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Synthesis and Structures of the Halogenated Tungsten(VI) Phosphoraniminate Complexes $WCl_5(N{=}PCl_3)$ and $WCl_4(N{=}PCl_2Ph)_2$ and the Weakly Coordinated Ion Pair $[WCl_4(N{=}PCl_3)][GaCl_4]$

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Halogen-substituted transition metal phosphoraniminate complexes have been synthesized via the reactions of WCl_6 with the phosphoranimines $Cl_2RP{=}NSiMe_3$ (R = Cl or Ph). The latter species were prepared from the reaction of the phosphoranes PCl_4R with $Li[N(SiMe_3)_2]$. The reaction of WCl_6 with 1 equiv of $Cl_3P{=}NSiMe_3$ yielded the perhalogenated (phosphoraniminato)tungsten(VI) species $WCl_5(N{=}PCl_3)$ (**1**), whereas with 2 equiv of $Cl_3P{=}NSiMe_3$, a product was isolated that was tentatively identified as *cis*-$WCl_4(N{=}PCl_3)_2$ (**2**). The analogous reaction of WCl_6 with 2 equiv of $Cl_2PhP{=}NSiMe_3$ yielded *cis*-$WCl_4(N{=}PCl_2Ph)_2$ (**3**). Compounds **1** and **3** were characterized by single-crystal X-ray diffraction. Attempts to abstract a chloride anion from **1** to yield a cationic tungsten(VI) phosphoraniminate complex via the reaction of this species with excess $GaCl_3$ yielded $[WCl_4(N{=}PCl_3)][GaCl_4]$ (**4**). An X-ray diffraction study of the latter species showed that the $[GaCl_4]^-$ anion is weakly coordinated to the cationic tungsten center through a single chloride bridge. Crystals of **1** are orthorhombic, space group *Pcmn*, with $a = 8.867(4)$ Å, $b = 10.749(2)$ Å, $c = 12.180(4)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1160.9(6)$ Å^3, and $Z = 4$. Crystals of **3** are triclinic, space group $P\bar{1}$, with $a = 9.461(4)$ Å, $b = 10.099(3)$ Å, $c = 14.506(3)$ Å, $\alpha = 109.65(2)°$, $\beta = 97.88(2)°$, $\gamma = 94.86(3)°$, $V = 1280.2(7)$ Å^3, and $Z = 2$. Crystals of **4** are monoclinic, space group $C2/m$, with $a = 13.099(3)$ Å, $b = 10.339(2)$ Å, $c = 12.540(3)$ Å, $\beta = 114.68(3)°$, $V = 1543.2(6)$ Å^3, and $Z = 4$.

Introduction

Monomeric, cyclic, and oligomeric transition metal nitrides have attracted considerable recent attention as compounds of intrinsic structural interest and as precursors to transition metal nitride ceramics and polymers.[1–10] Metal phosphoranimate complexes, which contain an $MNPR_3$ moiety, have also been well studied. However, their use as precursors to analogous transition metal phosphorus nitride materials is unexplored. Most known metal phosphoraniminate complexes possess organic substituents at phosphorus and so would be expected to give rise to a ceramic which contains carbon in addition to the transition metal, nitrogen, and phosphorus.[3,11] In order to create potentially useful precursors to carbon-free ceramics we have attempted to develop routes to halogenated species with transition metal–nitrogen–phosphorus skeletons. These compounds would be potentially useful as precursors to metal phosphorus nitride materials after ammonolysis and subsequent pyrolysis. In addition, such species might be expected to participate in cyclocondensation reactions in a similar way to species such as the cation $[Cl_3PNPCl_3]^+$ to yield potentially polymerizable inorganic heterocycles.[12–16]

In this paper we report full details of our attempts to synthesize halogenated tungsten(VI) phosphoraniminate complexes via the chlorosilane elimination reactions of WCl_6 with silylphosphoranimines.

Experimental Details

Equipment. All reactions and manipulations were carried out strictly under an atmosphere of prepurified nitrogen (Canox) using either Schlenk techniques or an inert-atmosphere glovebox (VAC Atmospheres). 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. ^{1}H NMR spectra (200 MHz) were obtained using a Varian Gemini 200 spectrometer and were referenced to $SiMe_4$ (TMS). ^{31}P NMR spectra were obtained using either a Varian XL 200 (80.0 MHz) or a Gemini 300 (121.5 MHz) spectrometer and were referenced externally to 85% H_3PO_4 in D_2O. ^{29}Si NMR spectra were obtained on a Varian XL 400 spectrometer (79.4 MHz) and were referenced externally to TMS. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer using an 70-eV electron impact ionization source.

