

# Synthesis and structural characterization of organometallic niobium(IV) amido complexes†

Simon G. Bott,<sup>a</sup> David M. Hoffman<sup>\*b</sup> and Sri Prakash Rangarajan<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of North Texas, Denton, Texas 76203, USA

<sup>b</sup> Department of Chemistry, University of Houston, Houston, Texas 77204, USA

New organometallic niobium(IV) amido complexes have been synthesized from  $[\text{NbCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$ .

Reaction with  $\text{ZnPh}_2$  gave the amidophenyl compound  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  and with  $\text{Zn}(\text{cp})_2$

( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ) gave  $[(\text{cp})_2\text{NbN}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2]$ . X-Ray crystallographic studies of both compounds have been carried out. In the solid state,  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  has a distorted-tetrahedral geometry and

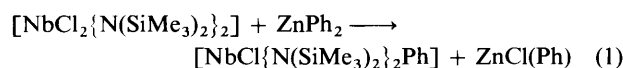
$[(\text{cp})_2\text{NbN}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2]$  has a planar four-membered metallaheterocyclic ring.

Relatively few well-characterized niobium(IV) amido compounds are known.<sup>1–3</sup> We recently reported a convenient synthesis of the niobium(IV) amido halides  $[\text{NbX}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  where  $\text{X} = \text{Cl}$  or  $\text{Br}$ .<sup>4–5</sup> We were interested in developing the chemistry of these compounds and, in particular, determining if substitution reactions could be carried out without inducing disproportionation to more stable niobium(V) and -(III) complexes. We report here on attempted substitution reactions of  $[\text{NbCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  leading to the isolation of two niobium(IV) complexes,  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  and the novel metallacycle  $[(\text{cp})_2\text{NbN}(\text{SiMe}_3)\text{SiMe}_2\text{CH}_2]$  ( $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ ).

## Results and Discussion

### Synthesis and characterization of $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$

Reaction of 1 equivalent of  $\text{ZnPh}_2$  with  $[\text{NbCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  (generated *in situ*) yielded dark-green plates (from hexane) of  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  in moderate yield [equation (1)].



Repeated attempts to prepare disubstituted  $[\text{Nb}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}_2]$  by treating  $[\text{NbCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  with 2 or 3 equivalents of  $\text{ZnPh}_2$  gave only  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$ . Refluxing a hexane–diethyl ether solution of  $[\text{NbCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  and 2 equivalents of  $\text{ZnPh}_2$  gave brown intractable products.

In the <sup>1</sup>H NMR spectrum of  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  a single broad resonance centred around  $\delta$  2.7 is observed, implying the compound is paramagnetic. The Evans' NMR method<sup>6,7</sup> gives a room-temperature magnetic moment of 1.02  $\mu_B$ , slightly lower than the spin-only value of 1.73  $\mu_B$ . The magnetic moments of  $[\text{NbCl}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  and  $\text{Nb}(\text{NPh}_2)_4$  are 1.03 and 0.98  $\mu_B$ , respectively. Low magnetic moments for niobium(IV) amides have also been observed by Bradley and Chisholm<sup>2</sup> who reported a magnetic moment of 0.8  $\mu_B$  for both  $\text{Nb}(\text{NEt}_2)_4$  and  $\text{Nb}(\text{NPr}^n)_4$ .

A thermal ellipsoid plot of  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  taken from an X-ray crystallographic study is shown in Fig. 1 and selected bond angles and distances are presented in Table 1. There are two independent molecules in the unit cell. The Nb–Cl bond distances are within the range found in other

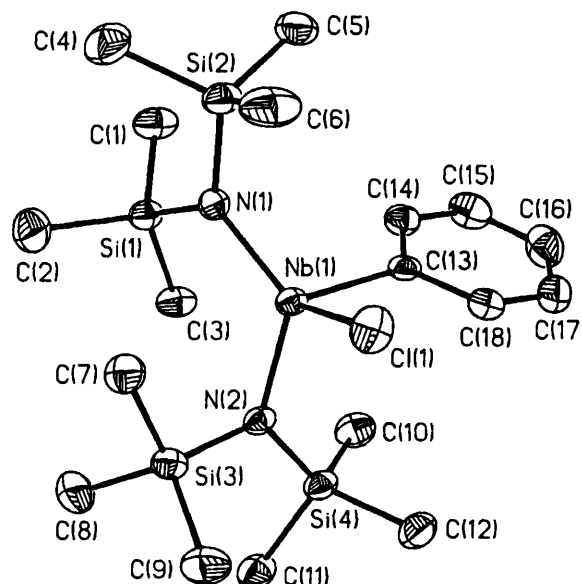


Fig. 1 Molecular structure of  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$  (40% probability ellipsoids)

