Inorg. Chem. **2001,** *40,* 1489−1495

Synthesis and Reactivity of Perhalogenated Acyclic and Metallacyclic Tantalum(V) Phosphoraniminato Complexes: Discovery of an Unexpected Ligand Coupling Reaction To Form the Novel Phosphazenium Salt $[N(PCl_2NH_2)_2][TaCl_6]$

Eric Rivard, Charles H. Honeyman,[†] Andrew R. McWilliams, Alan J. Lough, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto,
Ontario, Canada, M5S 3H6

Received August 30, 2000

The reaction of $TaCl_5$ with a single equivalent of $Cl_3P{=}NSiMe_3$ resulted in the isolation of the perhalogenated (phosphoraniminato) tantalum(V) complex $TaCl_4(N{=}PCl_3)$ (**1**). Reaction of **1** with an excess of THF and subsequent cooling produced crystals of $TaCl_4(N{=}PCl_3)(THF)$ (**1·THF**), which possesses a distorted octahedral Ta center with a THF molecule coordinated trans to the phosphoraniminato ligand. The reaction of **1** with the aminophosphoranimine, $(Me_3Si)_2NPCl_2{=}NSiMe_3$, resulted in a [3 + 1] cyclocondensation reaction to form the metallacyclic complex, $TaCl_3(N{=}PCl_3)[N(SiMe_3)PCl_2N(SiMe_3)]$ (**2**), which contains a TaNPN four-membered ring and a phosphoraniminato ligand ($N{=}PCl_3$). The analogous [3 + 1] cyclocondensation reaction between $(Me_3Si)_2NPCl_2{=}NSiMe_3$ and $TaCl_5$ led to the isolation of $TaCl_4[N(SiMe_3)PCl_2N(SiMe_3)]$ (**3**). An attempt to cleave the NPN ligand from the Ta center in **2** via protonolysis with HCl led to an unusual phosphoraniminato ligand coupling reaction to yield the novel phosphazenium salt $[N(PCl_2NH_2)_2][TaCl_6]$ (**4**). All new compounds (**1·THF** and complexes **1−4)** were characterized by single-crystal X-ray diffraction.

Introduction

Transition metal phosphoraniminato complexes have attracted attention as a result of their interesting and unusual structural characteristics,[1−6] and more recently as olefin polymerization catalysts.[7] In the vast majority of cases, phosphoraniminato ligands possess alkyl or aryl groups attached to phosphorus. If similar, but reactive (i.e., halogenated), complexes could be synthesized, they might prove useful as reagents for cyclocondensation syntheses of transition metal-containing cyclic heterophosphazenes, which are viable candidates for ring-opening polymerization (ROP) processes.[8−14] In addition, perhalogenated phosphoraniminato species are potential ceramic precursors as these compounds could lead to carbon-free ternary solids after chemical (e.g., ammonolysis) and thermal treatment.[15−17]

Consequently, we have previously reported the synthesis of the perhalogenated tungsten phosphoraniminato complex, $WCl_5(N{=}PCl_3)$, from the reaction of WCl_6 with the silylphosphoranimine, $Cl_3P{=}NSiMe_3$.[5] During the course of this work an unexpected, ambient-temperature, route to polyphosphazenes was discovered.[18] In this paper, we present full details of the synthesis and characterization of the analogous perhalogenated tantalum phosphoraniminato complex, $TaCl_4(N{=}PCl_3)$, and our investigations of its potential as a precursor to novel metallacycles and chains.

Results and Discussion

Conventional routes to phosphoraniminato transition metal complexes have employed the reaction of transition metal nitrido, azido, or nitrosyl reagents with phosphines.[4] In contrast,

---

* To whom correspondence should be addressed. E-mail: imanners@alchemy.chem.utoronto.ca.

[†] Current address: E-Ink Corporation, Cambridge, MA 02138.

(1) (a) Lichtenhan, J. D.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1992**, *31*, 2893. (b) Pohl-Ferry, C. E.; Ziller, J. W.; Doherty, N. M. *Chem. Commun.* **1999**, *18*, 1815.

(2) Aistars, A.; Doedens, R. J.; Doherty, N. M. *Inorg. Chem.* **1994**, *33*, 4360.

(3) Rentscheler, E.; Nu*β*här, D.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 999.

(4) (a) Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, *8*, 707. (b) Dehnicke, K.; Krieger, M.; Massa, W. *Coord. Chem. Rev.* **1999**, *182*, 19.

(5) Honeyman, C. H.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994**, *33*, 2988.

(6) Witt, M.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 1163.

(7) (a) Stephan, D. W.; Guérin, F.; Spence, R, E.; Koch, L.; Gao, X.; Brown, S. J.; Swabey, J. W.; Wang, Q.; Xu, W.; Zoricak, P.; Harrison, D. G. *Organometallics* **1999**, *18*, 2046. (b) Stephan, D. W.; Stewart, J. C.; Guérin, F.; Spence, R. E.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116. (c) Vollmerhaus, R.; Shao, P.; Taylor, N. J.; Collins, S. *Organometallics* **1999**, *18*, 2731.

(8) (a) Manners, I. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1602. (b) Nguyen, P.; Gómez-Elipe, P.; Manners, I. *Chem. Rev.* **1999**, *99*, 1515.

(9) Roesky, H. W.; Lücke, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 493.

(10) Roesky, H. W. *Polyhedron* **1989**, *8*, 1729.

(11) (a) Liang, M.; Manners, I. *J. Am. Chem. Soc.* **1991**, *113*, 4044. (b) Gates, D. P.; Liable-Sands, L. M.; Yap, G. P. A.; Rheingold, A. L.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1997**, *119*, 1125. (c) McWilliams, A. R.; Gates, D. P.; Edwards, M.; Liable-Sands, L. M.; Guzei, I.; Rheingold, A. L.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 8848.

(12) Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1989**, *111*, 5478.

(13) Dodge, J. A.; Manners, I.; Allcock, H. R.; Renner, G.; Nuyken, O. *J. Am. Chem. Soc.* **1990**, *112*, 1268.

(14) (a) Roy, A. K.; Burns, G. T.; Lie, G. C.; Grigoras, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 1268. (b) Chivers, T.; Gibson, M. P.; Parvez, M.; Vargas-Baca, I. *Inorg. Chem.* **2000**, *39*, 1697.

(15) Baldus, H.; Schnick, W.; Lücke, J.; Wannagat, U.; Bogedain, G. *Chem. Mater.* **1993**, *5*, 845.

(16) Holl, M. M. B.; Kersting, M.; Pendley, B. D.; Wolczanski, P. T. *Inorg. Chem.* **1990**, *29*, 1518.

(17) Parkin, I. P.; Rowley, A. T. *Adv. Mater.* **1994**, *6*, 780.