Materials. Phosphorus pentachloride, hexamethyldisilazane, 1.6 M butyllithium in hexanes, and dichlorophenylphosphine were supplied by Aldrich Chemicals. Hexamethyldisilazane and gallium trichloride were purified by distillation and sublimation, respectively. All other reagents purchased from Aldrich were used as received. Chlorine gas (Cl_2) was supplied in a lecture bottle by Matheson Gas Products, Canada, and used as supplied. Trichlorophosphine was supplied by BDH Inc. and was used without further purification. The metal halide WCl_6 was used as supplied by Aldrich Chemicals. The compounds $PhPCl_4$ and $Li[N(SiMe_3)_2]$ were prepared by literature procedures.[17,18]

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Synthesis of the Silylphosphoranimines $RCl_2P{=}NSiMe_3$ (R = Cl or Ph). Preparation of Trichloro(trimethylsilyl)phosphoranimine $Cl_3P{=}NSiMe_3$. This compound was prepared via a modification of the procedure reported by Niecke and Bitter.[19] To a mechanically stirred hexanes solution (1000 mL) containing phosphorus pentachloride (66.8 g, 0.32 mol) at −78 °C, was added dropwise a solution of lithium bis(trimethylsilyl)amide, $LiN(SiMe_3)_2$ (53.5 g, 0.32 mol) in hexanes (500 mL). After complete addition, the reaction solution was allowed to warm gradually to room temperature and was stirred for another 4 h. After this period the white precipitate of LiCl was allowed to settle and the clear yellow supernatent was decanted. The remaining precipitate was washed with dry hexanes (3 × 50 mL). The hexanes washings and decantate were combined and the hexanes was removed at reduced pressure (50 mmHg) at room temperature. This resulted in a clear yellow liquid. The pressure was then slowly further reduced to 10 mmHg at room temperature to remove chlorotrimethylsilane. The remaining crude product was a clear brown viscous liquid. This was then distilled to give a clear, colourless liquid (bp 24 °C, 0.2 mmHg) which was identified as $Cl_3P{=}NSiMe_3$. Yield: 43.0 g (60%). ^{29}Si NMR ($CDCl_3$): δ 0.27 ppm (d, $^2J_{PSi} = 11$ Hz). ^{31}P NMR (CH_2Cl_2): δ −54.3 ppm. ^1H NMR ($CDCl_3$): δ 0.16 ppm (s). ^{13}C NMR ($CDCl_3$): δ 2.27 ppm (d, $^3J_{PC} =$ 6 Hz).

Preparation of Dichlorophenyl(trimethylsilyl)phosphoranimine, $Cl_2PhP{=}NSiMe_3$. The procedure used to prepare this compound was analogous to that for $Cl_3P{=}NSiMe_3$ except for the following details. To tetrachlorophenylphosphorane (80 g, 0.32 mol) in hexanes (1000 mL) at −78 °C was added dropwise a solution of lithium bis(trimethylsilyl)amide, $LiN(SiMe_3)_2$ (53 g, 0.32 mol), in hexanes (500 mL) with mechanical stirring. The clear, colorless product was distilled (bp 53 °C, 0.02 mmHg) and was identified as $Cl_2PhP{=}NSiMe_3$. Yield: 47.0 g (55%). ^{31}P NMR (CH_2Cl_2): δ −11.8 ppm. ^{13}C NMR ($CDCl_3$): δ 133.2 ppm (d, $^4J_{CP} = 4$ Hz, *p*-Ph), δ 130.7 ppm (d, $^3J_{CP} = 13$ Hz, *m*-Ph), δ 128.7 ppm (d, $^2J_{CP} = 19$ Hz, *o*-Ph), δ 1.9 ppm (d, $^4J_{CP} = 7$ Hz, CH_3), ipso-Ph not observed. ^1H NMR ($CDCl_3$): δ 8.0 ppm (d of d, $^3J_{HP} = 19$ Hz, $^2J_{HH}$(o,m) = 8 Hz, 2 H, *o*-Ph), δ 7.5 ppm (br, 3 H, *p*- and *m*-Ph), δ 0.2 ppm (d, $^4J_{HP} = 3$ Hz, 9 H, CH_3).

Reaction of WCl_6 with 1 equiv of $Cl_3P{=}NSiMe_3$: Synthesis of $WCl_5(N{=}PCl_3)$ (1). Tungsten hexachloride (1.76 g, 4.4 mmol) was dissolved in dichloromethane (300 mL) with stirring and the resulting solution was brought to reflux. To this was added dropwise a solution of $Cl_3P{=}NSiMe_3$ (1.0 g, 4.4 mmol) in dichloromethane (100 mL) over 2 h. During the addition the initially opaque red solution gradually became virtually clear. The solution was filtered and the solvent was removed in vacuo to yield the fine orange product (2.0 g, 88%). X-ray diffraction quality crystals were grown from CH_2Cl_2/hexanes (4:1) at −20 °C for 5 days. ^{31}P NMR for **1** (CH_2Cl_2): δ 42.6 ppm (br). No satisfactory mass spectrum of this product could be obtained, but the assigned structure was confirmed by single-crystal X-ray diffraction.

Reaction of WCl_6 with 2 equiv of $Cl_3P{=}NSiMe_3$: Synthesis of *cis*-$WCl_4(N{=}PCl_3)_2$ (2). Tungsten hexachloride (1.58 g, 4.0 mmol) was dissolved in dichloromethane (175 mL) with stirring, and the resulting solution was brought to reflux. This gave a opaque red solution. Slightly more than 2 equiv of $Cl_3P{=}NSiMe_3$ (1.9 g, 8.5 mmol) in dichloromethane (20 mL) was then added dropwise over a 40-min period. During this addition the reaction solution gradually became clearer and bright red. A ^{31}P NMR spectrum of this reaction solution showed only one broad singlet at δ 30.9 ppm. Solvent was removed in vacuo to yield the product as an fine orange powder (2.0 g, 80%). Crystals for an X-ray crystallographic study were grown from CH_2Cl_2/hexanes (3:1 mixture at −20 °C for 2 days). However, these very quickly turned to a fine powder when removed from the solvent of crystallization. Data for **2**: ^{31}P NMR (CH_2Cl_2) $\delta = 30.9$ ppm (s, $^2J_{PW} = 55$ Hz), mass spectrum (EI, 70 eV) *m/z* (%) 593 (20, $M^+ - Cl$), 558 (50, $M^+ - 2Cl$), WCl_4^+ 326 (50, $M^+ - Cl$), 253 (100, WCl_2^+).