Table 1 Selected bond distances (Å) and angles (°) for  $[\text{NbCl}\{\text{N}(\text{SiMe}_3)_2\}_2\text{Ph}]$

Molecule A		Molecule B	
Nb(1)–Cl(1)	2.377(1)	Nb(2)–Cl(2)	2.373(2)
Nb(1)–N(1)	1.988(4)	Nb(2)–N(3)	1.983(4)
Nb(1)–N(2)	1.989(4)	Nb(2)–N(4)	1.973(4)
Nb(1)–C(13)	2.128(5)	Nb(2)–C(31)	2.141(5)
Cl(1)–Nb(1)–N(1)	130.2(1)	Cl(2)–Nb(2)–N(3)	134.9(1)
Cl(1)–Nb(1)–N(2)	101.6(1)	Cl(2)–Nb(2)–N(4)	98.7(1)
Cl(1)–Nb(1)–C(13)	95.2(1)	Cl(2)–Nb(1)–C(31)	97.3(2)
N(1)–Nb(1)–N(2)	118.6(1)	N(3)–Nb(2)–N(4)	115.3(2)
N(1)–Nb(1)–C(13)	99.3(2)	N(3)–Nb(2)–C(31)	98.6(2)
N(2)–Nb(1)–C(13)	107.0(2)	N(4)–Nb(2)–C(31)	108.7(2)
Nb(1)–N(1)–Si(1)	123.5(2)	Nb(2)–N(3)–Si(5)	125.4(2)
Nb(1)–N(1)–Si(2)	118.3(2)	Nb(2)–N(3)–Si(6)	113.5(2)
Nb(1)–N(2)–Si(3)	109.1(2)	Nb(2)–N(4)–Si(7)	110.1(2)
Nb(1)–N(2)–Si(4)	127.1(2)	Nb(2)–N(4)–Si(8)	126.7(2)
Si(1)–N(1)–Si(2)	118.2(3)	Si(5)–N(3)–Si(6)	121.1(2)
Si(3)–N(1)–Si(4)	121.8(2)	Si(7)–N(4)–Si(8)	120.6(2)

niobium compounds.<sup>8–11</sup> The Nb–N distances are similar to those in  $[\text{NbBr}_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  [1.957(4) Å],<sup>5</sup>  $\text{Nb}(\text{NMe}_2)_5$  [av.

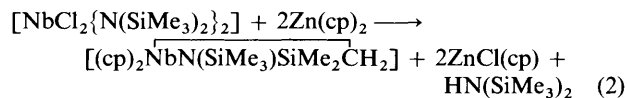
† Non-SI unit employed:  $\mu_B \approx 9.27402 \times 10^{-24} \text{ J T}^{-1}$ .

2.04 (15) Å] and Nb(NC<sub>5</sub>H<sub>10</sub>)<sub>5</sub> [av. 2.05(14) Å]<sup>12</sup> and the Si–N distances [av. 1.766(4) Å] are close to those in [NbBr<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] [av. 1.776(4) Å],<sup>5</sup> [TaCl<sub>3</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] [1.785–1.826(7) Å]<sup>13</sup> and [MCl{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>] [M = Ti, Zr or Hf; 1.759(12)–1.793(11) Å].<sup>14</sup> The Nb–C(phenyl) distances are significantly shorter than the Nb–C(alkyl) distances in [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>] [av. 2.304(3) Å],<sup>15</sup> [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Et(η-C<sub>2</sub>H<sub>4</sub>)] [2.316(8) Å]<sup>16</sup> and [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(=NBu<sup>t</sup>)(σ-C<sub>5</sub>H<sub>5</sub>)] [2.330(3) Å].<sup>17</sup> This can be attributed to the greater carbon 2s orbital character in the Nb–phenyl bond.