(18) (a) Honeyman, C. H. M.Sc. Thesis, University of Toronto, 1993. (b) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.

10.1021/ic000988y CCC: $20.00

Table 1. Crystal Data, and Intensity Collection Parameters, and Least-Squares Parameters for **1**, **1·THF**, **2**, **3**, and **4**

	1	**1·THF**	**2**	**3**	**4**
empirical formula	$Cl_{14}N_2P_2Ta_2$	$C_4H_8Cl_7NPTa$	$C_6H_{18}Cl_8N_3P_2Si_2Ta$	$C_6H_{18}Cl_6N_2PSi_2Ta$	$Cl_{10}H_4N_3P_2Ta$
fw	948.16	546.2	714.9	599.02	643.45
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a, Å	6.4014(3)	12.885(3)	16.823(4)	9.3107(4)	12.943(2)
b, Å	11.0400(5)	8.537(2)	9.040(2)	8.8168(4)	8.335(1)
c, Å	14.7275(6)	14.832(2)	17.757(3)	12.5402(4)	15.644(1)
β, deg	100.484(3)	113.95(2)	117.33(2)	104.774(3)	103.54(1)
V, Å^3	1023.44(8)	1491.0(8)	2399.2(15)	995.40(7)	1640.8(3)
Z	2	4	4	2	4
D_{calcd}, g cm^{-3}	3.077	2.433	1.979	1.999	2.605
μ (Mo Kα), mm^{-1}	12.654	8.708	5.702	6.513	8.499
F(000)	856	1016	1368	572	1192
θ range, deg	2.81−27.53	3.0−46.0	4.0−60.0	2.86−27.54	2.7−30.0
index ranges	$0 \le h \le 8$	$-14 \le h \le 12$	$0 \le h \le 21$	$-12 \le h \le 11$	$-9 \le h \le 18$
	$0 \le k \le 14$	$0 \le k \le 9$	$0 \le k \le 12$	$-11 \le k \le 11$	$-10 \le k \le 10$
	$-19 \le l \le 18$	$0 \le l \le 16$	$-24 \le l \le 22$	$-16 \le l \le 16$	$-22 \le l \le 21$
no. of reflns collcd	8496	2344	7293	13313	2414
no. of indep reflns/R_{int}	2347/ 0.097	1867/ 0.039	6665/ 0.023	4149/ 0.061	2322/ 0.045
temp, K	150	248	173	150	173
no. of refined params	92	136	200	171	75
goodness of fit (F^2)	1.062	1.13	1.04	1.066	1.08
R, % [$I > 2\sigma(I)$]^a	4.60	5.59	3.35	3.03	4.23
R_w, %^{b}	10.90	7.29	3.90	7.32	11.51
largest diff peak/hole, e/Å^3	1.77/−3.63	2.19/−1.77	0.93/−1.01	1.91/−1.54	2.35/−2.20

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

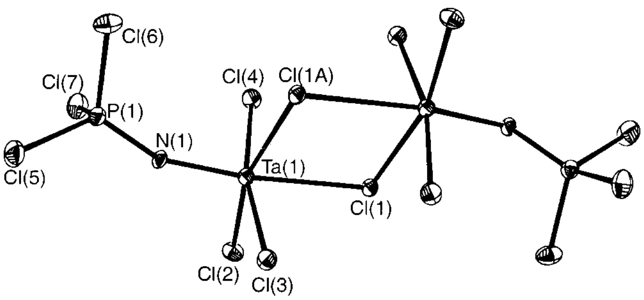


Figure 1. Molecular structure of **1** with thermal ellipsoids at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** with Estimated Standard Deviations in Parentheses^a

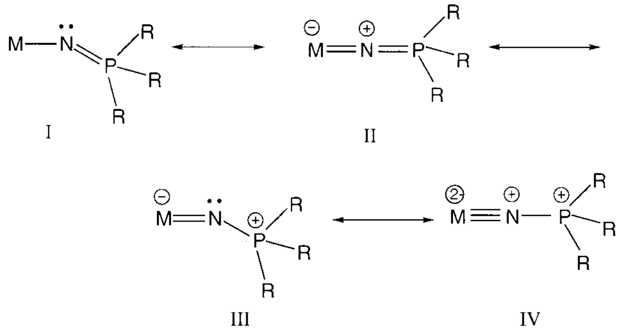
Ta(1)–Cl(1)	2.696(2)	Ta(1)–Cl(2)	2.306(2)
Ta(1)–Cl(3)	2.332(2)	Ta(1)–Cl(4)	2.332(2)
Ta(1)–Cl(1A)	2.483(2)	Ta(1)–N(1)	1.867(7)
P(1)–N(1)	1.547(8)	P(1)–Cl(5)	1.948(4)
P(1)–Cl(6)	1.962(4)	P(1)–Cl(7)	1.974(4)
N(1)–Ta(1)–Cl(1)	172.7(3)	N(1)–Ta(1)–Cl(2)	101.7(3)
N(1)–Ta(1)–Cl(3)	96.9(3)	N(1)–Ta(1)–Cl(4)	94.5(3)
N(1)–Ta(1)–Cl(1A)	94.9(3)	Ta(1)–Cl(1)–Ta(1A)	101.95(7)
Ta(1)–N(1)–P(1)	151.1(6)		

^{a} Alphabetized labels indicate symmetry-generated atoms.

the reaction of metal halides with silylphosphoranimines, $Cl_{3-n}R_nP{=}NSiMe_3$, has attracted less attention. However, this reaction pathway has been shown to be a facile route to alkyl- and aryl-substituted phosphoraniminato complexes.[1,4,5] In this paper we have explored this approach as an entry to halogenated tantalum phosphoraniminato complexes.

Synthesis and Characterization of $TaCl_4(N{=}PCl_3)$ (1). The reaction of $TaCl_5$ and $Cl_3P{=}NSiMe_3$ in a 1:1 ratio in CH_2Cl_2 produced a new phosphorus-containing product with a singlet resonance at $\delta = 16.2$ ppm by ^{31}P NMR. Furthermore, the characteristic signal of $Cl_3P{=}NSiMe_3$ was absent ($\delta = -54.3$ ppm), suggesting that the reaction was quantitative. Purification of the reaction product gave a fine white powder. Mass spectral analysis of this product was inconclusive; however, crystals suitable for a single-crystal X-ray diffraction study were obtained by slow evaporation of a solution of **1** in CH_2Cl_2. X-ray analysis indicated the structure of **1** to be dimeric in the solid state with one chlorine atom on each monomer participating in a Ta−Cl−Ta bridge, resulting in a distorted octahedral geometry about each Ta center; this structural arrangement has been observed in other tantalum phosphoraniminato complexes[19] (e.g., $TaCl_4(N{=}PPh_3)$). The summary of crystal data, intensity collection parameters, and structural refinement data for **1** can be found in Table 1. Figure 1 shows the molecular structure of **1**, and Table 2 contains selected bond lengths and angles for **1**.