Reaction of WCl_6 with 2 equiv of $Cl_2PhP{=}NSiMe_3$: Synthesis of *cis*-$WCl_4(N{=}PCl_2Ph)_2$ (3). Tungsten hexachloride (0.8 g, 2.0 mmol) was dissolved in dichloromethane (175 mL) with stirring and the solution was brought to reflux. This gave a dark red opaque solution to which a small excess of 2 equiv of $PhCl_2P{=}NSiMe_3$ (1.1 g, 4.1 mmol) in dichloromethane (20 mL) was added dropwise over 20 min. The reaction solution became progressively lighter and clearer and eventually became orange after 45 min. A ^{31}P NMR spectrum of the reaction mixture showed a major singlet at δ 46.4 ppm with tungsten satellites and weak signals at δ 39.7 ppm (d) and 25 ppm (m). The solvent was removed in vacuo at room temperature to give an orange powder (ca. 1.0 g). This product was washed with toluene and was then dissolved in dichloromethane (25 mL). Hexanes (5–10 mL) were then added, and subsequent cooling to −20 °C for 2 days resulted in the formation of greenish-yellow crystals of the product (0.3 g, 19%) adequate for an X-ray crystallographic analysis. ^{31}P NMR for **3**: δ 46.4 ppm (s, $^2J_{PW} = 60$ Hz). No satisfactory mass spectrum of this product could be obtained. However, the structure was confirmed by single-crystal X-ray diffraction.

Reaction of $WCl_5(N{=}PCl_3)$ (1) with $GaCl_3$: Synthesis of $[Cl_4WNPCl_3][GaCl_4]$ (4). All manipulations were carried out in an inert-atmosphere glovebox. Compound **1** (0.25 g, 0.49 mmol) was dissolved in a minimum (40 mL) of freshly distilled CH_2Cl_2 with stirring. To this, a solution of freshly sublimed $GaCl_3$ (0.10 g, 0.57 mmol) in 2 mL of CH_2Cl_2 was added dropwise by pipette. Within 5 min the solution became an amber color, after which it was stirred for another 30 min. After this time a ^{31}P NMR spectrum of the reaction solution revealed only a broad singlet resonance at δ 48.3 ppm. The reaction solution was then cooled to −15 °C for 12 h. This resulted in the formation of large clear orange crystals of the product. Yield: 0.12 g (34%). ^{31}P NMR (for **4**) of orange crystals (CH_2Cl_2) δ 48.3 ppm. The product was identified as $[Cl_4WNPCl_3][GaCl_4]$ by single-crystal X-ray diffraction.

X-ray Structure Determination Technique for $WCl_4(N{=}PCl_3)$ (1), $WCl_4(N{=}PCl_2Ph)_2$ (3), and $[WCl_4(N{=}PCl_3)][GaCl_4]$ (4). The compounds proved to be extremely sensitive to air and moisture; thus, the crystals of compounds **1** and **3** were mounted on glass fibers and encased in epoxy. A crystal of compound **4** was mounted on a glass fiber and maintained at a low temperature under nitrogen during data collection. All crystals had dimensions in the range 0.25–0.45 mm. Intensity data for all compounds were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The intensities of three standard reflections were measured every 2 h, and the data for each crystal were corrected for linear intensity decay based on the variation of these standards. The data were also corrected for Lorentz and polarization effects. Absorption corrections were also applied to **1**, **3**[20] and **4**.[21]

Each structure was solved by a combination of direct methods and difference Fourier calculations. All non-hydrogen atoms were refined anisotropically by full-matrix least squares to minimize $\sum w(F_0 - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. The hydrogen atoms in compound **3** were positioned on geometric grounds (C–H 0.96 Å) and an overall hydrogen atom thermal parameter refined to 0.091(8) Å^3. There were no chemically significant features in the final difference Fourier maps and the largest electron density peaks were in close proximity to the tungsten atoms. Crystal data, data collection, and least squares parameters are listed in Table 1. All calculations were performed and graphics created using SHELXTL PC on a 486-66 personal computer.

Results and Discussion

Previous routes to transition metal phosphoraniminate complexes have generally involved the reaction of nitrido, azido, or nitrosyl complexes with phosphines or the reactions of metal halides with silylphosphoranimines.[3,11] Virtually all of the species prepared by such reactions to date possess organic substituents such as alkyl or aryl groups at phosphorus. In order to prepare analogous complexes with halogen substituents at phosphorus we have explored the reactions of transition metal halides with the chloro(trimethyl)silylphosphoranimine $Cl_3P{=}NSiMe_3$. In this paper the reactions of the latter species with WCl_6 are discussed. The reactions of other main group or transition metal halides with chloro(trimethylsilyl)phosphoranimines will be discussed elsewhere.[22]