The amide nitrogen atoms in [NbCl{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Ph] are planar, but there are two significantly different Nb–N–Si angles, one greater than 120° and the other less. Similar ligand distortions were also observed in [TaCl<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] and the dimer [{TaCl(μ-NSiMe<sub>3</sub>)[N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>],<sup>18</sup> but [NbBr<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] is relatively undistorted.<sup>5</sup> Apparently the potential energy curve for bending the M–N–Si angles is shallow, allowing weak steric interactions to set the angle. The N–Nb–N/Cl–Nb–C planes are not mutually perpendicular (av. 78°), resulting in sets of large and small N–Nb–C and N–Nb–Cl angles. A similar 'C<sub>2</sub>' distortion was observed in [NbBr<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>], where the NbBr<sub>2</sub> and the NbN<sub>2</sub> planes are at an angle of 81°.<sup>5</sup>

### Synthesis and characterization of [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>]

In an attempt to prepare a σ-C<sub>5</sub>H<sub>5</sub> compound,<sup>17</sup> [NbCl<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>] was treated with two equivalents of Zn(cp)<sub>2</sub>. The complex [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>], presumably a result of amido-ligand γ-hydrogen-bond activation [equation (2)], was the only product that could be isolated.



In the <sup>1</sup>H NMR spectrum of [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>] (C<sub>6</sub>D<sub>6</sub>), only a single broad resonance centred around δ 1.2 is observed. The Evans' NMR method gives a room-temperature magnetic moment of 0.53 μ<sub>B</sub>. For comparison, the magnetic moments of [NbMe<sub>2</sub>(cp)<sub>2</sub>] and [TaMe<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>Me)<sub>2</sub>] are reported to be 1.5 and 1.1 μ<sub>B</sub>, respectively.<sup>19</sup>

A thermal ellipsoid plot from the crystal structure of [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>] is shown in Fig. 2 and selected bond distances and angles are given in Table 2.

The Nb–N and Nb–C(11) distances in the metallaheterocyclic ring are substantially longer than the Nb–N and Nb–C bond distances in [NbCl{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Ph]. The Nb–C(11) distance is close, however, to the Nb–C(alkyl) distances in [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>] [av. 2.304(3) Å],<sup>15</sup> [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Et(η-C<sub>2</sub>H<sub>4</sub>)] [2.316(8) Å]<sup>16</sup> and [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(=NBu<sup>t</sup>)(σ-C<sub>5</sub>H<sub>5</sub>)] [2.330(3) Å].<sup>17</sup>

The niobium cyclopentadienyl centroid distances and the cp–Nb–Cp angle are normal<sup>17</sup> and the C(11)–Nb–N angle is only slightly smaller than the analogous C–Nb–C angle in [Nb(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CH<sub>2</sub>Ph)<sub>2</sub>] [av. of two independent molecules: 79°].<sup>15</sup> The metallacycle ring in [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>] is essentially planar with the largest deviation being 0.03 Å, and the cp–Nb–cp and metallacycle planes are perpendicular [90.5(4)°].

### Conclusion

The niobium(IV) amidophenyl compound [NbCl{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Ph] was prepared in moderate yield by the reaction of ZnPh<sub>2</sub> with [NbCl<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]. A structure determination of [NbCl{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Ph] reveals it has a distorted tetrahedral geometry similar to [NbBr<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]. The compound

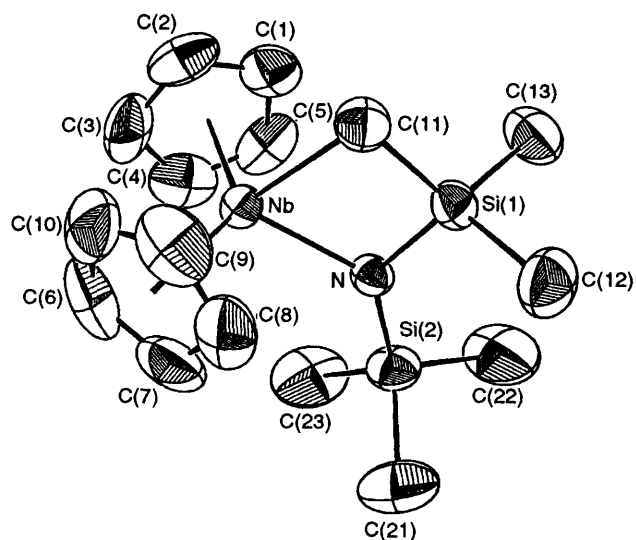


Fig. 2 Molecular structure of [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>] (50% probability ellipsoids)

