

Synthesis and characterization of perhalogenated diazaphosphametalletidines containing transition metals from group 4 and 5 †

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The preparation and characterization of the novel perhalogenated diazaphosphametalletidines, $\text{Cl}_3\text{M}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$, $\text{M} = \text{Ti, Zr and Hf}$ **2–4** and $\text{Cl}_4\text{Nb}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **5** are reported. In addition, a new high yield preparation of the previously synthesized metallacycle $\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **1** is described. All reported complexes were synthesized by [3 + 1] cyclocondensation reactions involving the aminoiminophosphorane, $(\text{Me}_3\text{Si})_2\text{NPCl}_2=\text{NSiMe}_3$, and corresponding metal halides in dichloromethane. When 2.5 equivalents of $(\text{Me}_3\text{Si})_2\text{NPCl}_2=\text{NSiMe}_3$ were reacted with NbCl_5 a complex series of products was identified by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy; crystals of the unusual heterocycles $[\text{Cl}_3\text{Nb}\{\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}\}_2\text{Cl}_2\text{Nb}\{\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)\}]$ **6** and $[\text{Cl}_2\text{Nb}\{\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)\}]_2\text{-}\mu\text{-Cl}(\text{NPCl}_2\text{N})$ **7** were isolated. Complex **7** contains the first example of a ClNbNPNb six-membered ring. Structural characterization by single-crystal X-ray diffraction is also reported for metallacycles **2, 3, and 5–7**.

Introduction

Heterocycles containing transition metals and main group elements are of interest from a structural perspective¹ and also as a result of their novel reactivity² and potential uses in catalysis,³ and as monomers for ring-opening polymerization (ROP) reactions.⁴ For example, we and others have shown that various cyclic heterophosphazenes readily undergo ring-opening polymerization to give new classes of inorganic polymers.^{5–9}

As part of our studies in this area we recently described the synthesis and reaction chemistry of perhalogenated acyclic and metallacyclic tantalum(v) phosphazenes.¹⁰ It was shown that treatment of the tantalum diazaphosphametalletidine, $\text{Cl}_3\text{-Ta}(\text{N}=\text{PCl}_2)[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$, with HCl produced the novel linear phosphazanium salt $[\text{N}(\text{PCl}_2\text{NH}_2)_2][\text{TaCl}_6]$, a potential synthon for the synthesis of other inorganic heterocycles. This reaction represents a formal coupling of a phosphoraniminato ligand ($\text{N}=\text{PCl}_3$) with a NPN chelate and further illustrates the chemical versatility of heterophosphazene rings.

This paper reports some of our related work on the synthesis of group 4 and 5 diazaphosphametalletidines *via* a [3 + 1] cyclocondensation reaction of various metal halides with the *N,N,N'*-tris(trimethylsilyl)dichloroaminoiminophosphorane, $(\text{Me}_3\text{Si})_2\text{NPCl}_2=\text{NSiMe}_3$.

Results and discussion

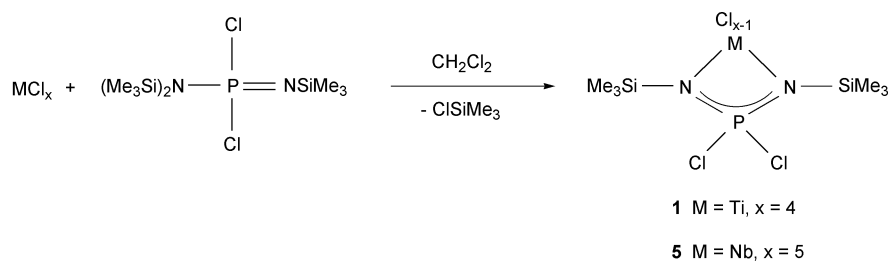
Synthesis and characterization of the perhalogenated titanium diazaphosphametalletidines, $\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **1** and $\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$ **2**

Roesky and coworkers have recently reported the synthesis of $\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **1** in a 58% yield by *in vacuo* condensation of Cl_2 and TiCl_4 onto a CFCl_3 solution of $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ at -196°C .¹¹ We have found that **1** can also be synthesized in a 83% yield by reacting a 1.0 M solution

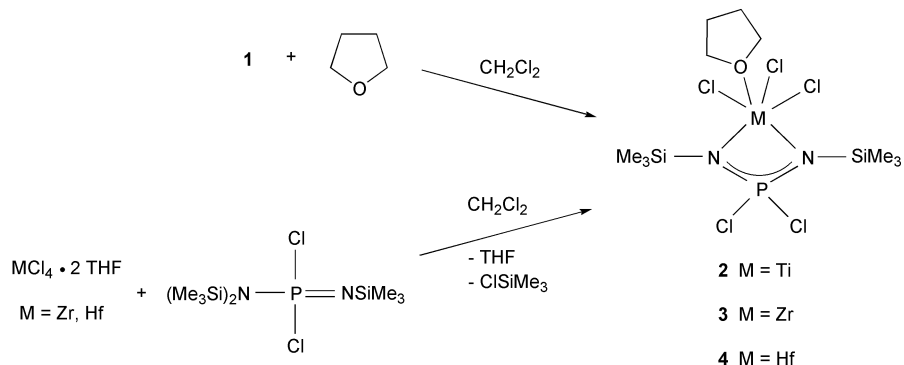
of TiCl_4 in CH_2Cl_2 with a solution of $(\text{Me}_3\text{Si})_2\text{NPCl}_2=\text{NSiMe}_3$ at -78°C (Scheme 1): this more convenient method obviates the use of corrosive chlorine gas and difficult experimental techniques. Characterization of **1**, a yellow solid, was achieved using NMR and IR spectroscopy, mass spectrometry and a melting point determination; this data was comparable to that previously reported.¹¹ In addition we found that the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** gave a doublet at 1.9 ppm ($^3J_{\text{PC}} = 5$ Hz) which was also consistent with the assigned structure.