Synthesis of the Silylphosphoranimines $RCl_2P{=}NSiMe_3$ (R = Cl or Ph). The synthesis of the phosphoranimine $Cl_3P{=}NSiMe_3$ was first reported from PCl_5 and $Li[N(SiMe_3)_2]$ in 1973 by Niecke and Bitter.[19] The only modification of the literature preparation for $Cl_3P{=}NSiMe_3$ in our work involved the lowering of the temperature of reaction from +10 to −78 °C. However, this alteration in reaction conditions resulted in a dramatic increase

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Table 1. Summary of Crystal Data and Intensity Collection Parameters for **1**, **3**, and **4**

	1	**3**	**4**
empirical formula	Cl_8NPW	$C_{12}H_{10}Cl_8N_2P_2W\cdot CH_2Cl_2$	$Cl_{11}GaNPW$
M_r	512.4	796.5	688.5
cryst class	orthorhombic	triclinic	monoclinic
space group	*Pcmn*	$P\bar{1}$	*C*2/*m*
a, Å	8.867(4)	9.461(4)	13.099(3)
b, Å	10.749(2)	10.099(3)	10.339(2)
c, Å	12.180(4)	14.506(3)	12.540(3)
α, deg	90	109.65(2)	90
β, deg	90	97.88(2)	114.68(3)
γ, deg	90	94.86(3)	90
V, $Å^3$	1160.9(6)	1280.2(7)	1543.2(6)
Z	4	2	4
D_{calc}, g cm^{-3}	2.932	2.066	2.963
μ(Mo Kα), cm^{-1}	118.71	56.86	111.68
F(000)	928	756	1256
temp, K	294	294	193
scan type	ω–2θ	ω–2θ	ω
ω scan width, deg	0.80 + 0.35 tan θ	0.75 + 0.35 tan θ	1.45 + 1.07 tan θ
scan speed range, deg/min in ω	2.35–5.49	2.35–5.49	4.12–16.48
range 2θ collcd, deg	3.3–50.0	3.0–50.0	6.3–52.6
variation in stds.	1.00–0.89	1.00–0.74	1.00–0.93
octants, *h*,*k*,*l*	0 to *h*, 0 to *k*, 0 to *l*	–*h* to +*h*, –*k* to +*k*, –*l* to *l*	–*h* to +*h*, –*k* to 0, –*l* to +*l*
tot. no of reflcns.	1233	4555	3415
no. of unique reflcns	1079	4492	1664
R_{int}	0.00	0.00	0.15
no. of obsd. data [$I > 3\sigma(I)$]	517	3636	1307
type of abs cor	DIFABS	DIFABS	semi-empirical
min/max corr	0.770/1.446	0.794/1.359	0.160/0.960
weighting *g*	0.0003	0.0004	0.0045
R	0.038	0.029	0.048
R_w	0.035	0.035	0.072
goodness of fit	1.00	1.24	0.94
largest/mean Δ/σ	0.00/0.00	0.01/0.00	0.02/0.00
params refined	58	254	79
max/min density in ΔF map, e/$Å^3$	0.99/–1.14	0.93/–0.99	2.62/–4.79

in the yield of the product from 20% to 60%. The new phosphoranimine $PhCl_2P{=}NSiMe_3$ was prepared from $PhPCl_4$ using an analogous procedure. Purification of the silylphosphoranimines was carried out by vacuum distillation, which yielded clear, colorless highly moisture-sensitive liquid products. Identification of $Cl_3P{=}NSiMe_3$ was achieved by comparison of the ^{31}P NMR spectrum of this species with that reported in the literature.[19] The new species $PhCl_2P{=}NSiMe_3$ was characterized by ^{31}P, ^1H, and ^{13}C NMR spectroscopy. Particularly important features of the characterization data for this species were the presence of a single, singlet ^{31}P NMR resonance at –11.8 ppm and the correct ^1H NMR integration ratio for the resonances assigned to the phenyl and the trimethylsilyl groups.

Reaction of WCl_6 with 1 equiv of $Cl_3P{=}N\text{-}SiMe_3$: Synthesis of $WCl_5(N{=}PCl_3)$ (1). In order to synthesize a perhalogenated compound with a WNP skeleton the reaction of WCl_6 with $Cl_3P{=}NSiMe_3$ was explored. When the latter reagents were reacted in a 1:1 molar ratio in CH_2Cl_2, analysis of the reaction mixture by ^{31}P NMR showed that a single new product with a broad singlet resonance at δ = 42.6 ppm was formed. Crystallization from CH_2Cl_2–hexanes at –20 °C over 5 days yielded small red crystals of the product, which was assumed to have the structure $WCl_5(N{=}PCl_3)$ (**1**). However, attempts to obtain useful mass spectra to verify the structure of the product were unsuccessful, probably as a consequence of the acute moisture sensitivity of this species. In order to characterize this product completely, a single-crystal X-ray diffraction study was performed.

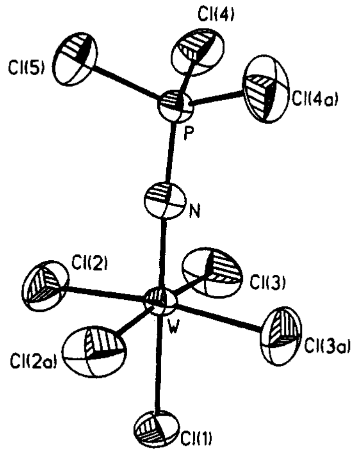


Figure 1. Molecular structural diagram of **1** with thermal ellipsoids at the 50% probability level.