Table 2 Selected bond distances (Å) and angles (°) for [(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>]

Nb–N	2.120(4)	N–Si(1)	1.717(4)
N–Si(2)	1.696(5)	Nb–C(11)	2.277(6)
Nb–cp(1) <sub>cent</sub>	2.113(8)	Nb–cp(2) <sub>cent</sub>	2.111(8)
N–Si(1)–C(11)	97.8(2)	N–Si(2)–C(21)	112.9(3)
N–Si(1)–C(12)	112.3(3)	N–Si(2)–C(22)	111.4(3)
N–Si(1)–C(13)	113.4(2)	N–Si(2)–C(23)	112.0(3)
C(11)–Si(1)–C(12)	113.7(3)	Nb–N–Si(1)	97.9(2)
C(11)–Si(1)–C(13)	112.6(3)	Nb–N–Si(2)	133.2(2)
C(12)–Si(1)–C(13)	107.1(3)	Si(1)–N–Si(2)	128.8(3)
Nb–C(11)–Si(1)	89.5(2)	C(11)–Nb–N	74.8(2)
cp(1) <sub>cent</sub> –Nb–cp(2) <sub>cent</sub>	132.4(3)	cp(1) <sub>cent</sub> –Nb–N	109.9(2)
cp(2) <sub>cent</sub> –Nb–N	111.6(2)	cp(1) <sub>cent</sub> –Nb–C(11)	106.3(2)
cp(2) <sub>cent</sub> –Nb–C(11)	106.3(2)		

cp(1)<sub>cent</sub> and cp(2)<sub>cent</sub> are the centroids of the C(1)–C(5) and C(6)–C(10) rings respectively.

[(cp)<sub>2</sub>NbN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>], which has a planar metallaheterocyclic ring, was prepared by the reaction of Zn(cp)<sub>2</sub> with [NbCl<sub>2</sub>{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]. An analogous compound is known for titanium [(cp)<sub>2</sub>TiN(SiMe<sub>3</sub>)SiMe<sub>2</sub>CH<sub>2</sub>], which was prepared by the reaction of [TiCl<sub>2</sub>(cp)<sub>2</sub>] with 2 equivalents of LiN(SiMe<sub>3</sub>)<sub>2</sub>.<sup>20</sup> The structure of the titanium complex was proposed on the basis of spectroscopic studies. Other examples of organometallic niobium or tantalum amido compounds are [TaBr(NMe<sub>2</sub>)<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>Me-p)], [Ta(NMe<sub>2</sub>)<sub>4</sub>R] (R = Bu<sup>t</sup>, Pr<sup>i</sup>, Et and CH<sub>2</sub>SiMe<sub>3</sub>)<sup>21</sup> and [Nb(NMe<sub>2</sub>)<sub>3</sub>(cp)]<sup>3</sup>.

### Experimental

#### General techniques and reagents

All manipulations were carried out in a nitrogen-filled glove box or by using standard Schlenk techniques. The solvents diethyl ether and hexane were distilled from sodium–benzophenone and then stored in the dry-box over 4 Å molecular sieves. The compounds [NbCl<sub>4</sub>(thf)<sub>2</sub>] (thf = tetrahydrofuran),<sup>19</sup> ZnPh<sub>2</sub>,<sup>22</sup> and Zn(cp)<sub>2</sub> were synthesized by literature methods,<sup>23</sup> and LiN(SiMe<sub>3</sub>)<sub>2</sub> was purchased from Aldrich.