Despite numerous attempts, crystals of **1** suitable for single-crystal X-ray diffraction could not be obtained. In order to facilitate crystal growth and subsequent structural characterization of the titanium metallacycle by X-ray crystallography, one equivalent of THF was added to a solution of **1** in CH_2Cl_2 . Upon the addition of the coordinating THF, a new singlet resonance was observed when the reaction mixture was analyzed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy ($\delta = 13.1$ ppm). This resonance was shifted upfield when compared to the resonance associated with **1** ($\delta = 17.4$ ppm) indicating the formation of the new THF adduct $\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$ **2** (Scheme 2). Additional support for the assigned structure was obtained by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The ^1H NMR spectrum displayed a singlet resonance at $\delta = 0.42$ ppm, attributable to the SiMe_3 protons of the ring, and two multiplet resonances centered at $\delta = 2.08$ and 4.37 ppm which were assigned to the two methylene environments of the THF ligand. Furthermore, integration of these signals produced a 9 : 2 : 2 ratio, consistent with the presence of one molecule of THF coordinated to each titanium center. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2** also indicated the presence of coordinated THF with two signals observed for the THF ligand at 25.8 and 75.8 ppm (downfield compared to free THF), and a doublet at 1.9 ppm ($^3J_{\text{PC}} = 5$ Hz) due to the trimethylsilyl (SiMe_3) carbons. Further characterization of **2** was provided by a single-crystal X-ray diffraction study involving crystals which were grown from a 1 : 1 CH_2Cl_2 -hexanes solution at -30°C . The molecular structure of **2** is shown in Fig. 1. Table 1 contains relevant X-ray data collection and refinement parameters for **2**, while Table 2 lists selected bond lengths and angles within **2**.

† Electronic supplementary information (ESI) available: molecular structure of **3**. See <http://www.rsc.org/suppdata/dt/b1/b109905c/>



Scheme 1 Syntheses of complexes 1 and 5.



Scheme 2 Syntheses of complexes 2–4.

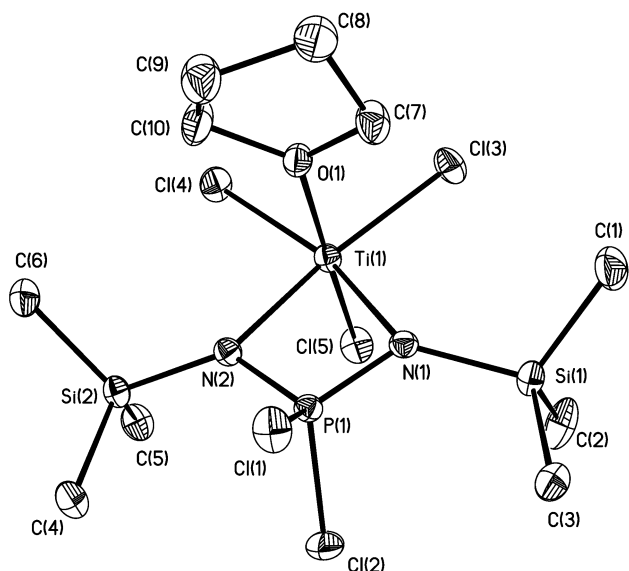


Fig. 1 Molecular structure of **2** with thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity.

The geometry about the titanium center in **2** can be described as distorted octahedral with the THF ligand and a chlorine atom occupying the two axial positions, while two chlorine and two nitrogen atoms (NPN chelate) occupy the remaining equatorial positions about the titanium center. The Ti–N bond lengths in **2** [2.0978(15) Å avg.] were slightly longer than those of previously reported four-membered TiNPN chelates: e.g. 2.066(4) Å avg. for the P–CCl₃ substituted chelate, Cl₃Ti–[N(SiMe₃)P(CCl₃)CIN(SiMe₃)],¹¹ and 2.030(3) Å avg. for the P–Ph substituted species, Cl₃Ti[N(SiMe₃)PPh₂N(SiMe₃)]·CH₃CN.¹² The P–N bond lengths in **2** [1.581(2) Å avg.] were also similar to those in other TiNPN rings and suggest significant π-electron density within the N–P–N moiety. For comparison, typical P–N single bonds range from 1.69 to 1.72 Å,¹³ while the phosphorus–nitrogen double bonds in the chlorophosphazene cation, [Cl₃P=N=P(Cl)₃]⁺, range between 1.51 and 1.56 Å.¹⁴ The bite angle of the NPN chelate was found to be 72.73(6)° (*endo* NTiN) and is similar to those found in other known four-membered metallaphosphazene rings.

Synthesis and characterization of Cl₃Zr[N(SiMe₃)PCl₂–N(SiMe₃)]·THF **3** and Cl₃Hf[N(SiMe₃)PCl₂–N(SiMe₃)]·THF **4**

Initial attempts to react (Me₃Si)₂NPCl₂=NSiMe₃ with either ZrCl₄ or HfCl₄ in CH₂Cl₂ gave complicated reaction mixtures from which no well-defined compounds could be extracted. We then selected the CH₂Cl₂ soluble THF adducts, ZrCl₄·2THF and HfCl₄·2THF as precursors with the goal of obtaining soluble, crystallizable metallacycles analogous to the titanium heterocycle **2** described above.

When (Me₃Si)₂NPCl₂=NSiMe₃ was allowed to react with one equivalent of ZrCl₄·2THF and HfCl₄·2THF in CH₂Cl₂, new products were observed by ³¹P{¹H} NMR spectroscopy at 11.8 and 12.4 ppm, respectively. These resonances were considerably shifted from that of the starting phosphoranimine, (Me₃Si)₂NPCl₂=NSiMe₃ (δ = –23.0 ppm) and were consistent with the formation of metallacycles Cl₃Zr[N(SiMe₃)PCl₂–N(SiMe₃)]·THF **3** and Cl₃Hf[N(SiMe₃)PCl₂–N(SiMe₃)]·THF **4** (Scheme 2). Work-up of the reactions afforded white moisture-sensitive solids in moderate yields (67% for **3**; 70% for **4**). The ¹H and ¹³C{¹H} NMR of **3** and **4** were similar to the Ti analogue **2** with resonances observed for the SiMe₃ groups and the THF ligands. Furthermore, integration of the ¹H NMR signals revealed that one molecule of THF was coordinated to each metal site in both **3** and **4**. Crystals of **3** (colorless needles) suitable for a single-crystal X-ray diffraction study were grown from a 3 : 1 CH₂Cl₂–hexanes solution at –30 °C. The molecular structure of **3** is quite similar to **2**, therefore the ORTEP diagram of **3** has been included as ESI†. A summary of crystal data, intensity collection parameters, and structural refinement data can be found in Table 1, while Table 2 contains selected bond lengths and angles for **3**. Due to the similar nature of **4**, an X-ray diffraction study was not performed on this compound.