Scheme 1. Possible Canonical Forms for the M−N−P Linkage in Phosphoraniminato Complexes



Typical features of a transition metal phosphoraniminato complex include short metal−nitrogen and phosphorus−nitrogen bond lengths and wide M−N−P bond angles.[2,4] These features have been ascribed to the ability of the nitrogen atom in the M−N−P linkage to form π-bonds with both phosphorus and transition metal centers. Moreover, the degree to which the nitrogen interacts with either element can be described by the resonance hybrid of several canonical forms (see Scheme 1). The P−N bond length of the phosphoraniminato ligand in **1**

---

(19) Bezler, H.; Strähle, J. *Z. Naturforsch.* **1983**, *38b*, 317.

was determined to be 1.547(8) Å and is similar to the accepted P−N double bond length of 1.56 Å.[20,21] The Ta−N bond length [1.867(7) Å] was also found to be in agreement with the assessment that forms I and II in Scheme 1 best represent the bonding within the phosphoraniminato ligand in **1**. Moreover, the Ta−N bond length is similar to those found in the cyclic compound $[(Cp^*)Ta(Cl)N]_3$ ($Cp^* = \eta^5$-C_5Me_5) which has Ta−N bond lengths ranging from 1.84(2) to 1.92(2) Å.[22] The Ta−N bond lengths in both this ring and **1** have considerable multiple-bond character as typical single Ta−N bonds range from 1.95 to 2.03 Å and Ta−N triple bonds from 1.61 to 1.78 Å.[22,23] The Ta−N−P bond angle in **1** [151.1(6)°] is substantially narrower than that in the dimer of $TaCl_4(N{=}PPh_3)$, which has an average Ta−N−P bond angle of 176.8(7)° and a shorter Ta−N bond length of 1.801(8) Å.[19] This supports the observation that perhalogenated phosphoraniminato complexes of high oxidation state metals are best represented by canonical forms I and II,[5] whereas alkylated (and phenylated) analogues are represented by forms III and IV.[2,4]

Synthesis and Characterization of $TaCl_4(N{=}PCl_3)(THF)$ (1·THF). In order to probe the lability of the bridging interactions in **1**, we attempted to cleave the dimer using a donor molecule (THF). The synthesis of the adduct **1·THF** was accomplished by the dissolution of **1** in a minimum of CH_2Cl_2 followed by the slow addition of THF. This gave a reaction solution whose ^{31}P NMR spectrum exhibited a new resonance at $\delta = 7.2$ ppm. Interestingly, if the synthesis of **1·THF** was attempted with high THF concentrations (>3 M), a vigorous reaction occurred which resulted in an extremely viscous solution which presumably contained poly(tetrahydrofuran). This reaction is consistent with the observation that many Lewis acids (e.g., $TaCl_5$) are known to initiate the ring-opening polymerization of THF.[24] Isolation of the adduct **1·THF** and subsequent recrystallization from CH_2Cl_2 and hexanes at low temperature produced crystals suitable for X-ray analysis. This analysis confirmed the identity of **1·THF**, and all relevant crystallographic parameters and refinement data can be found in Table 1. The structure of **1·THF** is depicted in Figure 2, while selected bond lengths and angles are listed in Table 3.

As shown in Figure 2, the Ta(V) center in **1·THF** has a distorted octahedral geometry with the donating THF and phosphoraniminato ligands adopting a trans arrangement. Competition between the coordinated THF and the phosphoraniminato ligand for the vacant d-orbitals on Ta (d^0) should lead to the weakening of the Ta−N bond. However, the Ta−N bond lengths in the dimer of **1** and its THF adduct (**1·THF**) were not significantly different [1.867(7) Å in **1** vs 1.895(13) Å in **1·THF**]. Despite this, the P−N bond length in the THF adduct was considerably shorter [1.485(15) Å] than in **1** [1.547(8) Å], suggesting that the presence of the THF molecule stabilizes canonical form I depicted in Scheme 1. The M−N−P bond angle is unexpectedly wider [158.2(13)°] in **1·THF**, which is congruent with the observation that the bond angles at nitrogen in transition metal phosphoraniminato complexes tend not to bear a relation to the M−N and P−N bond lengths (as previously noted by Dehnicke and Strähle[4] and subsequently observed by ourselves[5]).

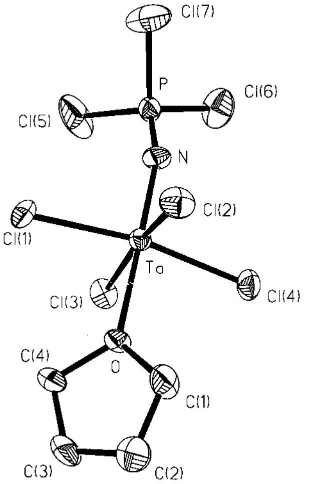


Figure 2. Molecular structure of **1**·THF with thermal ellipsoids at the 50% probability level (H atoms are omitted for clarity).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1·THF** with Estimated Standard Deviations in Parentheses

Ta−Cl(1)	2.361(5)	Ta−Cl(2)	2.333(7)
Ta−Cl(3)	2.346(7)	Ta−Cl(4)	2.348(5)
Ta−O	2.213(9)	Ta−N	1.895(13)
Cl(5)−P	1.927(13)	Cl(6)−P	1.949(10)
Cl(7)−P	1.959(10)	P−N	1.485(15)
O−C(1)	1.469(27)	O−C(4)	1.454(23)
C(1)−C(2)	1.434(30)	C(2)−C(3)	1.441(45)
Cl(1)−Ta−N	94.9(5)	Cl(2)−Ta−N	96.8(6)
Cl(3)−Ta−N	95.8(6)	Cl(4)−Ta−N	96.1(5)
O−Ta−N	179.0(5)	Ta−N−P	158.2(13)
Ta−O−C(1)	126.2(11)	Ta−O−C(4)	126.2(11)
C(1)−O−C(4)	107.3(14)		

Synthesis and Characterization of $TaCl_3(N{=}PCl_3)[N(SiMe_3)PCl_2N(SiMe_3)]$ (2). Of major interest to us was the potential use of **1** in the synthesis of perhalogenated metallacycles, which are possible candidates for ROP.[8,10,25] We therefore attempted to use a [3 + 3] cyclocondensation route to synthesize the metallacycle, $[Cl_2TaNPCl_2NPCl_2N]$, employing $(Me_3Si)_2NPCl_2{=}NSiMe_3$ and **1** as reactants (Scheme 2).