Elemental analyses were performed by Oneida Research Services, Whitesboro, NY. Infrared spectra were obtained for Nujol mulls between KBr plates in the 500–4000 cm<sup>-1</sup> range on a Mattson Galaxy 5000 FTIR. NMR spectra were collected on a GE 300 MHz instrument. Chemical shifts were internally

referenced to the residual protons in the solvent. Magnetic susceptibilities were determined for  $C_6D_6$  solutions at room temperature by the Evans' method using tetramethylsilane as the standard.

### Preparations

**Bis[bis(trimethylsilyl)amido]chloro(phenyl)niobium.** In the glove box,  $LiN(SiMe_3)_2$  (0.44 g, 2.6 mmol) was slowly added to a yellow suspension of  $[NbCl_4(thf)_2]$  (0.50 g, 1.3 mmol) in hexane–diethyl ether (2:1, 20 cm<sup>3</sup>). The solution was left to stir for 30 min during which time the colour of the solution turned to the characteristic blue colour of  $[NbCl_2\{N(SiMe_3)_2\}_2]$ . The solution was then filtered through Celite. To the blue filtrate,  $ZnPh_2$  (0.28 g, 1.3 mmol) was slowly added. The colour of the solution turned dark green after stirring for ca. 1 h. The solution was stripped to dryness, and the residue was extracted with hexane (1 × 15 cm<sup>3</sup>). The extract was filtered through Celite. On reducing the volume of the green filtrate to ca. 5 cm<sup>3</sup>, a white precipitate formed. The green liquid was separated from the precipitate by using a glass pipette, transferred to another flask and cooled to –35 °C. After 24 h dark green plates formed, which were isolated by removing the mother-liquor with a glass pipette. Yield, 0.38 g (55%) (Found: C, 40.85; H, 7.35; N, 4.70.  $C_{18}H_{41}ClN_2NbSi_4$  requires C, 41.0; H, 7.85; N, 5.30%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  2.7 (br). IR (cm<sup>-1</sup>): 1562w, 1253s, 860s, 785s, 765m, 696s, 667s and 617w.

**The metallacycle  $[(cp)_2NbN(SiMe_3)SiMe_2CH_2]$ .** In the glove box,  $LiN(SiMe_3)_2$  (0.44 g, 2.6 mmol) was slowly added to a yellow suspension of  $[NbCl_4(thf)_2]$  (0.50 g, 1.3 mmol) in hexane–diethyl ether (2:1, 20 cm<sup>3</sup>). The solution was left to stir for 30 min during which time the colour of the solution turned blue. The solution was then filtered through Celite. To the blue filtrate  $Zn(cp)_2$  (0.51 g, 2.6 mmol) was slowly added. The colour of the solution turned brown after stirring for ca. 2 h. The solution was then stripped to dryness, and the residue was extracted with hexane (1 × 15 cm<sup>3</sup>). The extract was filtered through Celite. On reducing the volume of the brown filtrate to ca. 5 cm<sup>3</sup>, a white precipitate formed. The brown liquid was separated from the precipitate with a glass pipette, transferred to another flask, and then cooled to –35 °C. After 24 h brown needles formed, which were isolated by removing the mother-liquor with a glass pipette. Yield, 0.18 g (36%) (Found: C, 49.85; H, 7.05; N, 3.45.  $C_{16}H_{27}NNbSi_2$  requires C, 50.25; H, 7.10; N, 3.65%). <sup>1</sup>H NMR ( $C_6D_6$ ):  $\delta$  1.2 (br). IR (cm<sup>-1</sup>): 1242s, 1001s, 866s, 841s, 798s, 756m, 694w, 669m, 617w and 597w.

### Crystal structure determination of $[NbCl\{N(SiMe_3)_2\}_2Ph] \cdot 0.25C_6H_{14}$

**Crystal data.**  $C_{18}H_{41}ClN_2NbSi_4 \cdot 0.25C_6H_{14}$ ,  $M = 547.88$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.200(2)$ ,  $b = 11.382(4)$ ,  $c = 26.557(6)$  Å,  $\alpha = 85.76(2)$ ,  $\beta = 80.64(2)$ ,  $\gamma = 74.78(2)^\circ$ ,  $U = 2934$  Å<sup>3</sup>,  $T = -50$  °C, Mo-K $\alpha$  ( $\lambda = 0.71073$  Å),  $Z = 4$ ,  $D_c = 1.24$  g cm<sup>-3</sup>,  $F(000) = 1156$ ,  $\mu = 6.53$  cm<sup>-1</sup>. Crystal size 0.5 × 0.5 × 0.1 mm.

