

***cis*-Bis[*N*¹,*N*²-bis(trimethylsilyl)benzamidinato- κ^2 *N*¹,*N*²]chloro(4-tolylimido- κ *N*)vanadium(V)**

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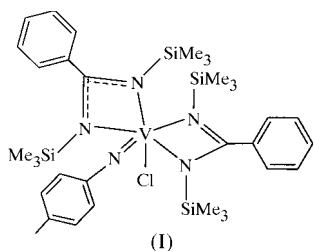
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The title complex, $[V(C_7H_7N)(C_{13}H_{23}N_2Si_2)_2Cl]$, consists of a V metal centre coordinated to five N atoms and a Cl^- ion in a pseudo-octahedral arrangement. The N atoms of the benzamidinate ligands form two four-membered chelate rings to V, with bite angles of $63.59(8)$ and $64.36(8)^\circ$, whilst the fifth N atom is from a *p*-tolylimido ligand [$V-N-C$ $172.2(2)^\circ$] located *cis* with respect to the Cl^- ion [$Cl-V-N_{imido}$ $96.96(8)^\circ$].

Comment

Vanadium complexes play a pivotal role in several diverse biological systems, but until recently they have not been as extensively studied as complexes containing zinc or iron (Rehder, 1999). Vanadium compounds coordinated to various biologically important functionalities, such as N_2 and nitrogen-containing ligands (*e.g.* pyrrole), have been proposed as functional models for nitrogenases (Veith, 1976; Bultitude *et al.*, 1986). Other studies have probed the varying oxidation states of vanadium (essential in these biological processes) by coordinating bidentate nitrogen ligands with numerous halogen and oxo ligands (Mohan *et al.*, 1995).

The title complex, (I), has a vanadium centre surrounded by two nitrogen-bound $PhC(NSiMe_3)_2$ ligands, a *p*-tolylimine group and a Cl^- ligand. The distorted octahedral geometry of the metal is clearly shown by the dissimilar *trans* angles of $151.71(6)$, $155.68(9)$ and $165.27(9)^\circ$, and the small $N-V-N$



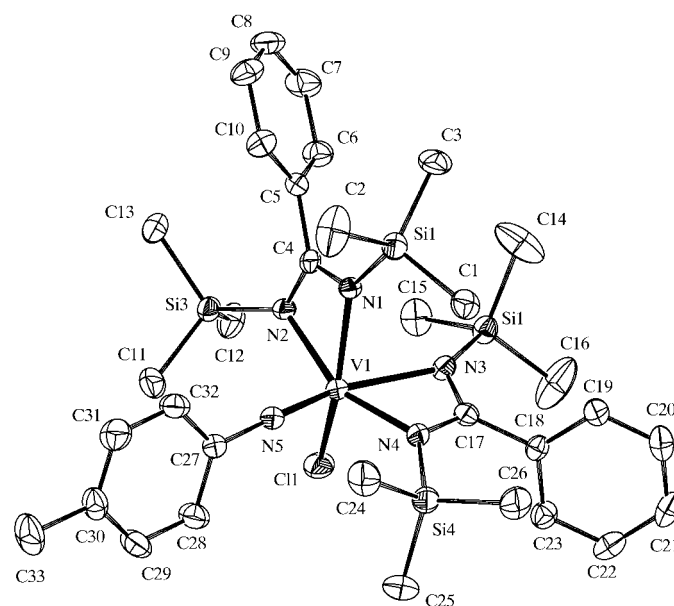
ligand bite angles of $63.59(8)$ and $64.36(8)^\circ$. The chelate bond angles are considerably smaller than the other *cis* $N-V-N$ and $N=V-N$ bond angles, ranging from $83.93(8)$ to

$101.7(1)^\circ$, but are comparable with those in other bis(trimethylsilyl)benzamidinate complexes (Hao *et al.*, 1996; Patt-Siebel *et al.*, 1990).

The $V-N$ and $C-N$ bonds within the two benzamidinate ligands (bound to V) are distinct. Each ligand forms a non-planar four-membered $V-N-C-N$ ring and the two are non-equivalent: the $V1-N3-C17-N4$ group is more puckered than the $V1-N1-C4-N2$ group [mean deviations from the least-squares plane of $0.045(16)$ and $0.011(3)^\circ$, respectively]. The $C-N$ distances in the $N1-C4-N2$ group have partial bond orders of 1.5, suggesting electron delocalization within the NCN group, whilst those for $N3-C17-N4$ are more localized. The phenyl groups at C4 and C17 are almost orthogonal to the NCN plane [dihedral angles of $61.2(3)$ and $77.2(3)^\circ$, respectively], and this therefore excludes the possibility of extending the π -conjugation. The two chelate groups are essentially perpendicular with respect to each other [$83.17(13)^\circ$], presumably to minimize the repulsion of the trimethylsilyl groups.

The $V1-N3$ distance is significantly longer than either $V1-N1$ or $V1-N2$. The $V1-N4$ distance is significantly shorter than any other $V-N$ bonds in benzamidinate ligands. These distances in (I), however, are generally in accord with those observed previously in $[(Me_3Si)NC(Ph)N(SiMe_3)]_2-V(allyl)$ [Brussee *et al.*, 1998; $V-N$ $2.051(1)$ – $2.164(1)$ Å] and in $[V(C_{18}H_{32}Cl_2N_3OSi)]$ [Brandsma *et al.*, 1998; $V-N$ $2.124(1)$ and $2.016(1)$ Å]. Thus, the $V1-N3$ and $V1-N4$ distances in (I) also reflect the general asymmetry of this ligand and presumably the greater *trans* influence, or steric bulk, of the *p*-tolylimino group compared with the Cl^- ligand.