Reaction of **1** with 1 equiv of $(Me_3Si)_2NPCl_2{=}NSiMe_3$ produced a product which was isolated as a fine white powder. A ^{31}P NMR spectrum of this powder revealed two singlets at $\delta = 15.2$ and -2.7 ppm that were not characteristic of either of the starting materials. To unambiguously assign a structure to **2**, crystals suitable for a single-crystal X-ray diffraction study were grown from a CH_2Cl_2 solution by adding hexanes and cooling to −30 °C for 3 days. The X-ray diffraction study revealed that **2** contained a four-membered TaNPN ring with a further phosphoraniminato ligand bound to the Ta center. The molecular structure of **2** is shown in Figure 3. Table 1 contains a summary of crystal data, intensity collection parameters, and structural refinement data for **2**. Selected bond lengths and angles are shown in Tables 4 and 5.

The TaNPN ring system in **2** warrants some discussion. Within the ring, the Ta−N bond lengths are significantly different from each other, as are the lengths of the two P−N

---

(20) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 1st ed.; Pergamon Press: Oxford, 1984; p 1542.

(21) Although π-bonding arguments are often used to explain the bonding in MNP complexes, other factors such as the inductive effects of neighboring substituents may also play a significant role. For example, the P−N bond in $[TaCl_4(N{=}PPh_3)]_2$ is considerably longer [1.593(9) Å] than that in **1**.[19] It is certainly reasonable to assume that the inductive nature of the Cl substituents in **1** also contributes to the shortening of the P−N bond by increasing the s-orbital character of the σ-bond.

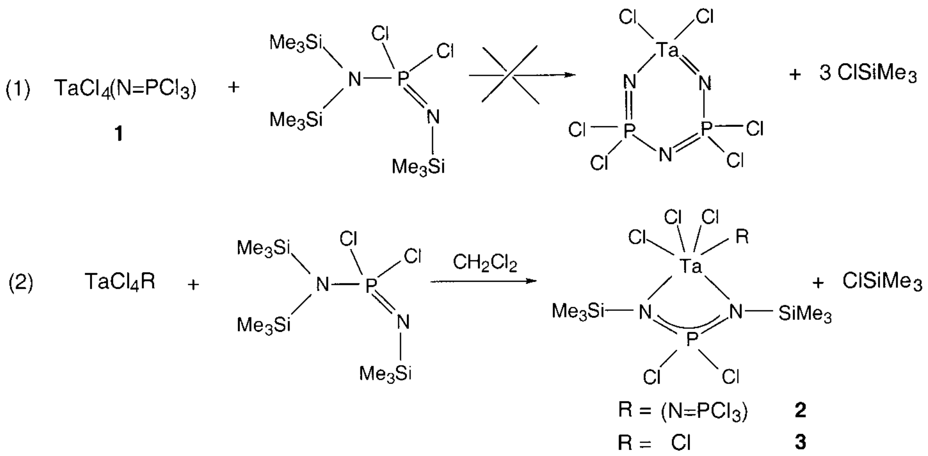
(22) Plenio, H.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1330.

(23) Wheeler, R. A.; Hoffmann, R.; Strähle, J. *J. Am. Chem. Soc.* **1986**, *108*, 5381.

(24) McGrath, J. E. *Ring-Opening Polymerization*; ACS Symposium Series 286; American Chemical Society: Washington, DC, 1985; p 183.

(25) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: New Jersey, 1992.

Scheme 2



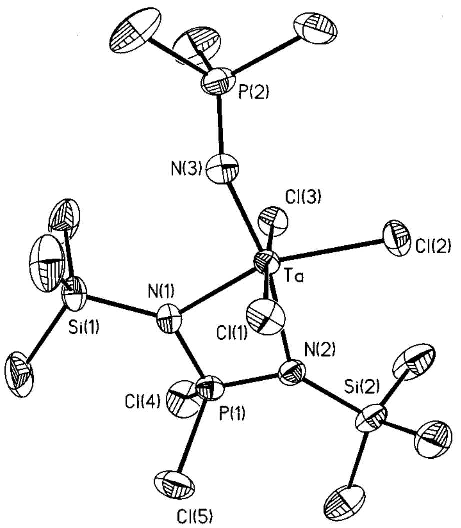


Figure 3. Molecular structure of **2** with thermal ellipsoids at the 50% probability level (H atoms are omitted for clarity).

Table 4. Selected Bond Lengths (Å) for **2** with Estimated Standard Deviations in Parentheses

Ta−Cl(1)	2.355(2)	Ta−Cl(2)	2.344(1)
Ta−Cl(3)	2.405(1)	Ta−N(1)	2.095(4)
Ta−N(2)	2.246(4)	Ta−N(3)	1.890(5)
Cl(4)−P(1)	2.011(2)	Cl(5)−P(1)	2.003(2)
Cl(6)−P(2)	1.961(2)	Cl(7)−P(2)	1.976(2)
Cl(8)−P(2)	1.979(3)	P(1)−N(1)	1.598(4)
P(1)−N(2)	1.559(5)	P(2)−N(3)	1.537(4)
Si(1)−N(1)	1.775(5)	Si(2)−N(2)	1.763(5)

Table 5. Selected Bond Angles (deg) for **2** with Estimated Standard Deviations in Parentheses

Cl(1)−Ta−N(1)	89.8(1)	Cl(2)−Ta−N(1)	159.7(1)
Cl(3)−Ta−N(1)	90.3(1)	Cl(1)−Ta−N(2)	90.1(1)
Cl(2)−Ta−N(2)	90.0(1)	Cl(3)−Ta−N(2)	85.9(1)
Cl(1)−Ta−N(3)	94.0(1)	Cl(2)−Ta−N(3)	102.7(1)
Cl(3)−Ta−N(3)	90.3(1)	N(1)−Ta−N(2)	69.7(2)
N(1)−Ta−N(3)	97.6(2)	N(2)−Ta−N(3)	166.7(2)
N(1)−P(1)−N(2)	103.8(2)	Ta−N(1)−P(1)	95.5(2)
Ta−N(2)−P(1)	90.9(2)	Ta−N(3)−P(2)	152.2(3)
Ta−N(1)−Si(1)	132.0(2)	Ta−N(2)−Si(2)	135.2(2)
P(1)−N(1)−Si(1)	132.5(2)	P(1)−N(2)−Si(2)	133.8(2)