Table 2. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients ($Å^2$) for the Atoms of **1**

	x	*y*	*z*	*U*(eq)[a]
W	0.1305(1)	0.2500	0.2172(1)	0.0300(3)
Cl(1)	0.3545(7)	0.2500	0.1099(6)	0.063(3)
Cl(2)	0.0401(5)	0.3973(6)	0.0989(5)	0.080(2)
Cl(3)	0.2449(7)	0.4022(7)	0.3178(4)	0.095(3)
Cl(4)	–0.1689(5)	0.3955(6)	0.4712(5)	0.082(3)
Cl(5)	–0.3599(8)	0.2500	0.2997(6)	0.070(3)
P	–0.1732(6)	0.2500	0.3803(6)	0.035(2)
N	–0.0340(19)	0.2500	0.2999(15)	0.035(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond Angles (deg) for **1** with Estimated Standard Deviations in Parentheses

Cl(1)–W–Cl(2)	87.0(2)	Cl(1)–W–Cl(3)	85.6(2)
Cl(2)–W–Cl(3)	89.9(2)	Cl(1)–W–N	178.7(6)
Cl(2)–W–N	94.0(4)	Cl(3)–W–N	93.5(4)
Cl(1)–W–Cl(2A)	87.0(2)	Cl(2)–W–Cl(2A)	87.7(3)
Cl(3)–W–Cl(2A)	172.3(2)	N–W–Cl(2A)	94.0(4)
Cl(1)–W–Cl(3A)	85.6(2)	Cl(2)–W–Cl(3A)	172.3(2)
Cl(3)–W–Cl(3A)	91.6(3)	N–W–Cl(3A)	93.5(4)
Cl(2A)–W–Cl(3A)	89.9(2)	Cl(4)–P–Cl(5)	108.2(3)
Cl(4)–P–N	110.1(4)	Cl(5)–P–N	110.9(8)
Cl(4)–P–Cl(4A)	109.4(5)	Cl(5)–P–Cl(4A)	108.2(3)
N–P–Cl(4A)	110.1(4)	W–N–P	176.2(12)

Table 4. Bond Lengths (Å) for **1** with Estimated Standard Deviations in Parentheses

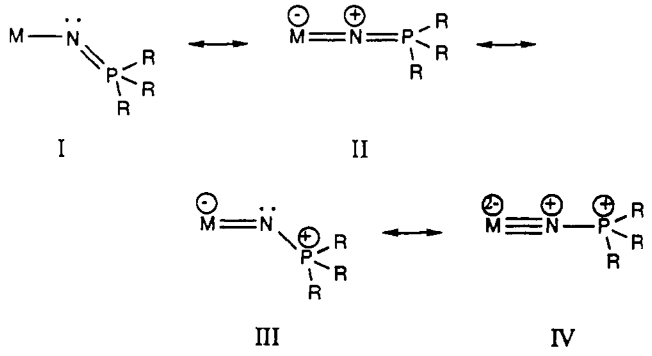
W–Cl(1)	2.377(7)	W–Cl(2)	2.285(6)
W–Cl(3)	2.282(6)	W–N	1.773(17)
W–Cl(2A)	2.285(6)	W–Cl(3A)	2.282(6)
Cl(4)–P	1.916(8)	Cl(5)–P	1.925(9)
P–N	1.576(18)	P–Cl(4A)	1.916(8)

The X-ray structural determination confirmed that **1** was indeed a perchlorinated tungsten(VI) phosphoraniminate complex. The molecular structure of **1** is shown in Figure 1. A summary of the crystal data, intensity collection parameters and structural refinement data for **1** is shown in Table 1. The fractional atomic coordinates, selected bond angles, and bond lengths for **1** are found in Tables 2–4, respectively.

The general features of the structure of **1** are quite typical for transition metal phosphoraniminate complexes;[3,11] however, several details are noteworthy. The tungsten center in **1** possesses a pseudooctahedral configuration where the chlorine atoms which form an equatorial plane orthogonal to the N–W–Cl(1) axis are bent away from the phosphoraniminate ligand. Thus the N–W–Cl_{eq} bond angles are significantly widened from the expected value of 90° for an ideal octahedral complex to 93.5(4)–94.0(4)°. The W–N–P bond angle is almost linear with a value of 176.2(12)°, which clearly suggests that the nitrogen lone pair is extensively involved in π-bonding with the tungsten center. This angle is significantly greater than that found in the analogous complex with methyl substituents at phosphorus, $Cl_5W(NPMe_3)$, which was recently reported by Doherty and co-workers where the value is 164.1(12)°.[3] The W–N bond length found in **1** (1.773 (17) Å) is longer than that in both $Cl_5W(N{=}PMe_3)$ (1.736(18) Å) and the linear species $Cl_5WN{=}PCl_2N{=}PCl_3$ (1.71(2) Å)[23] and is similar in length to those found in the cyclometallophosphazene $(Cl_3WNPPh_2NPPh_2N){\cdot}CH_3CN$ (1.798(6) and 1.773-(5) Å).[24] In contrast, a typical W–N single bond length is considered to fall in the range 2.10–2.15 Å.[25]

The geometry about the phosphorus atom is that of a slightly distorted tetrahedron. The P–N bond length of 1.576(18) Å in **1** is consistent with the presence of a normal P–N double bond, which has an accepted length of 1.56 Å,[26] and is considerably shorter than the length of a typical P–N single bond, which ranges from 1.75–1.80 Å.[27]

The reasons for these differences in bond lengths and angles between **1** and related species are not obvious. However, the factors that influence the observed geometry of the M–N–P linkage in phosphoraniminato complexes, whose bonding is best described as a resonance hybrid of several canonical forms (I–IV), are known to be quite complex[11] and the influence of steric factors may also be crucial. In addition, in the solid state the importance of crystal packing forces cannot be overlooked. Nevertheless, the structural data for **1** suggests that the most realistic formulation for this species is a resonance hybrid where canonical form II makes a dominant contribution. In contrast, the data for $Cl_5W(N{=}PMe_3)^3$ suggest that form III and possibly IV are also important.