The *p*-tolylimido ligand is almost linearly bound [$V1-N5-C27$ $172.2(2)^\circ$] and is located *cis* to the Cl^- ligand. Although the $V1=N5$ distance of $1.659(2)$ Å falls within the range of

**Figure 1**

The molecular view of (I) showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

V–N_{imido} values found in the Cambridge Structural Database (Allen & Kennard, 1993), the majority of vanadium complexes contain different geometric environments to that of (I). The V–Cl bond length [2.3082 (8) Å] is of a similar magnitude to that found in the related vanadium complex [V(C₁₈H₃₂Cl₂N₃OSi)] (Brandsma *et al.*, 1998).

Experimental

Detailed experimental procedures for the precursors to this complex and related species, namely [(Me₃Si)NC(Ph)N(SiMe₃)₂V(allyl)] (Brussee *et al.*, 1998) and [(Me₃Si)NC(Ph)N(SiMe₃)₂VCl] (Hao *et al.*, 1996), have been described. Complex (I) was recrystallized from hexane/dichloromethane solution.

Crystal data

[V(C ₇ H ₇ N)(C ₁₃ H ₂₃ N ₂ Si ₂) ₂ Cl]	$D_x = 1.197 \text{ Mg m}^{-3}$
$M_r = 718.55$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 10.1600 (5) \text{ \AA}$	$\theta = 11.5\text{--}14.0^\circ$
$b = 18.4257 (10) \text{ \AA}$	$\mu = 0.464 \text{ mm}^{-1}$
$c = 22.6430 (13) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 109.808 (5)^\circ$	Block, dark red
$V = 3988.1 (4) \text{ \AA}^3$	$0.25 \times 0.25 \times 0.25 \text{ mm}$
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.027$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 27.48^\circ$
Absorption correction: refined from ΔF (PLATON; Spek, 2000)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.819$, $T_{\text{max}} = 0.890$	$k = 0 \rightarrow 23$
11 788 measured reflections	$l = -19 \rightarrow 29$
9132 independent reflections	2 standard reflections
5838 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: 1%

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$
$wR(F^2) = 0.108$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} = 0.002$
9132 reflections	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
410 parameters	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Two of the methyl groups on Si3 display large displacement parameters, but no suitable refinement model for disorder was found. Aromatic H atoms were constrained and allowed to ride on their C atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Methyl H atoms (except those on C33) were constrained to an ideal geometry with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$, and allowed to rotate freely about the C–C bonds. The H atoms on C33 were equally disordered over two positions and were refined with 50% site-occupancy factors.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF97* (Beurskens *et al.*, 1997); program(s) used to refine

Table 1

Selected geometric parameters (Å, °).

V1–Cl1	2.3082 (8)	N1–C4	1.329 (3)
V1–N1	2.094 (2)	N2–C4	1.325 (3)
V1–N2	2.092 (2)	N3–C17	1.292 (3)
V1–N3	2.291 (2)	N4–C17	1.379 (3)
V1–N4	1.944 (2)	N5–C27	1.379 (3)
V1–N5	1.659 (2)		
N1–V1–N2	64.36 (8)	N3–V1–N5	165.27 (9)
N1–V1–N3	83.93 (8)	N4–V1–N5	101.70 (10)
N1–V1–N4	99.57 (9)	N1–V1–Cl1	151.71 (6)
N1–V1–N5	100.12 (10)	N2–V1–Cl1	90.82 (6)
N2–V1–N3	95.33 (8)	N3–V1–Cl1	85.24 (6)
N2–V1–N4	155.68 (9)	N4–V1–Cl1	98.82 (7)
N2–V1–N5	99.19 (9)	N5–V1–Cl1	96.96 (8)
N3–V1–N4	63.59 (8)	C27–N5–V1	172.2 (2)

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1031). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., García-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1997). *The DIRDIF97 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Brandsma, M. J. R., Brussee, E. A. C., Meetsma, A., Hessen, B. & Teuben, J. H. (1998). *Eur. J. Inorg. Chem.* pp. 1867–1870.
- Brussee, E. A. C., Meetsma, A., Hessen, B. & Teuben, J. H. (1998). *Organometallics*, **17**, 4090–4095.
- Bultitude, J., Larkworthy, L. F., Povey, D. C., Smith, G. W., Dilworth, J. R. & Leigh, G. J. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1748–1750.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Hao, S., Berno, P., Minhas, R. K. & Gambarotta, S. (1996). *Inorg. Chim. Acta*, **244**, 37–47.
- Mohan, M., Bond, M. R., Otieno, T. & Carrano, C. J. (1995). *Inorg. Chem.* **34**, 1233–1242.
- Patt-Siebel, U., Müller, U., Ergezinger, C., Borgsen, B., Dehnicke, K., Fenske, D. & Baum, G. (1990). *Z. Anorg. Allg. Chem.* **582**, 30–36.
- Rehder, D. (1999). *Coord. Chem. Rev.* **182**, 297–322.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *HELENA*. University of Utrecht, The Netherlands.
- Spek, A. L. (2000). *PLATON*. University of Utrecht, The Netherlands.
- Veith, M. (1976). *Angew. Chem. Int. Ed. Engl.* **15**, 387–388.