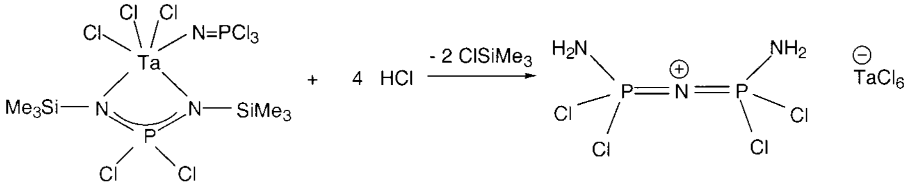
bonds. The variation in Ta−N$_{ring}$ bond lengths is a result of N(2) being trans to the phosphoraniminato ligand whereas N(1) is trans to a chlorine atom. Phosphoraniminato ligands have a substantial trans influence,[4,5] and hence the Ta−N(2) bond [2.246(4) Å] is lengthened in comparison to the Ta−N(1) [2.095(4) Å]. Both of the Ta−N$_{ring}$ bonds in **2** are longer than the Ta−N bond in **1**; this represents a substantial reduction in the degree of π-donation from the N$_{ring}$ atoms to the tantalum center, and the Ta−N$_{ring}$ bonds in **2** can be considered to be single bonds. As a consequence, the nitrogen atoms were found to be preferentially π-bonded to the P(1) atom. The P(1)−N$_{ring}$ bonds [1.598(4) and 1.559(5) Å] are similar to the accepted double-bond length of 1.56 Å, indicative of an appreciable amount of π-bonding within the N(1)−P(1)−N(2) ring fragment. The phosphoraniminato ligand (N═PCl$_3$) in **2** displays bonding characteristics similar to those in **1**, with comparable P−N [1.537(4) Å] and Ta−N [1.890(5) Å] bond lengths.

Synthesis and Characterization of TaCl$_4$[N(SiMe$_3$)PCl$_2$N(SiMe$_3$)] (3). In light of the synthesis of **2**, we attempted to synthesize an analogous metallacycle directly from the reaction of TaCl$_5$ with (Me$_3$Si)$_2$NPCl$_2$═NSiMe$_3$. Reaction of TaCl$_5$ with (Me$_3$Si)$_2$NPCl$_2$═NSiMe$_3$ produced a new product observable in the ^{31}P NMR spectrum of the reaction mixture after 24 h. The product was isolated as a pale yellow solid that was characterized by NMR, IR, melting point, mass spectroscopy, elemental analysis, and a single-crystal X-ray diffraction study.

The ^{31}P NMR in CDCl$_3$ of **3** consists of a broad resonance at 19.7 ppm (ascribed to the P atom of the TaNPN ring), whereas a similar resonance is observed at 15.2 ppm for the P$_{ring}$ in **2**. In addition, the ^{1}H NMR spectrum of **3** displays a singlet resonance at 0.55 ppm attributable to the trimethylsilyl (SiMe$_3$) protons, while the SiMe$_3$ protons of **2** gave a resonance at 0.48 ppm. This slight difference in the chemical shifts can be attributed to the electron-donating nature of the phosphoraniminato ligand in **2** which causes a small increase in the shielding about the SiMe$_3$ protons. The ^{13}C NMR spectra of **2** and **3** both consist of doublets ($^3J_{PC}$ = 4 Hz) at 1.64 ppm. On the basis of the similarities between the NMR spectra of **2** and **3**, it appeared that a TaNPN heterocycle was present in **3**. An X-ray diffraction study was subsequently undertaken which confirmed the presence of a four-membered TaNPN ring (see Figure 4). Table 1 contains a summary of crystal data, intensity collection parameters, and structural refinement data for **3**, while Tables 6 and 7 list selected bond lengths and angles within **3**.

As seen from the X-ray data, substitution of a Cl atom for the N═PCl$_3$ ligand results in the lengthening of the trans Ta−N$_{ring}$ bond to 2.117(5) Å (average) in **3** from 2.246(4) Å in **2**. This structural change can be ascribed to the trans effect described earlier and represents an interesting example of how the electronic nature of the ligands about the Ta center can influence the structure of the TaNPN ring. The geometry about the Ta centers in **2** and **3** can be considered as distorted

Scheme 3



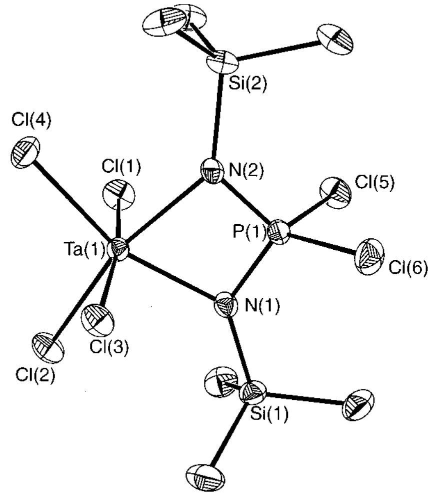


Figure 4. Molecular structure of **3** with thermal ellipsoids at the 50% probability level (H atoms are omitted for clarity).

Table 6. Selected Bond Lengths (Å) for **3** with Estimated Standard Deviations in Parentheses

Ta(1)−Cl(1)	2.3514(15)	Ta(1)−Cl(2)	2.3391(15)
Ta(1)−Cl(3)	2.3459(14)	Ta(1)−Cl(4)	2.3101(15)
Ta(1)−N(1)	2.103(5)	Ta(1)−N(2)	2.130(5)
Cl(5)−P	1.993(2)	Cl(6)−P	1.983(2)
P−N(1)	1.591(5)	P−N(2)	1.593(5)
Si(1)−N(1)	1.793(5)	Si(2)−N(2)	1.800(5)

Table 7. Selected Bond Angles (deg) for **3** with Estimated Standard Deviations in Parentheses

Cl(1)−Ta−N(1)	93.34(13)	Cl(2)−Ta−N(1)	93.70(13)
Cl(3)−Ta−N(1)	91.61(13)	Cl(4)−Ta−N(1)	159.06(13)
Cl(1)−Ta−N(2)	90.74(13)	Cl(2)−Ta−N(2)	164.11(14)
Cl(3)−Ta−N(2)	97.13(13)	Cl(4)−Ta−N(2)	88.19(14)
N(1)−Ta−N(2)	70.01(19)	N(1)−P−N(2)	101.1(3)
Cl(5)−P−Cl(6)	102.60(10)	Ta−N(1)−P	94.4(2)
Ta−N(2)−P	93.3(2)	Ta−N(1)−Si(1)	135.1(3)
Ta−N(2)−Si(2)	135.9(3)	P−N(1)−Si(1)	130.4(3)
P−N(2)−Si(2)	128.2(3)		

octahedral with a NPN bidentate chelate in half of the four equatorial sites. The bite angles of the NPN chelates (endo N−Ta−N bond angle) within **2** and **3** are 69.7(2)° and 71.01 (19)°, respectively, and have values similar to those found in other MNPN chelates (M = transition metal).[7,26] The electrophilic nature of the Ta(V) center, coupled with the acute bite angle of the NPN ligand, makes **2** and **3** of possible interest as olefin polymerization catalysts.[7]

Reaction of 2 with Excess Gaseous HCl. Unexpected Synthesis of [N(PCl$_2$NH$_2$)$_2$][TaCl$_6$] (4). As discussed before, the Ta−N bonds within the TaNPN ring of **2** are significantly longer than the Ta−N(3) bond of the N=PCl$_3$ ligand [2.246(4) vs 1.890(5) Å]. This suggests that the former moiety is less strongly bound to the Ta center than the phosphoraniminato ligand in **2**. Consequently, an attempt was made to chemically remove the NPN ligand from **2** using HCl as ring nitrogens N(1) and N(2) were expected to be more Lewis basic than N(3).

