i>	Mo K α radiation
<i>a</i> = 14.981 (1) Å	μ = 1.11 mm ⁻¹
<i>b</i> = 15.423 (1) Å	<i>T</i> = 147 (2) K
<i>c</i> = 11.3884 (8) Å	Prism, red
<i>V</i> = 2631.4 (3) Å ³	0.27 × 0.21 × 0.17 mm

Data collection

Bruker SMART 1000 CCD
diffractometer
 ω scans
Absorption correction: multi-scan
(Blessing, 1995)
 $T_{\min} = 0.728$, $T_{\max} = 0.828$

11979 measured reflections
2332 independent reflections
1752 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 24.7^\circ$

Refinement

Refinement on *F*
 $R[F > 2\sigma(F)] = 0.027$
 $wR(F) = 0.035$
S = 1.55
1752 reflections
157 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{Å}^{-3}$

Table 1

Selected bond lengths (Å).

Fe1–C1	2.040 (2)	V1–Cl1	2.257 (1)
Fe1–C2	2.042 (3)	V1–N1	1.861 (2)
Fe1–C3	2.047 (3)	V1–N1 ⁱ	1.861 (2)
Fe1–C4	2.055 (3)	V1–N2	1.658 (3)
Fe1–C5	2.050 (3)	Si1–N1	1.759 (2)

Symmetry code: (i) *x*, $-y + \frac{1}{2}$, *z*.

H atoms were included in the riding-model approximation with C–H = 0.94–0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation & Rigaku Corporation, 1998); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN*.

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References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Bruker (1999). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2002). *SAINT*. Version 6.40. Bruker AXS Inc., Madison, Wisconsin, USA.
- Devore, D. D., Lichtenhan, J. D., Takusagawa, F. & Maatta, E. A. (1987). *J. Am. Chem. Soc.* **109**, 7408–7416.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gambartotta, S., Chiesi-Villa, A. & Guastini, C. (1984). *J. Organomet. Chem.* **270**, C49–C52.
- Molecular Structure Corporation & Rigaku Corporation (1998). *TEXSAN*. MSC, The Woodlands, Texas, USA, and Rigaku, Tokyo, Japan.
- Shafir, A. & Arnold, J. (2001). *J. Am. Chem. Soc.* **123**, 9212–9213.
- Shafir, A. & Arnold, J. (2003). *Inorg. Chim. Acta*, **345**, 216–220.
- Shafir, A., Fiedler, D. & Arnold, J. (2002). *J. Chem. Soc. Dalton Trans.* pp. 555–560.
- Togni, A. & Hayashi, T. (1995). *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*. Weinheim/New York: VCH Publishers.