Reaction of WCl_6 with 2 equiv of $RCl_2P{=}NSiMe_3$: Synthesis of $WCl_4(N{=}PCl_3)_2$ (2) and $WCl_4(N{=}PPhCl_2)_2$ (3). In order to synthesize a perhalogenated species with a PNWNP skeleton, the reaction of WCl_6 with 2 equiv of $Cl_3P{=}NSiMe_3$ was investigated. This yielded a red crystalline product, which was tentatively assigned the structure $WCl_4(N{=}PCl_3)_2$ (**2**). The ^{31}P NMR spectrum of the product in CH_2Cl_2 consisted of a singlet resonance at 30.9 ppm accompanied by two ^{183}W satellites ($^2J_{PW}$ = 55 Hz). In contrast to the situation for **1**, a mass spectrum of the product did yield some useful characterization information and showed peaks corresponding to $M^+ - Cl$ and $M^+ - 2Cl$ in addition to a large number of peaks which could not be assigned. No peaks assignable to WCl_6^+ or WCl_5^+ were detected. The samples of **2** supplied for mass spectra were not handled strictly under anaerobic conditions and thus they may have partially decomposed during the mass spectrometry experiments. Attempts to prove the structure of **2** conclusively by X-ray diffraction were frustrated by the powdering of crystals grown from dichloromethane-hexanes after their removal from the solution from which they were crystallized.

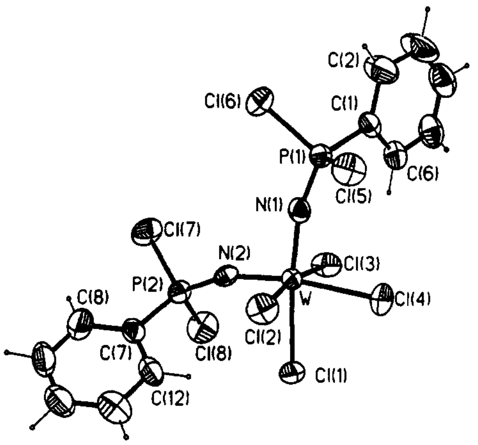


Figure 2. Molecular structural diagram of **3** with thermal ellipsoids at the 50% probability level and the solvent molecule (CH_2Cl_2) omitted for clarity.

Table 5. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å²) for the Atoms of **3**

	x	*y*	*z*	*U*(eq)[a]
W	–0.18872(2)	–0.26448(2)	–0.29002(2)	0.0291(1)
Cl(1)	–0.4355(2)	–0.2291(2)	–0.3420(1)	0.044(1)
Cl(2)	–0.1369(2)	–0.0138(2)	–0.2240(1)	0.049(1)
Cl(3)	–0.2772(2)	–0.5084(2)	–0.3453(2)	0.050(1)
Cl(4)	–0.2759(2)	–0.2481(2)	–0.1384(1)	0.062(1)
Cl(5)	0.1419(2)	–0.1073(2)	–0.0354(1)	0.053(1)
Cl(6)	0.3052(2)	–0.2496(2)	–0.2077(1)	0.050(1)
Cl(7)	–0.0376(2)	–0.3900(2)	–0.5947(1)	0.061(1)
Cl(8)	–0.3683(2)	–0.4278(2)	–0.5917(2)	0.063(1)
P(1)	0.1253(2)	–0.2766(2)	–0.1568(1)	0.031(1)
P(2)	–0.1882(2)	–0.2958(2)	–0.5259(1)	0.037(1)
N(1)	–0.0107(5)	–0.2830(5)	–0.2351(4)	0.035(2)
N(2)	–0.1546(5)	–0.2764(5)	–0.4131(4)	0.033(2)
C(1)	0.1242(6)	–0.4313(6)	–0.1269(5)	0.036(2)
C(2)	0.2512(9)	–0.4632(8)	–0.0846(7)	0.069(4)
C(3)	0.2475(10)	–0.5859(9)	–0.0599(8)	0.082(5)
C(4)	0.1193(10)	–0.6747(8)	–0.0806(6)	0.066(4)
C(5)	–0.0041(8)	–0.6430(7)	–0.1225(6)	0.055(3)
C(6)	–0.0040(7)	–0.5192(6)	–0.1454(5)	0.045(3)
C(7)	–0.2014(6)	–0.1343(7)	–0.5464(5)	0.041(2)
C(8)	–0.1437(8)	–0.1020(10)	–0.6211(6)	0.067(4)
C(9)	–0.1619(9)	0.0272(10)	–0.6325(7)	0.076(5)
C(10)	–0.2337(9)	0.1210(9)	–0.5725(7)	0.071(4)
C(11)	–0.2899(9)	0.0892(9)	–0.4994(7)	0.070(4)
C(12)	–0.2731(8)	–0.0368(8)	–0.4847(6)	0.056(3)
Cl(1S)	–0.5341(3)	0.1320(3)	–0.0746(3)	0.104(1)
Cl(2S)	–0.4371(4)	0.2711(4)	–0.2058(3)	0.147(2)
C(1S)	–0.4763(12)	0.1175(10)	–0.1823(10)	0.130(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In order to prepare a similar product to **2** which could be fully characterized, the reaction of WCl_6 with the phenylated phosphoranimine $PhCl_2P{=}NSiMe_3$ was also studied. The product was isolated as a yellow powder having a single ^{31}P NMR resonance at δ 46.4 ppm with tungsten satellites ($^2J_{WP}$ = 60 Hz) in CH_2Cl_2. The subsequent addition of hexanes to this solution and cooling to –20 °C for 2 days induced greenish-yellow crystals to form.