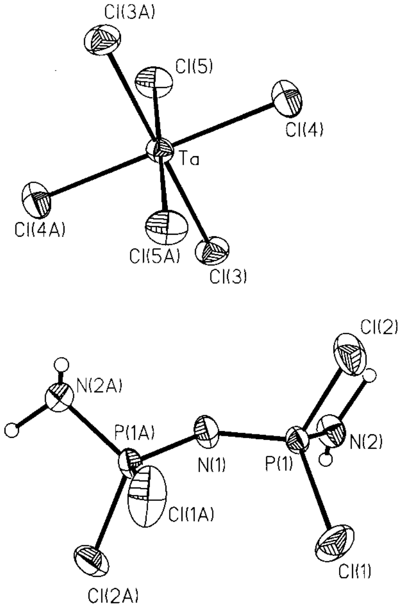


Figure 5. Molecular structure of **4** with thermal ellipsoids at the 50% probability level.

Table 8. Bond Lengths (Å) and Angles (deg) for the Cation present in **4** with Estimated Standard Deviations in Parentheses[a]

P(1)−N(1)	1.553(3)	P(1A)−N(1)	1.553(3)
P(1)−N(2)	1.629(2)	P(1)−Cl(1)	1.975(2)
P(1)−Cl(2)	1.964(2)		
N(1)−P(1)−N(2)	109.7(3)	N(1)−P(1)−Cl(2)	112.44(10)
N(2)−P(1)−Cl(2)	106.3(2)	N(1)−P(1)−Cl(1)	112.9(3)
N(2)−P(1)−Cl(1)	111.6(2)	Cl(2)−P(1)−Cl(1)	103.62(14)
P(1)−N(1)−P(1A)	138.2(5)		

[a] Alphabetized atom labels indicate symmetry-generated atoms.

Reaction of **2** in CH$_2$Cl$_2$ with a purge of gaseous HCl for 1 h resulted in a reaction solution which exhibited a single ^{31}P NMR resonance at $\delta = 18.5$ ppm. At this point the reaction was deemed complete as further addition of HCl did not result in any change in the ^{31}P NMR spectrum of the reaction solution. The product was isolated as a white solid, and crystals suitable for single-crystal X-ray diffraction were grown from CH$_2$Cl$_2$ and hexanes. This analysis identified the structure of **4** as the phosphazenium salt, [N(PCl$_2$NH$_2$)$_2$][TaCl$_6$]. A summary of crystal data, intensity collection parameters, and structural refinement data for **4** can be found in Table 1. Figure 5 shows the molecular structure of **4**, and Table 8 lists selected bond lengths and bond angles within the NPNPN cation of **4**.

The P−N bond lengths in **4** were found to be 1.553(3) Å for the internal P−N bonds and 1.629(6) Å for external (P−NH$_2$) bonds. The internal nitrogen atom [N(1)] forms a shorter P−N bond than that of the external amino group as the former is only two-coordinate and can more readily donate electron

---

(26) Witt, M.; Noltemeyer, M.; Schmidt, H.; Lübben, T.; Roesky, H. W. *J. Organomet. Chem.* **1999**, *591*, 138.

density to the phosphorus centers. Bond angles about both the amino nitrogen and the phosphorus centers are characteristic of a distorted tetrahedron and fall in the range 104−113°; the internal nitrogen was found to be somewhat more distorted and has a P(1)−N(1)−P(1A) angle of 138.2(5)°. This wide angle is a further indication of the ability of N(1) to π-bond strongly and equally to both phosphorus centers.

The reaction of **2** with excess HCl(g) resulted in the formal coupling of the phosphoraniminato ligand with the NPN fragment accompanied by the elimination of $ClSiMe_3$ (Scheme 3). However, the sequence of steps resulting in the formation of **4** by the attack of HCl is unclear and is currently under investigation. While the structural features of **4** are not unusual, the composition of the phosphazenium cation is. Roesky and co-workers have used a similar phenylated phosphazenium salt $[N(PPh_2NH_2)_2]Cl$ and WCl_6 to synthesize the first transition metal containing cyclic heterophosphazene, $Cl_3WNPPh_2NPPh_2N\cdot CH_3CN$.[27] Of note, the synthetic route to the salt $[N(PPh_2NH_2)_2]Cl$ involves the reaction of Ph_2PCl_3 and NH_3.[28] Adaptation of this method to yield the perchlorinated phosphazenium salt is most likely not possible as the required reactants (i.e., PCl_5 and NH_3) would undoubtedly produce a mixture of highly branched oligomeric products. The isolation of **4** indicates that a salt containing the cation required for the synthesis of the perhalogenated cyclometallaphosphazenes is accessible and does not eliminate HCl under ambient conditions. Thus, we are currently exploring **4** as a possible reagent for the synthesis of perhalogenated transition metal containing cyclic heterophosphazenes via cyclocondensation processes.

Summary

The perhalogenated phosphoraniminato tantalum(V) complex (**1**) has been prepared, and some of the reaction chemistry of this specie has been explored. These studies demonstrated that **1** is a suitable reagent for the synthesis of novel tantalum-based metallacycles and subsequently the novel phosphazenium salt (**4**) via an unexpected ligand coupling reaction. This phosphazenium salt holds promise as a precursor for inorganic heterocycles as it is the perhalogenated analogue of the salt used by Roesky and co-workers to synthesize a wide range of phenylated six-membered cyclometallaphosphazenes.[10,27] We are currently exploring the synthesis of other metallacycles using species such as **4**, and we are also attempting to elucidate the mechanism by which **4** is formed.