As mentioned, the molecular structure of **3** mimics that of the Ti analogue with a single THF molecule coordinated to the Zr center. A similar coordination geometry is also observed within the CH₃CN adduct of the P–Ph substituted zirconium metallacycle, Cl₃Zr[N(SiMe₃)PPh₂N(SiMe₃)]·NCCH₃, synthesized by Roesky and coworkers.¹⁵ The Zr–N bond lengths in **3** [2.2337(13) Å avg.] were found to be significantly longer than the Ti–N bond lengths in **2** [2.0978(15) Å avg.]. In addition, the Zr–N bonds within **3** were longer than in other reported ZrNPN rings: e.g. 2.187(19) Å avg. for Cl₃Zr[N(SiMe₃)P(OMe)₂–

Table 1 Crystal data, data and intensity collection parameters, and least squares parameters for **2**, **3**, and **5**

	2	3	5
Empirical formula	C ₁₀ H ₂₆ Cl ₅ N ₂ OPSi ₂ Ti	C ₁₀ H ₂₆ Cl ₅ N ₂ OPSi ₂ Zr	C ₆ H ₁₈ Cl ₆ N ₂ NbPSi ₂
<i>M</i>	502.63	545.95	510.98
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁
<i>a</i> /Å	10.0677(3)	10.1372(4)	9.3280(9)
<i>b</i> /Å	14.8866(5)	15.1405(8)	8.7650(8)
<i>c</i> /Å	15.0835(4)	15.1927(8)	12.4990(12)
β /deg	105.576(2)	104.642(3)	104.679(4)
<i>V</i> /Å ³	2177.60(11)	2256.08(19)	988.56(16)
<i>Z</i>	4	4	2
μ (Mo K α)/mm ⁻¹	1.191	1.258	1.608
θ range/deg	2.58–27.50	2.57–30.07	2.87–25.06
No. of reflns colld	17345	30447	5845
No. of indep reflns/ <i>R</i> _{int}	4952/0.030	6514/0.026	2963/0.067
<i>T</i> /K	150(1)	110(1)	150(2)
No. of refined params	205	205	171
<i>R</i> (%) (<i>I</i> > 2 σ [<i>I</i>]) ^a	2.80	2.65	4.31
<i>R</i> _w (%) ^b	6.75	5.94	10.83

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

N(SiMe₃)₂·NCCH₃,¹¹ 2.178(4) Å avg. for Cl₃Zr[N(SiMe₃)₂·PPh₂N(SiMe₃)₂·NCCH₃].¹⁵ The P–N bond lengths in **3** were determined to be 1.5798(14) and 1.5847(14) Å and are typical for diazaphosphametallidines incorporating phosphorus(v) centers.

Reaction of NbCl₅ with one equivalent of (Me₃Si)₂NPCl₂=NSiMe₃: synthesis and characterization of Cl₄Nb[N(SiMe₃)₂PCl₂-N(SiMe₃)] **5**

In order to complete our study of group 4 and 5 perhalogenated phosphazene metallacycles, we investigated the synthesis of a Nb analogue and compared its structural characteristics to both **2** and **3**, and to the previously reported Ta derivative, Cl₄Ta[N(SiMe₃)₂PCl₂N(SiMe₃)].¹⁰

Reaction of NbCl₅ with one equivalent of (Me₃Si)₂NPCl₂=N-SiMe₃ in CH₂Cl₂ produced a new product observable in the ³¹P{¹H} NMR spectrum (δ = 22.0 ppm) after 24 h. A bright yellow solid was isolated and characterized by multinuclear NMR, IR, elemental analysis, melting point and a single-crystal X-ray diffraction study.

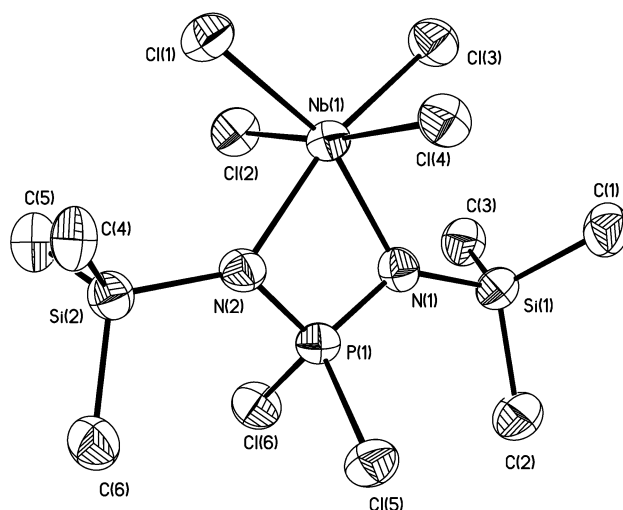
The NMR spectra of **5** were consistent with the formation of a NbNPN four-membered ring with a singlet resonance observed in the ¹H NMR at 0.57 ppm attributable to the SiMe₃ protons, and a doublet at 1.6 ppm in the ¹³C{¹H} NMR spectrum (³*J*_{PC} = 5 Hz) associated with the trimethylsilyl carbons. Unlike the Ta, Ti and Zr analogues, **5** proved too involatile for conventional mass spectrometry, hence no identifiable mass fragments were observed. Conclusive structural evidence for the presence of a monomeric NbNPN heterocycle was obtained by a single-crystal X-ray crystallographic study performed on yellow needles of **5** grown from a 1 : 1 CH₂Cl₂–hexanes solution (–30 °C). The molecular structure of **5** is shown as Fig. 2. Table 1 contains a summary of crystal data, intensity collection parameters, and structural refinement data for **5**, while Table 2 lists selected bond lengths and angles within **5**.

Compound **5** is a monomeric metallacycle with similar structural features as the analogous perhalogenated TaNPN chelate, reflecting the comparable size of niobium and tantalum. The NbNPN ring within **5** is planar with N–Nb–N and N–P–N angles (*endo*) of 71.1(2) and 102.1(3)° respectively, and average Nb–N and P–N bond lengths of 2.132(9) and 1.595(8) Å. The Nb–N bond lengths are similar to the Ta–N bond within the tantalum analogue [2.117(5) Å avg.],¹⁰ and the P–N bond lengths are consistent with the presence of multiple-bond character within the N–P–N chelate. The geometry about the Nb center can be described as distorted octahedral with the

Table 2 Selected bond lengths (Å) and angles (deg) for **2** (M = Ti), **3** (M = Zr), **5** and **7** (M = Nb) with estimated standard deviations in parentheses

	2	3	5	7
M–N	2.0947(14) 2.1016(15)	2.2299(13) 2.2375(13)	2.117(7) 2.147(6)	2.102(3) 2.255(3) 1.844(2) ^a
Si–N	1.7784(14) 1.7769(15)	1.7766(14) 1.7759(13)	1.786(7) 1.790(6)	1.788(3) 1.765(3)
P–N	1.5830(15) 1.5787(14)	1.5847(14) 1.5798(14)	1.589(6) 1.601(6)	1.595(3) 1.558(3) 1.585(2) ^a
M–O	2.1766(13)	2.2651(12)		
N–M–N (<i>endo</i>)	72.73(6) 103.81(8)	68.54(5) 105.30(7)	71.1(2) 102.1(3)	69.22(9) 103.60(14) 115.93(19) ^a
M–N–P (<i>endo</i>)	91.64(7) 91.51(6)	93.00(6) 92.85(6)	94.0(3) 92.6(3)	95.95(12) 91.20(12) 154.26(16) ^a
M–N–Si (<i>exo</i>)	133.72(7) 133.20(7)	134.42(8) 134.36(8)	134.1(3) 136.0(4)	133.12(14) 136.31(14) 125.71(4) ^a
M–Cl–M				

^a Within the NbNPNNb bridge of **7**.