An X-ray diffraction study showed this product, **3**, to be a bis(phosphoriminato)tungsten(VI) complex. A summary of the crystal data, intensity collection parameters, and structural refinement data for **3** is shown in Table 1. Figure 2 shows the molecular structure of **3** (the CH_2Cl_2 solvent molecule of crystallization has been removed for clarity), and Table 5 lists the fractional atomic coordinates for this structure. Tables 6 and 7 contain selected bond angles and bond lengths, respectively.

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Table 6. Bond Angles (deg) for **3** with Estimated Standard Deviations in Parentheses

Cl(1)–W–Cl(2)	85.9(1)	Cl(1)–W–Cl(3)	86.6(1)
Cl(2)–W–Cl(3)	170.3(1)	Cl(1)–W–Cl(4)	82.4(1)
Cl(2)–W–Cl(4)	86.7(1)	Cl(3)–W–Cl(4)	86.1(1)
Cl(1)–W–N(1)	172.6(2)	Cl(2)–W–N(1)	91.8(1)
Cl(3)–W–N(1)	94.9(1)	Cl(4)–W–N(1)	90.4(2)
Cl(1)–W–N(2)	87.9(1)	Cl(2)–W–N(2)	93.8(1)
Cl(3)–W–N(2)	92.2(1)	Cl(4)–W–N(2)	170.3(1)
N(1)–W–N(2)	99.3(2)	Cl(5)–P(1)–Cl(6)	104.0(1)
Cl(5)–P(1)–N(1)	110.7(2)	Cl(6)–P(1)–N(1)	110.8(2)
Cl(5)–P(1)–C(1)	110.6(2)	Cl(6)–P(1)–C(1)	107.9(2)
N(1)–P(1)–C(1)	112.5(3)	Cl(7)–P(2)–Cl(8)	104.6(1)
Cl(7)–P(2)–N(2)	109.8(2)	Cl(8)–P(2)–N(2)	110.4(2)
Cl(7)–P(2)–C(7)	109.2(2)	Cl(8)–P(2)–C(7)	109.3(2)
N(2)–P(2)–C(7)	113.2(3)	W–N(1)–P(1)	162.0(3)
W–N(2)–P(2)	158.5(3)	P(1)–C(1)–C(2)	119.9(5)
P(1)–C(1)–C(6)	119.2(5)	C(2)–C(1)–C(6)	120.8(7)
C(1)–C(2)–C(3)	119.0(7)	C(2)–C(3)–C(4)	119.7(9)
C(3)–C(4)–C(5)	120.8(9)	C(4)–C(5)–C(6)	120.6(7)
C(1)–C(6)–C(5)	119.1(6)	P(2)–C(7)–C(8)	123.1(6)
P(2)–C(7)–C(12)	117.4(6)	C(8)–C(7)–C(12)	119.5(7)
C(7)–C(8)–C(9)	118.8(8)	C(8)–C(9)–C(10)	121.1(10)
C(9)–C(10)–C(11)	120.0(10)	C(10)–C(11)–C(12)	120.9(8)
C(7)–C(12)–C(11)	119.7(8)	Cl(1S)–C(1S)–Cl(2S)	117.6(6)

Table 7. Bond Lengths (Å) for **3** with Estimated Standard Deviations in Parentheses

W–Cl(1)	2.447(2)	W–Cl(2)	2.366(1)
W–Cl(3)	2.356(2)	W–Cl(4)	2.412(2)
W–N(1)	1.815(5)	W–N(2)	1.823(5)
Cl(5)–P(1)	1.975(2)	Cl(6)–P(1)	1.979(2)
Cl(7)–P(2)	1.978(3)	Cl(8)–P(2)	1.976(2)
P(1)–N(1)	1.577(5)	P(1)–C(1)	1.757(7)
P(2)–N(2)	1.565(6)	P(2)–C(7)	1.765(8)
C(1)–C(2)	1.386(11)	C(1)–C(6)	1.377(9)
C(2)–C(3)	1.400(15)	C(3)–C(4)	1.378(12)
C(4)–C(5)	1.354(12)	C(5)–C(6)	1.397(11)
C(7)–C(8)	1.396(13)	C(7)–C(12)	1.385(10)
C(8)–C(9)	1.392(15)	C(9)–C(10)	1.354(13)
C(10)–C(11)	1.366(16)	C(11)–C(12)	1.378(13)
Cl(1S)–C(1S)	1.691(15)	Cl(2S)–C(1S)	1.718(14)