Experimental Section

Materials and Instrumentation. All reactions and manipulations were carried out strictly under an atmosphere of prepurified nitrogen (Canox) using either Schlenk techniques or an inert atmosphere glovebox (Innovative Technologies). Solvents were all dried and distilled using standard methods, and 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 MHz) and referenced to protio impurities in the solvent. ^{31}P and ^{13}C NMR spectra were obtained using a Gemini 300 spectrometer (122.1 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. 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. Melting points (uncorrected) were obtained in sealed glass capillaries (0.5 mm o.d.) which were flame sealed under a nitrogen atmosphere. Infrared spectra were obtained as Nujol mulls between KBr plates with a Nicolet Magna-IR 550 spectrometer. $TaCl_5$ (Strem) was sublimed prior to use. Hydrogen chloride gas (HCl) was supplied in lecture bottles by Aldrich and was used as received. Phosphoranimines $Cl_3P{=}NSiMe_3$[5,29] and $(Me_3Si)_2NPCl_2{=}NSiMe_3$[30] were prepared according to literature methods.

Preparation of $TaCl_4(N{=}PCl_3)$ (1). A suspension of $TaCl_5$ (4.50 g, 12.6 mmol) in CH_2Cl_2 (350 mL) was prepared and cooled to 0 °C. To this stirred suspension was added a solution of $Cl_3P{=}NSiMe_3$ (3.33 g, 14.8 mmol) in CH_2Cl_2 (100 mL) dropwise by cannula over 15 min, and the reaction solution was then allowed to warm to room temperature. After 24 h, a broad resonance at 16.2 ppm was detected by ^{31}P NMR spectroscopy, and the solvent was removed by vacuum yielding a pale brown powder. This powder was washed with 10 mL of CH_2Cl_2, leaving a fine white powder (5.12 g, 86%). Mass spectral analysis of this product was inconclusive; however, the assigned structure was confirmed by a single-crystal X-ray diffraction study (Figure 1).

Data for 1. ^{31}P NMR ($CDCl_3$): $\delta = 14.4$ ppm (s). Mp (°C): 133−5 (dec). IR (ν, cm^{-1}): 1829 (w), 1200 (vs), 1103 (sh), 1019 (sh), 801 (m), 724 (m), 613 (vs). Anal. Calcd for Cl_7NPTa (474.1): N, 2.95. Found: N, 2.88.

Preparation of $TaCl_4(N{=}PCl_3)(THF)$ (1·THF). THF (0.50 mL) was slowly added dropwise by syringe to a solution of **1** (0.52 g, 1.1 mmol) in CH_2Cl_2 (40 mL). A ^{31}P NMR spectrum of the resulting colorless solution after 10 min showed only one singlet resonance at $\delta = 7.2$ ppm. The solvent was then removed by vacuum, and a fine white powder was isolated (0.54 g, 90%). The powder was redissolved in a minimum of CH_2Cl_2 (ca. 25 mL) and cooled to −30 °C for 4 h. Hexanes (5 mL) was slowly added, and this mixture was cooled for a further 2 days. This resulted in the growth of large colorless plate-shaped crystals suitable for a single-crystal X-ray diffraction study which confirmed that **1·THF** had the assigned structure (Figure 2).

Data for 1·THF. ^{31}P NMR ($CDCl_3$): $\delta = 6.4$ ppm (s). ^1H NMR ($CDCl_3$): $\delta = 4.71$ ppm (t, OCH_2, $^3J_{HH} = 7$ Hz) and 2.14 ppm (pentet, CH_2, $^3J_{HH} = 4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 76.8$ ppm (s, OCH_2) and 26.1 ppm (s, CH_2). Mp (°C): 89−90 (dec). IR (ν, cm^{-1}): 1345 (w), 1263 (vs), 1094 (br), 1046 (m), 1000 (m), 961 (w), 927 (w), 841 (s), 804 (m), 726 (w), 680 (w), 671 (w), 699 (vs). Anal. Calcd for $Cl_7C_4H_8NOPTa$ (546.2): C, 8.80; H, 1.48; N, 2.56. Found: C, 8.96; H, 1.59; N, 2.56.

Reaction of 1 with 1 Equiv of $(Me_3Si)_2NPCl_2{=}NSiMe_3$. Synthesis of $TaCl_3(N{=}PCl_3)[N(SiMe_3)PCl_2N(SiMe_3)]$ (2). Compound **1** (1.61 g, 3.40 mmol) was dissolved in CH_2Cl_2 (200 mL) to give a clear, colorless solution. A solution of $(Me_3Si)_2NPCl_2{=}NSiMe_3$ (1.29 g, 3.68 mmol) in CH_2Cl_2 (20 mL) was prepared and added dropwise to the $[TaCl_4(N{=}PCl_3)]_2$. The reaction mixture was stirred for 24 h, resulting in a pale beige solution. A ^{31}P NMR spectrum of this solution exhibited two singlets at $\delta = 14.9$ and -2.0 ppm, respectively, with no trace of starting materials. The solvent was then removed under vacuum to yield a beige residue. The residue was extracted with toluene (2 × 25 mL) and filtered. Removal of the volatiles gave a fine white solid when vacuum-dried (1.41 g, 58%). Dissolution of this material in a minimum of CH_2Cl_2 and cooling to −30 °C, followed by subsequent addition of an equal volume of hexanes, yielded clear, colorless, needle-shaped crystals after 3 days.

Data for 2. ^1H NMR ($CDCl_3$): $\delta = 0.48$ ppm (s, $SiMe_3$). ^{31}P NMR ($CDCl_3$): $\delta = 15.2$ ppm (s, $N{=}PCl_3$), -2.7 ppm (s, PCl_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 1.61$ ppm (d, $SiMe_3$, $^3J_{PC} = 4$ Hz). MS 70 eV, EI (m/z, %): 715 (M^+, 5), 700 ($M^+ - Me$, 46), 680 ($M^+ - Cl$, 23), 607 ($M^+ - ClSiMe_3$, 2), 592 ($M^+ - Me - ClSiMe_3$, 35), 93 ($ClSiMe_2^+$,

---

(27) (a) Witt, M.; Roesky, H. W. *Polyhedron* **1989**, *8*, 1736. (b) Witt, M.; Roesky, H. W.; Noltemeyer, M.; Schmidpeter, A. *New J. Chem.* **1989**, *13*, 403. (c) Roesky, H. W.; Katti, K. V.; Seseke, U.; Witt, M.; Egert, E.; Herbst, R.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 477. (d) Katti, K.; Seseke, U.; Roesky, H. W. *Inorg. Chem.* **1987**, *26*, 814.

(28) Herring, D. L.; Douglas, C. M. *Inorg. Chem.* **1964**, *3*, 428.

(29) Original preparation of $Cl_3P{=}NSiMe_3$: Niecke, E.; Bitter, W. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 127. We prepared $Cl_3P{=}NSiMe_3$ from PCl_5 and $LiN(SiMe_3)_2$ in hexanes at an initial temperature of −78 °C, followed by 4−5 h at room temperature (see ref 5).