**Fig. 2** Molecular structure of **5** with thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity.

axial chlorine atoms [Cl(2) and Cl(4)] being further away from the Nb center [2.355(3) Å avg.] than the equatorial chlorine atoms [Cl(1) and Cl(3): 2.326(3) Å avg.]; lengthening of the axial Nb–Cl bonds can be partially attributed to the *trans* effect of the chelating nitrogen atoms of the NPN ligand.

Reaction of NbCl₅ with an excess of (Me₃Si)₂NPCl₂=NSiMe₃: synthesis of the unusual complex [Cl₃Nb{N(SiMe₃)PCl₂N}₂-Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}] 6

When NbCl₅ was reacted with 2.5 equivalents of (Me₃Si)₂NPCl₂=NSiMe₃ (in CH₂Cl₂), a complex mixture of products was detected after 16 h by ³¹P{¹H} NMR spectroscopy. Specifically, a small amount of **5** (ca. 5%) was observed (δ = 22.0 ppm in CH₂Cl₂) along with various species with NMR signals in the range 29 to 6.5 ppm (ca. 75%) and unreacted (Me₃Si)₂NPCl₂=NSiMe₃ (ca. 20%; δ = -23.0 ppm in CH₂Cl₂). Removal of the volatiles gave a dark yellow–brown residue from which a yellow solid could be isolated when the residue was washed with small amounts of hexanes. Re-crystallization of this product from CH₂Cl₂ at -30 °C gave the unexpected metallacycle [Cl₃Nb{N(SiMe₃)PCl₂N}₂-Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}] **6** (24% yield) as yellow needles. Characterization of **6** was accomplished by NMR and IR spectroscopy, mass spectrometry, melting point, elemental analysis and a single-crystal X-ray diffraction study.

The NMR spectra of **6** reflect the structural complexity of this unique bimetallic phosphazene.¹⁶ Namely, three distinct resonances (δ = 29.0, 21.0 and 20.5 ppm; 1 : 1 : 1 ratio, CH₂Cl₂) were observed in the ³¹P{¹H} NMR spectrum and could be assigned to the presence of three different NPN chelates. In addition, three distinct trimethylsilyl (SiMe₃) environments were present (¹³C{¹H} and ¹H NMR) with an intensity ratio of 1 : 1 : 2 as determined by ¹H NMR spectroscopy, and consistent with the structure of **6**. Furthermore, mass fragments attributable to loss of Cl and Me from **6** (*m/z* = 1010 and 1030 amu) were detected in the mass spectrum of this compound. Conclusive structural characterization of **6** was achieved by single-crystal X-ray diffraction and the molecular structure of **6** is depicted as Fig. 3. Table 3 lists relevant parameters associated with crystal data collection and refinement, while Table 4 contains selected bond lengths and angles within **6**.

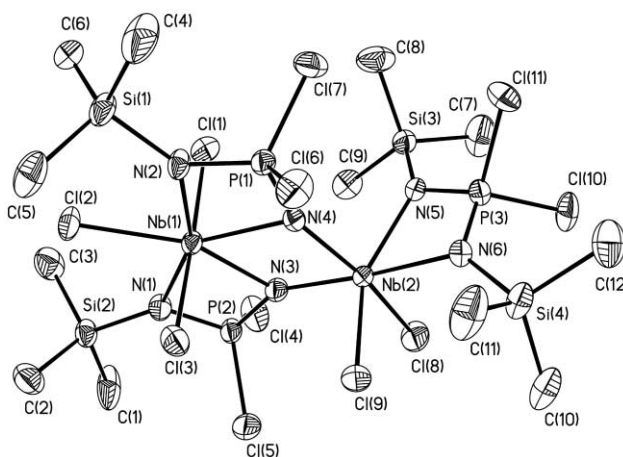
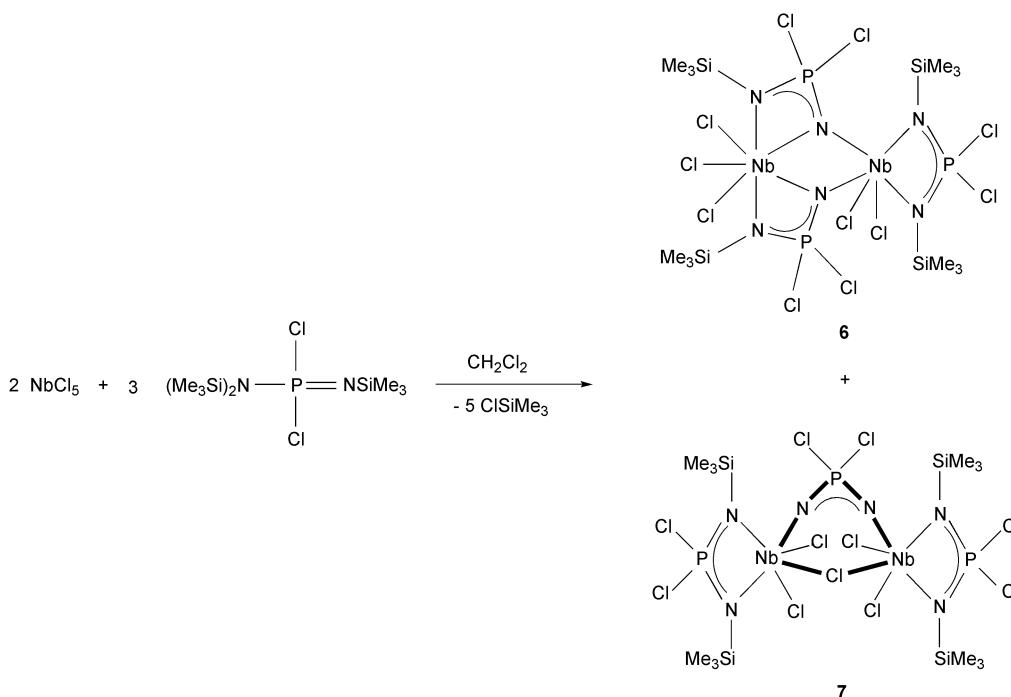


Fig. 3 Molecular structure of **6** with thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity.