**Data collection.** The air-sensitive dark green plates were manipulated under mineral oil. Nicolet R3 four-circle diffractometer equipped with a LT-1 low-temperature device,  $\omega$  mode with scan width  $\Delta\theta = 1.25 + (K\alpha_2 - K\alpha_1)^\circ$ , scan-speed range 1.5–15.0° min<sup>-1</sup>, graphite-monochromated Mo-K $\alpha$  radiation; 6264 reflections measured ( $4 \leq 2\theta \leq 42^\circ$ ;  $\pm h$ ,  $\pm k$ ,  $l$ ), 5512 independent with  $I > 3\sigma(I)$ . Lorentz and polarization corrections were applied; however, no correction for absorption was made due to the small absorption coefficient. Two standard reflections were measured every 2 h or after every 100 data collected, and these showed no significant variation.

**Structure solution and refinement.** The Laue symmetry was determined to be  $\bar{1}$  and the space group was shown to be either  $P1$  or  $P\bar{1}$ ; because the unitary factors displayed centric statistics, space group  $P\bar{1}$  was assumed to be correct from the beginning. The structure was solved by interpretation of the Patterson map, which revealed the positions of both Nb atoms in the asymmetric unit. Remaining atoms were found in subsequent Fourier-difference syntheses. A molecule of hexane solvent was also located, situated about an inversion centre. The hydrogen atoms were placed in calculated positions and constrained to riding motion, with a single variable isotropic thermal parameter for all of them. After all the shift/e.s.d. ratios were less than 0.1 (except for the rigid bodies) convergence was reached with  $R$ ,  $R' = 0.032$ , 0.036 (goodness-of-fit = 3.3). The weighting scheme was  $w = [\sigma(F)]^{-2}$ . No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference-density map showed a maximum peak of about 0.50 e Å<sup>-3</sup>. All calculations were made using the SHELXTL PLUS package of programs.<sup>24</sup>

### Crystal structure determination of $[(cp)_2NbN(SiMe_3)SiMe_2CH_2]$

**Crystal data.**  $C_{16}H_{27}NNbSi_2$ ,  $M = 382.48$ , monoclinic, space group  $P2_1/c$ ,  $a = 14.5702(9)$ ,  $b = 9.7654(7)$ ,  $c = 14.039(1)$  Å,  $\beta = 109.838(6)^\circ$ ,  $U = 1879.0(3)$  Å<sup>3</sup>,  $T = 23$  °C, Mo-K $\alpha$  ( $\lambda = 0.71073$  Å),  $Z = 4$ ,  $D_c = 1.35$  g cm<sup>-3</sup>,  $F(000) = 796$ ,  $\mu = 7.31$  cm<sup>-1</sup>. Crystal size 0.08 × 0.10 × 0.42 mm.

**Data collection.** A brown rod-shaped crystal was mounted in a 0.7 mm outside-diameter Lindemann capillary under nitrogen. Enraf-Nonius CAD-4 diffractometer,  $\theta$ – $2\theta$  scan mode with scan width  $\Delta\theta = 0.8 + 0.35 \tan \theta$ , scan-speed range 0.67–8° min<sup>-1</sup>, graphite-monochromated Mo-K $\alpha$  radiation; 2565 reflections measured ( $2 \leq 2\theta \leq 44^\circ$ ;  $h$ ,  $k$ ,  $\pm l$ ), 2464 unique ( $R_{int} = 0.021$ ), 1539 observed with  $I > 3\sigma(I)$ . Lorentz and polarization corrections were applied. Three standard reflections were measured every 3600 s and these showed no significant variation.