(30) Niecke, E.; Bitter, W. *Chem. Ber.* **1976**, *109*, 415.

100), 73 ($SiMe_3^+$, 75). Mp (°C): 152−4. IR (ν, cm^{-1}): 1256 (s), 1232 (s), 1172(s), 1122 (w), 1099 (s), 1019 (w), 851 (s), 795 (s), 769 (w), 738 (m), 696 (w), 657 (m), 607 (s), 594 (s), 561 (s). Anal. Calcd for $C_6H_{18}Cl_8N_3P_2Si_2Ta$ (714.9): C, 10.08; H, 2.54; N, 5.88. Found: C, 10.37; H, 2.52; N, 5.85.

Reaction of $TaCl_5$ with 1 Equiv of $(Me_3Si)_2NPCl_2{=}NSiMe_3$. Synthesis of $TaCl_4[N(SiMe_3)PCl_2N(SiMe_3)]$ (3). A solution of $TaCl_5$ (0.45 g, 1.2 mmol) in CH_2Cl_2 (75 mL) was prepared, and a solution of $(Me_3Si)_2NPCl_2{=}NSiMe_3$ (0.44 g, 1.3 mmol) in 10 mL of CH_2Cl_2 was then added dropwise (20 min). The reaction mixture was stirred for 24 h, and the ^{31}P NMR spectrum of the pale yellow solution showed a new singlet resonance at $\delta = 20.3$ ppm. The volatiles were removed under reduced pressure, and the residue was extracted with hexanes (50 mL) and filtered through Celite. Removal of the hexanes afforded a pale yellow solid when vacuum-dried (0.54 g, 73%). Large, colorless needle-shaped crystals of **3** were obtained by slow evaporation (24 h at room temperature, under N_2) of a 1:3 hexanes/CH_2Cl_2 solution.

Data for 3. ^1H NMR ($CDCl_3$): $\delta = 0.55$ ppm (s, $SiMe_3$). ^{31}P NMR ($CDCl_3$): $\delta = 19.7$ ppm (s, PCl_2). $^{13}C\{^1H\}$ NMR: ($CDCl_3$) $\delta = 1.62$ ppm (d, $SiMe_3$, $^3J_{PC} = 4$ Hz). MS 70 eV, EI (*m*/*z*, %): 583 ($M^+ - Me$, 52), 563 ($M^+ - Cl$, 30), 475 ($M^+ - Me - ClSiMe_3$, 78), 455 ($M^+ - Cl - ClSiMe_3$, 17), 73 ($SiMe_3^+$, 100). Mp (°C): 142−4. IR (ν, cm^{-1}): 1259 (vs), 1171 (w), 1127 (m), 1094 (vs), 1020 (w), 855 (s), 802 (s), 772 (w), 741 (m), 695 (m), 614 (m), 588 (s). Anal. Calcd for $C_6H_{18}Cl_6N_2PSi_2Ta$ (599.0): C, 12.03; H, 3.03; N, 4.68. Found: C, 11.63; H, 2.85; N, 4.36.

Reaction of 2 with Excess Gaseous HCl: Preparation of $[N(PCl_2NH_2)_2][TaCl_6]$ (4). HCl(g) was bubbled through a solution of **2** (125 mg, 0.175 mmol) dissolved in ca. 5 mL of CH_2Cl_2 for 1 h. A ^{31}P NMR spectrum of the colorless solution exhibited a singlet at $\delta = 18.4$ ppm. Removal of solvent resulted in the isolation of a white solid (50 mg, 44%). Dissolution in a minimum of CH_2Cl_2 and cooling (−30 °C) for several hours resulted the formation of crystals suitable for a single-crystal X-ray diffraction study which identified **4** as the phosphazenium salt (Figure 5).

Data for 4. ^{31}P NMR (CD_2Cl_2): $\delta = 18.4$ ppm (s). ^1H NMR (CD_2Cl_2): $\delta = 5.21$ ppm (br, NH_2). Mp (°C): 125−130 (dec). IR (ν, cm^{-1}): 3396 (s), 3300 (s), 1521 (m), 1339 (vs), 1262 (w), 1094 (br), 1018 (m), 992 (s), 801 (m), 765 (m), 601 (vs). Anal. Calcd for $Cl_{10}H_4N_3P_2Ta$ (643.5): H, 0.63; N, 6.53. Found: H, 0.70; N, 6.49.

Single-Crystal X-ray Structural Determination of 1·THF, 2, and 4. Intensity data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The intensities of three standard reflections for each structure were monitored periodically and used to apply corrections where necessary. Data were corrected for Lorentz and polarization effects and for absorption. The structures were solved using SHELXTL-PC.[31] For all structures non-hydrogen atoms were refined anisotropically by least squares to minimize $\sum w(F_o - F_c)^2$ for **1·THF**, **2**, and **4**. All hydrogen atoms were visible in difference Fourier maps and were positioned on geometric grounds and included in the refinement as riding atoms (C−H 0.96 Å, N−H 0.90 Å, $U_{iso} = 0.80(6)$, 0.76(6), and 0.08 Å^2 for **1·THF**, **2**, and **4** respectively). There were no chemically significant features in the difference Fourier map. Crystal data, data collection, and least-squares parameters for **1·THF**, **2**, and **4** are listed in Table 1. All calculations and graphics were performed using SHELXTL-PC or SHELXL-93.[31,32]

Single-Crystal X-ray Structural Determination of 1 and 3. Diffraction data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° ϕ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[33] The structures were solved and refined with the SHELXTL-PC v5.1 software package.[34] Refinement was by full-matrix least squares on F^2 using all data (including negative intensities). Molecular structures are presented with ellipsoids at a 50% probability level. In all structures, hydrogen atoms bonded to carbon atoms were included in calculated positions and treated as riding atoms.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council of Canada (NSERC). E.R. thanks NSERC for a Graduate Fellowship (1999−2001), and A.R.M. thanks the University of Toronto for a U of T Open Fellowship (1999). I.M. is grateful to NSERC for an E.W.R. Steacie Fellowhip (1997−1999), the University of Toronto for a McLean Fellowhip (1997−2003), and the Ontario Government for a PREA Award (1997−2003). The authors also thank Dr. Alex Young for obtaining the mass spectra of **2** and **3**.

Supporting Information Available: Tables listing detailed crystallographic data, atomic position parameters, and bond lengths and angles for all reported complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000988Y

---

(31) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1994.

(32) Sheldrick, G. M. *SHELXTL-PC*; Siemens Analytical X-ray Instruments, Inc.: Madison Wisconsin, 1990.

(33) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(34) Sheldrick, G. M. *SHELXTL-PC V5.1*; Bruker Analytical X-ray Systems Inc.: Madison, Wisconsin, 1997.