The molecular structure of [Cl₃Nb{N(SiMe₃)PCl₂N}₂-Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}] **6** illustrates some of the unusual binding modes available to diazaphosphametallidene chelates.^{1a} Besides the typical MNPN chelate involving atoms Nb(2)–N(5)–P(3)–N(6) (with both nitrogen atoms silylated), the two NPN moieties about Nb(1) only have one silylated nitrogen atom per chelate [(Me₃Si)NPCl₂N] which enables μ-bonding to occur between the non-silylated nitrogen atoms [N(3) and N(4)] and two niobium centers [Nb(1) and Nb(2)]. This results in the formation of a Nb₂N₂ four-membered ring which lies at the core of **6** with long Nb(1)–N [2.188(6) Å avg.] and short Nb(2)–N [1.983(6) Å avg.] distances; the Nb–N distances within the Nb₂N₂ unit in **6** may be compared with the average Nb–N single (2.04–2.08 Å) and double (1.7–1.8 Å) bond lengths observed in various amino and imido niobium complexes.¹⁷ The geometry about Nb(2) is similar to **5** (distorted octahedral), however the adjacent niobium atom, Nb(1), lies at the center of a pentagonal bipyramid with two chlorine atoms at the axial positions [Cl(1)–Nb(1)–Cl(3) = 177.33(4)°], and two bidentate NPN chelates and a chlorine atom [Cl(2)] occupying the five remaining planar equatorial positions [angle sum of equatorial ligands about Nb(1) = 360.23(26)°]. Despite



Scheme 3 Syntheses of complexes **6** and **7**.

Table 3 Crystal data, data and intensity collection parameters, and least squares parameters for **6** and **7**

	6	7
Empirical formula	C ₁₂ H ₃₆ Cl ₁₁ N ₆ Nb ₂ P ₃ Si ₄	C ₁₂ H ₃₆ Cl ₁₁ N ₆ Nb ₂ P ₃ Si ₄
<i>M</i>	1045.51	1045.51
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	9.1891(2)	26.3658(9)
<i>b</i> /Å	24.4588(6)	10.4749(5)
<i>c</i> /Å	18.0989(5)	16.1779(7)
β /deg	98.50(3)	114.783(2)
<i>V</i> /Å ³	4023.07(17)	4056.5(3)
<i>Z</i>	4	4
μ (Mo K α)/mm ⁻¹	1.558	1.545
θ range/deg	2.66–27.44	2.58–26.06
No. of reflns collcd	28732	58454
No. of indep reflns/ <i>R</i> _{int}	9011/0.049	4004/0.038
<i>T</i> /K	150(1)	100(1)
No. of refined params	356	180
<i>R</i> (%) (<i>I</i> > 2 σ [<i>I</i>]) ^a	4.66	3.22
<i>R</i> _w (%) ^b	10.08	7.88

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, ^b R_w = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}.$$

the structural differences between the doubly- and singly-silylated NPN chelates, the MNPN (*endo*) bite angles [67.64(14), 67.76(13) and 69.06(13)°] and P–N bond lengths [1.565(4) to 1.594(4) Å] were similar for all three rings.

Formation of [Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}]₂- μ -Cl(NPCl₂N) **7**: a structural analogue to **6**

In one reaction between NbCl₅ and excess (Me₃Si)₂NPCl₂=NSiMe₃, we were able to isolate an intriguing niobium metallacycle [Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}]₂- μ -Cl(NPCl₂N) **7** as yellow crystals which were coated with an intractable brown tar that precluded conclusive characterization of **7** by spectroscopic techniques. However, one of the crystals was suitable for single-crystal X-ray diffraction and identified the product as the novel metallacycle **7**. The molecular structure of **7** is shown in Fig. 4, while Table 3 contains a summary of crystal data, inten-

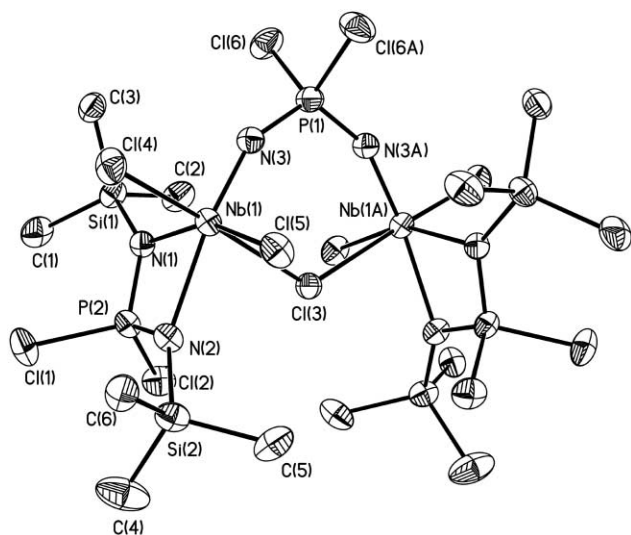


Fig. 4 Molecular structure of **7** with thermal ellipsoids at the 50% probability level. All hydrogen atoms have been omitted for clarity.

sity collection parameters, and structural refinement data for **7**. Table 2 lists selected bond lengths and angles within **7**.