**Structure solution and refinement.** The structure was solved by interpretation of the Patterson map, which revealed the position of the Nb atom. Remaining atoms were found in subsequent Fourier-difference syntheses. Hydrogen atoms were located on a difference map, their geometries idealized, and allowed to ride on the appropriate carbon atom [ $U(H) = 1.3U_{eq}(C)$ ]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Convergence was reached with  $R$ ,  $R' = 0.0313$ , 0.0376 (goodness-of-fit = 1.20). The weighting scheme was  $w = [0.03F^2 + (\sigma F)^2]^{-1}$ . The final difference map showed a maximum peak of about 0.35 e Å<sup>3</sup> near Nb. All calculations were made using the MolEN package of programs.<sup>25</sup>

Atomic coordinates, thermal parameters, and bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/11.

### Acknowledgements

Acknowledgement for support is made to the Petroleum Research Fund, administered by the American Chemical Society, and the Robert A. Welch Foundation. D. M. H. is a Alfred P. Sloan Research Fellow (1992–1994). We are grateful to J. Korp for his technical assistance with the X-ray crystallographic analysis of  $[NbCl\{N(SiMe_3)_2\}_2Ph]$  and his helpful discussions.

## References

- 1 D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, 1962, **40**, 449.
- 2 D. C. Bradley and M. H. Chisholm, *J. Chem. Soc. A*, 1971, 1511.
- 3 A. D. Jenkins, M. F. Lappert and R. C. Srivastava, *J. Organomet. Chem.*, 1970, **23**, 165.
- 4 D. M. Hoffman and S. P. Rangarajan, *Polyhedron*, 1993, **12**, 2899.
- 5 S. G. Bott, D. M. Hoffman and S. P. Rangarajan, *Inorg. Chem.*, 1995, **34**, 4305.
- 6 D. F. Evans, *J. Chem. Soc.*, 1959, 2003.
- 7 D. H. Live and S. I. Chan, *Anal. Chem.*, 1970, **42**, 791.
- 8 A. Zalkin and D. E. Sands, *Acta Crystallogr.*, 1958, **11**, 615.
- 9 W. Clegg, R. J. Errington, D. C. R. Hockless and C. Redshaw, *Polyhedron*, 1991, **10**, 1959.
- 10 A. N. Chernega, M. L. H. Green and A. G. Suárez, *J. Chem. Soc., Dalton Trans.*, 1993, 3031.
- 11 F. A. Cotton, S. A. Duraj and W. J. Roth, *J. Am. Chem. Soc.*, 1984, **106**, 4749.
- 12 C. Heath and M. B. Hursthouse, *J. Chem. Soc., Chem. Commun.*, 1971, 143.
- 13 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik and G. B. C. Vuru, *Inorg. Chim. Acta*, 1980, **44**, L5.
- 14 C. Airoldi, D. C. Bradley, H. Chudzynska, M. B. Hursthouse, K. M. A. Malik and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 2010.
- 15 P. B. Hitchcock, M. F. Lappert and C. R. C. Milne, *J. Chem. Soc., Dalton Trans.*, 1981, 180.
- 16 L. J. Guggenberger, P. Meakin and F. N. Tebbe, *J. Am. Chem. Soc.*, 1974, **96**, 5420.
- 17 M. L. H. Green, D. M. Michaelidou, P. Mountford, A. G. Suárez and L.-L. Wong, *J. Chem. Soc., Dalton Trans.*, 1993, 1593.
- 18 D. M. Hoffman and S. Suh, *J. Chem. Soc., Chem. Commun.*, 1993, 714.
- 19 L. E. Manzer, *Inorg. Chem.*, 1977, **16**, 525.
- 20 C. R. Bennett and D. C. Bradley, *J. Chem. Soc., Chem. Commun.*, 1974, 29.
- 21 M. H. Chisholm, L.-S. Tan and J. C. Huffman, *J. Am. Chem. Soc.*, 1982, **104**, 4879.
- 22 S. Cai, D. M. Hoffman and D. A. Wierda, *Organometallics*, 1996, **15**, 1023.
- 23 J. Lorberth, *J. Organomet. Chem.*, 1969, **19**, 189.
- 24 G. M. Sheldrick, SHELXTL PLUS, Release 3.4 for the Nicolet R3m/v Crystallographic System, Nicolet Instrument Corp., Madison, 1987.
- 25 MolEN, An Interactive Structure Solution Program, Enraf-Nonius, Delft, 1990.

Received 1st November 1995; Paper 5/07207G