The structure of **7** consists of two NbNPN four-membered rings linked by bridging Cl and NPN units in between the two niobium centers to form a previously unknown, planar ClNbNPNNb 6-membered ring. The bonding within the two NbNPN four-membered rings within **7** is comparable to the NbNPN chelates in **5** and **6**. The Nb–N bond lengths within the NbNPN rings of **7** are 2.102(3) and 2.255(3) Å, respectively,

Table 4 Selected bond lengths (Å) and angles (deg) for **6**

Nb(1)–N(1)	2.227(3)	P(1)–N(4)	1.590(4)
Nb(1)–N(2)	2.223(3)	P(2)–N(1)	1.571(4)
Nb(1)–N(3)	2.180(4)	P(2)–N(3)	1.594(4)
Nb(1)–N(4)	2.197(4)	P(3)–N(5)	1.580(4)
Nb(2)–N(3)	1.987(4)	P(3)–N(6)	1.568(4)
Nb(2)–N(4)	1.979(4)	Si(1)–N(2)	1.786(4)
Nb(2)–N(5)	2.153(4)	Si(2)–N(1)	1.793(4)
Nb(2)–N(6)	2.219(4)	Si(3)–N(5)	1.785(4)
P(1)–N(2)	1.565(4)	Si(4)–N(6)	1.786(4)
N(1)–Nb(1)–N(3)	67.64(14)	Nb(1)–N(3)–P(2)	95.79(18)
N(2)–Nb(1)–N(4)	67.91(13)	Nb(2)–N(5)–P(3)	94.52(16)
N(3)–Nb(1)–N(4)	67.76(13)	Nb(2)–N(6)–P(3)	92.36(17)
N(3)–Nb(2)–N(4)	75.95(14)	Nb(1)–N(1)–Si(2)	137.8(2)
N(5)–Nb(2)–N(6)	69.03(13)	Nb(1)–N(2)–Si(1)	129.5(2)
Nb(1)–N(3)–Nb(2)	107.90(15)	Nb(2)–N(5)–Si(3)	129.7(2)
Nb(1)–N(4)–Nb(2)	107.56(15)	Nb(2)–N(6)–Si(4)	128.9(2)
Nb(1)–N(2)–P(1)	94.39(17)	Cl(1)–Nb(1)–Cl(3)	177.33(4)
Nb(1)–N(4)–P(1)	94.67(17)	Cl(2)–Nb(1)–N(1)	78.92(10)
Nb(1)–N(1)–P(2)	94.67(18)	Cl(2)–Nb(1)–N(2)	78.00(10)

with the longest bond [Nb(1)–N(2)] located *trans* to the donating nitrogen atoms of the N(3)–P(1)–N(3A) bridging unit. The P–N bonds of the NbNPN ring are also influenced by the neighboring bridging NPN fragment, as one bond is significantly lengthened with respect to the other [N(1)–P(2) = 1.595(3) Å; N(2)–P(2) = 1.558(3) Å]. The bite angle [N(1)–Nb(1)–N(2) = 69.22(9)°] is slightly more acute in comparison with that of **5** [71.1(2)°].

The planar six-membered ClNbNPNNb ring in **7** represents the first structurally characterized example of this ring type and warrants further discussion. The Nb–N and P–N bond lengths within this ring are 1.844(2) and 1.585(2) Å, respectively, and suggest significant multiple bonding throughout the NbNPNNb framework. Consequently, the N(3)–P(1)–N(3A) angle within this moiety [115.93(19)°] is much wider than in the two adjacent NbNPN four-membered rings [N(1)–P(2)–N(2) = 103.60(14)°].

Based on the ³¹P{¹H} NMR spectrum of the reaction mixture obtained during the synthesis of **6** (see above), it appears that **7** could be one of the remaining unidentified products (*ca.* 25%, several signals between δ = 14.5 to 6.5 ppm). As illustrated in Scheme 3, complexes **6** and **7** are related by a SiMe₃ migration from a silylated nitrogen atom to a non-silylated nitrogen atom within **6**, to give the NbNPNNb moiety and the two doubly-silylated NPN chelates found in **7**. This structural relationship suggests a rational synthesis of **7** from **6** is possible, however our efforts to thermally induce a SiMe₃

rearrangement within **6** have yet to produce **7**. We are currently further exploring the chemistry of these more complex metallacycles.

Summary

Various diazaphosphametallidines containing early transition metals of group 4 and 5 have been prepared and structurally characterized. It has been shown that the group 4 derivatives crystallize with one coordinating molecule of THF to form the distorted octahedral complexes $\text{Cl}_3\text{M}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$, $\text{M} = \text{Ti}$, Zr and Hf **2–4**. The unsolvated Nb derivative, $\text{Cl}_4\text{Nb}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **5** was also synthesized and shown to possess structural and chemical features similar to the previously known tantalum analogue. In addition, the unusual metallacycles $[\text{Cl}_3\text{Nb}\{\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}\}_2\text{Cl}_2\text{Nb}\{\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)\}]$ **6** and $[\text{Cl}_2\text{Nb}\{\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)\}]_2\text{-}\mu\text{-Cl}(\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N})$ **7** were both isolated from the reaction of NbCl_5 with 2.5 equivalents of $(\text{Me}_3\text{Si})_2\text{NPCL}_2=\text{NSiMe}_3$. Compound **7** represents the first example of a structurally characterized complex containing a ClNbNPNNb ring. The reproducible isolation of significant amounts of **6** suggests that related higher order metallacycles might be synthesized in significant quantity using controlled synthetic procedures. We are currently focusing our efforts towards the isolation of compound **7** in a high yield, and the exploration of the potential chemistry of perhalogenated diazaphosphametallidines. These metallacycles should tolerate various chemical modification strategies, and thus represent possible precursors to new olefin polymerization catalysts¹⁸ and inorganic materials.

Experimental

General procedures

All reactions and manipulations were carried out strictly under an atmosphere of prepurified nitrogen (Matheson) using either Schlenk techniques or an inert atmosphere glove box (Innovative Technology). Solvents were dried and collected using a Grubbs-type solvent system manufactured by Innovative Technology.¹⁹ All reactions were carried out with solvents that had been stored under an inert atmosphere for less than 24 h. ^1H NMR spectra were obtained on a Varian Gemini 300 spectrometer (300.1 Hz) and referenced to protio impurities in the solvent. $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained using a Gemini 300 spectrometer (122.1 MHz and 75.5 MHz) and were referenced externally to 85% H_3PO_4 and SiMe_4 (TMS) in either CDCl_3 , CD_2Cl_2 or D_2O (insert). Mass spectra were obtained with the use of a VG 70–250S mass spectrometer using a 70 eV electron impact ionization source. Elemental analyses were performed by Quantitative Technologies Inc, Whitehouse, NJ. Although complexes **1–6** gave satisfactory elemental analyses for hydrogen and nitrogen content, the amount of carbon determined was consistently lower than anticipated (1–2%). This may be the result of the formation of combustion-resistant M_xC_y ceramics. Melting points (uncorrected) were obtained under a nitrogen atmosphere in flame-sealed glass capillaries (0.5 mm o.d.). Infrared spectra were obtained as Nujol mulls between KBr plates with a Nicolet Magna-IR 550 spectrometer. NbCl_5 (Strem) was sublimed prior to use, while TiCl_4 (1.0 M solution in CH_2Cl_2) was supplied by Aldrich and used as received. $\text{ZrCl}_4\cdot 2\text{THF}$,²⁰ $\text{HfCl}_4\cdot 2\text{THF}$ ²⁰ and the aminoiminophosphorane $(\text{Me}_3\text{Si})_2\text{NPCL}_2=\text{NSiMe}_3$ ²¹ were prepared according to literature methods.

Syntheses

$\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **1.** A 1.0 M solution of TiCl_4 in CH_2Cl_2 (4.6 mL, 4.6 mmol) was added dropwise to a solution of $(\text{Me}_3\text{Si})_2\text{NPCL}_2=\text{NSiMe}_3$ (1.61 g, 4.6 mmol) in 75 mL of

CH_2Cl_2 at -78°C . The resulting yellow solution was warmed to room temperature and stirred for 12 h, and subsequent removal of the volatiles gave a yellow powder. Pure **1** was obtained by slow removal of solvent (24 h) from a 5 mL solution in CH_2Cl_2 (1.64 g, 83%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 17.0 (s). ^1H NMR (CDCl_3): δ 0.49 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.9 (d, $^3J_{\text{PC}} = 5$ Hz). mp $77\text{--}78^\circ\text{C}$ (lit.,¹¹ 78°C). MS EI, 70 eV (m/z , %): 415 ($\text{M}^+ - \text{Me}$, 2), 397 ($\text{M}^+ - \text{Cl}$, 1), 380 ($\text{M}^+ - \text{Cl} - \text{Me}$, 1), 365 ($\text{M}^+ - \text{Cl} - 2$ Me, 4), 93 (Me_2SiCl^+ , 100). IR (ν_{max} , cm^{-1}): 1255s, 1161m, 1129vs, 852vs, 780s, 733s, 652s, 566m. Anal. Calc. for $\text{C}_6\text{H}_{18}\text{Cl}_5\text{N}_2\text{PSi}_2\text{Ti}$ (430.5): C, 16.74; H, 4.21; N, 6.51. Found: C, 14.46; H, 3.66; N, 6.86%.

$\text{Cl}_3\text{Ti}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$ **2.** Dry THF (0.11 g, 1.5 mmol) was added dropwise to a solution of **1** (0.62 g, 1.4 mmol) in CH_2Cl_2 (20 mL). After stirring the reaction for 12 h, the volatiles were removed *in vacuo* leaving a bright yellow solid. The powder was re-crystallized from CH_2Cl_2 –hexanes (3 : 1) at -30°C giving bright yellow needles, suitable for a single-crystal X-ray diffraction study (0.56, 78%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 13.4 (s). ^1H NMR (CDCl_3): δ 0.42 (s, 18 H, SiMe_3), 2.08 (m, 4 H, $-\text{CH}_2\text{CH}_2\text{O}-$), and 4.37 (m, 4 H, $-\text{CH}_2\text{O}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.9 (d, SiMe_3 , $^3J_{\text{PC}} = 5$ Hz), 25.8 (s, $-\text{CH}_2\text{CH}_2\text{O}-$), and 75.8 (s, $-\text{CH}_2\text{O}-$). mp $109\text{--}111^\circ\text{C}$. MS EI, 70 eV (m/z , %): 414 ($\text{M}^+ - \text{THF} - \text{Me}$, 3), 188 (TiCl_4^+ , 65), 153 (TiCl_3^+ , 100), 93 (Me_2SiCl^+ , 45), 73 (Me_3Si^+ , 15), 72 (THF^+ , 16). IR (ν_{max} , cm^{-1}): 1378m, 1252s, 1240s, 1139m, 1113vs, 1011m, 849vs, 785s, 734s, 651s, 589m. Anal. Calc. for $\text{C}_{10}\text{H}_{26}\text{Cl}_5\text{N}_2\text{OPSi}_2\text{Ti}$ (502.6): C, 23.90; H, 5.21; N, 5.57. Found: C, 22.64; H, 5.11; N, 5.81%.

$\text{Cl}_3\text{Zr}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$ **3.** A solution of $\text{ZrCl}_4\cdot 2\text{THF}$ (1.61 g, 4.27 mmol) in CH_2Cl_2 (15 mL) was added dropwise to a solution of $(\text{Me}_3\text{Si})_2\text{NPCL}_2=\text{NSiMe}_3$ (1.49 g, 4.26 mmol) in CH_2Cl_2 at -78°C . The resulting colorless solution was allowed to warm to room temperature and stirred for 12 h. The solvent was then removed *in vacuo* leaving a white solid. The powder was re-crystallized from CH_2Cl_2 –hexanes (3 : 1) at -30°C giving colorless needles, suitable for a single-crystal X-ray diffraction study (1.56 g, 67%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 11.8 (s). ^1H NMR (CDCl_3): δ 0.42 (s, 18 H, SiMe_3), 2.08 (m, 4 H, $-\text{CH}_2\text{CH}_2\text{O}-$), and 4.37 (m, 4 H, $-\text{CH}_2\text{O}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 1.9 (d, SiMe_3 , $^3J_{\text{PC}} = 5$ Hz), 25.8 (s, $-\text{CH}_2\text{CH}_2\text{O}-$), and 75.8 (s, $-\text{CH}_2\text{O}-$). mp $137\text{--}139^\circ\text{C}$. MS EI, 70 eV (m/z , %): 511 ($\text{M}^+ - \text{Cl}$, 4), 93 (Me_2SiCl^+ , 100), 73 (Me_3Si^+ , 71), 72 (THF^+ , 23). IR (ν_{max} , cm^{-1}): 1265s, 1255vs, 1122m, 1122vs, 1040m, 1002vs, 767m, 736s, 621m, 564m. Anal. Calc. for $\text{C}_{10}\text{H}_{26}\text{Cl}_5\text{N}_2\text{OPSi}_2\text{Zr}$ (546.0): C, 22.00; H, 4.80; N, 5.13. Found: C, 20.10; H, 4.50; N, 4.92%.

$\text{Cl}_3\text{Hf}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]\cdot\text{THF}$ **4.** A solution of $\text{HfCl}_4\cdot 2\text{THF}$ (0.40 g, 0.86 mmol) in CH_2Cl_2 (20 mL) was cooled to 0°C , and a solution of $(\text{Me}_3\text{Si})_2\text{NPCL}_2=\text{NSiMe}_3$ (0.32 g, 0.92 mmol) in 3 mL of CH_2Cl_2 was then added dropwise. The resulting colorless solution was warmed to room temperature and stirred for 2 days. The volatiles were then removed *in vacuo* leaving a white solid (0.38 g, 70%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 12.4 (s). ^1H NMR (CDCl_3): δ 0.42 (s, 18 H, SiMe_3), 2.09 (m, 4 H, $-\text{CH}_2\text{CH}_2\text{O}-$), and 4.42 (m, 4 H, $-\text{CH}_2\text{O}-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 2.1 (d, SiMe_3 , $^3J_{\text{PC}} = 5$ Hz), 26.0 (s, $-\text{CH}_2\text{CH}_2\text{O}-$), and 76.0 (s, $-\text{CH}_2\text{O}-$). mp $155\text{--}158^\circ\text{C}$. IR (ν_{max} , cm^{-1}): 1347m, 1267s, 1254vs, 1121vs, 1041w, 1000m, 959br, 928w, 851vs, 792s, 764m, 739m, 693m, 666s, 632m, 606w, 571s. Anal. Calc. for $\text{C}_{10}\text{H}_{26}\text{Cl}_5\text{HfN}_2\text{OPSi}_2$ (633.2): C, 18.97; H, 4.14; N, 4.42. Found: C, 18.13; H, 3.72; N, 4.18%.

$\text{Cl}_4\text{Nb}[\text{N}(\text{SiMe}_3)\text{PCl}_2\text{N}(\text{SiMe}_3)]$ **5.** A yellow solution of NbCl_5 (0.82 g, 3.0 mmol) in 100 mL of CH_2Cl_2 was cooled to 0°C , and a solution of $(\text{Me}_3\text{Si})_2\text{NPCL}_2=\text{NSiMe}_3$ (1.07 g, 3.1 mmol) in 5 mL of CH_2Cl_2 was then added dropwise. The

mixture was warmed to room temperature and stirred for 16 h to give a dark yellow solution. The volatiles were removed and the resulting yellow oil was taken up in hexanes-CH₂Cl₂ (1 : 2, 15 mL) and filtered. Removal of the volatiles from the filtrate afforded a bright yellow solid when vacuum dried (0.70 g, 46%). Yellow needles suitable for a single-crystal X-ray crystallographic study were subsequently grown from hexanes-CH₂Cl₂ (1 : 1) at -30 °C. ³¹P{¹H} NMR (CDCl₃): δ 21.6 (s). ¹H NMR (CDCl₃): δ 0.57 (s). ¹³C{¹H} NMR (CDCl₃): δ 1.6 (d, ³J_{PC} = 5 Hz). mp 107–109 °C. IR (ν_{max}, cm⁻¹): 1259s, 1155w, 1113m, 1089vs, 1031w, 856s, 790s, 732m, 695m, 642m, 591s. Anal. Calc. for C₆H₁₈Cl₆N₂NbPSi₂ (511.0): C, 14.10; H, 3.55; N, 5.48. Found: C, 12.60; H, 3.14; N, 5.60%.

[Cl₃Nb{N(SiMe₃)PCl₂N₂Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}] 6. A solution of (Me₃Si)₂NPCl₂=NSiMe₃ (1.45 g, 4.1 mmol) in 5 mL of CH₂Cl₂ was added dropwise to a solution of NbCl₅ (0.52 g, 1.9 mmol) in 125 mL of CH₂Cl₂ at room temperature. Upon the addition of the phosphoranimine, the reaction mixture went from bright yellow to amber, and the reaction was stirred for 16 h. Removal of the volatiles afforded a yellow-brown residue which was washed with hexanes (3 × 2 mL), leaving a bright yellow solid when vacuum dried. Recrystallization from 1 mL of CH₂Cl₂ (-30 °C) gave a crop of pure **6** (0.24 g, 24%) as yellow-needles of sufficient quality for a single-crystal X-ray diffraction study. ³¹P{¹H} NMR (CDCl₃): δ 20.6 (s), 21.1 (br) and 28.6 (s). ¹H NMR (CDCl₃): δ 0.52 (s, 18H), 0.58 (s, 9H) and 0.60 (s, 9H). ¹³C{¹H} NMR (CDCl₃): δ 2.9 (d, ³J_{PC} = 5 Hz), 3.3 (d, ³J_{PC} = 5 Hz) and 3.5 (d, ³J_{PC} = 5 Hz). mp > 300 °C (turned brown > 140 °C). MS EI, 70 eV (m/z, %): 1030 (M⁺ - Me, 1), 1010 (M⁺ - Cl, 1), 975 (M⁺ - 2 Cl, < 1), 938 (M⁺ - ClSiMe₃, < 1), 93 (Me₂SiCl⁺, 44), 73 (SiMe₃⁺, 100). IR (ν_{max}, cm⁻¹): 1256s, 1135s, 1113m, 1100m, 1048s, 851s, 786m, 766w, 733w, 695m, 681m, 655w, 631w, 623w, 584w, 576w and 565w. Anal. Calc. for C₁₂H₃₆Cl₁₁N₆Nb₂P₃Si₄ (1045.5): C, 13.79; H, 3.47; N, 8.04. Found: C, 13.13; H, 3.22; N, 7.94%.

[Cl₂Nb{N(SiMe₃)PCl₂N(SiMe₃)}]₂-μ-Cl(NPCl₂N) 7. A yellow solution of NbCl₅ (0.17 g, 0.63 mmol) in 25 mL of CH₂Cl₂ was cooled to 0 °C, and a solution of (Me₃Si)₂NPCl₂=NSiMe₃ (0.52 g, 1.5 mmol) in 10 mL of CH₂Cl₂ was then added dropwise. The mixture was warmed to room temperature and stirred for 16 h to give a dark yellow solution. The volatiles were removed and the resulting dark yellow oil afforded a few (< 10 mg) yellow needle-shaped crystals upon standing for one week. These crystals were coated with an intractable tar which precluded conclusive characterization by spectroscopic techniques. However, one of these crystals was suitable for a single-crystal X-ray crystallographic study which identified the needle as **7**.

Single-crystal X-ray structural determination of **2**, **3**, **5**–**7**

Diffraction data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A combination of $1^\circ \phi$ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.²² The structures were solved and refined with the SHELXTL-PC v5.1 software package.²³ Refinement was by full-matrix least squares on F^2 using data (including negative intensities) with hydrogen atoms bonded to carbon atoms included in calculated positions and treated as riding atoms.

CCDC reference numbers 173273–173276 and 179458.

See <http://www.rsc.org/suppdata/dt/b1/b109905c/> for crystallographic data in CIF or other electronic format.

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