The X-ray structure determination indicated that **3** was indeed a tungsten(VI) complex with two phosphoraniminate ligands cis to one another. As with the case of **1**, the general features of the structure of **3** are fairly typical for transition metal phosphoraniminate complexes. The N–W–N bond angle is 99.3(2)°, which is significantly wider than the 90° angle expected for ideal octahedral complexes. The W–N–P bond angles for **3** (162.0(3) and 158.5(3)°) are significantly smaller than that found in **1** (176.2(12)°). This difference is expected as two nitrogen centers can donate electron density to the electron deficient tungsten(VI) metal center in **3**. This translates into weaker, and hence longer, W–N bonds in **3** (average 1.819(5) Å compared to 1.773(17) Å in **1**). The P–N bond lengths in **3** (1.577(5) and 1.565(6) Å) are similar to that in **1** (1.576(18) Å) and are comparable to the accepted value of 1.56 Å for a P–N double bond. Thus, the bond angle at nitrogen seems relatively unrelated to the P–N bond length as previously noted.[11]

Reaction of $WCl_5(N{=}PCl_3)$ (1) with $GaCl_3$: Synthesis of $[Cl_4WNPCl_3][GaCl_4]$ (4). The well-characterized cation $[Cl_3PNPCl_3]^+$ is an excellent precursor to potentially polymerizable inorganic heterocycles via cyclocondensation reactions.[12-16] The tungsten analogue $[Cl_4WNPCl_3]^+$ might also be expected to function in a similar way to provide a route to transition metal containing rings. We therefore attempted to synthesize such a tungsten(VI) cation from **1** via halide ion abstraction.

The chloride abstracting reagent used was $GaCl_3$ and was chosen for its excellent solubility in CH_2Cl_2 and its relative ease of purification compared to the more common chloride abstractor $AlCl_3$. Addition of a solution of $GaCl_3$ in CH_2Cl_2 dropwise to a concentrated solution of **1** and subsequent cooling of the reaction solution to −15 °C for 12 h yielded large orange crystals which proved to be extremely air sensitive. The ^{31}P NMR spectrum of these crystals in CH_2Cl_2 yielded a singlet resonance at $\delta = 48.3$ ppm which is significantly shifted to low field compared to the singlet resonance of the starting material **1** ($\delta = 42.6$ ppm). In order to investigate the structure of the orange product a single-crystal X-ray diffraction study was undertaken.

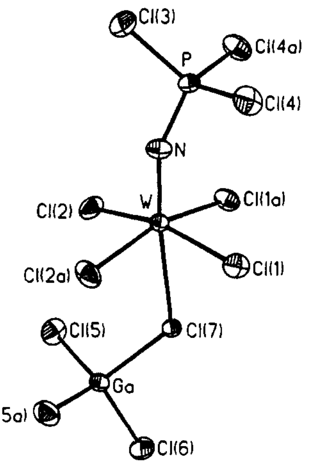

Figure 3. Molecular structural diagram for **4** with thermal ellipsoids at the 50% probability level.

Table 8. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for the Atoms of **4**

	x	y	z	U(eq)[a]
W	0.05386(4)	0.0000	0.76633(5)	0.0172(3)
Ga	−0.2976(1)	0.0000	0.7204(2)	0.021(1)
P	0.3029(3)	0.0000	0.7610(4)	0.020(1)
N	0.1709(10)	0.0000	0.7332(14)	0.025(5)
Cl(1)	0.1195(2)	0.1549(2)	0.9091(3)	0.028(1)
Cl(2)	−0.0518(2)	−0.1538(3)	0.6392(3)	0.036(1)
Cl(3)	0.3216(3)	0.0000	0.6177(4)	0.040(2)
Cl(4)	0.3750(2)	0.1508(2)	0.8535(3)	0.034(1)
Cl(5)	−0.3331(2)	−0.1716(2)	0.6146(3)	0.037(1)
Cl(6)	−0.3748(3)	0.0000	0.8417(4)	0.035(2)
Cl(7)	−0.1126(3)	0.0000	0.8405(3)	0.021(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 9. Bond Angles (deg) for **4** with Estimated Standard Deviations in Parentheses

N–W–Cl(1)	96.1(3)	N–W–Cl(2)	99.9(3)
Cl(1)–W–Cl(2)	164.0(1)	N–W–Cl(7)	174.3(5)
Cl(1)–W–Cl(7)	79.9(1)	Cl(2)–W–Cl(7)	84.2(1)
N–W–Cl(1A)	96.1(3)	Cl(1)–W–Cl(1A)	88.9(1)
Cl(2)–W–Cl(1A)	88.8(1)	Cl(7)–W–Cl(1A)	79.9(1)
N–W–Cl(2A)	99.9(3)	Cl(1)–W–Cl(2A)	88.8(1)
Cl(2)–W–Cl(2A)	89.0(1)	Cl(7)–W–Cl(2A)	84.2(1)
Cl(1A)–W–Cl(2A)	164.0(1)	Cl(7)–Ga–Cl(5)	107.9(1)
Cl(5)–Ga–Cl(6)	113.1(1)	Cl(7)–Ga–Cl(6)	102.6(2)
Cl(5)–Ga–Cl(5A)	111.5(2)	Cl(7)–Ga–Cl(5A)	107.9(1)
Cl(6)–Ga–Cl(5A)	113.1(1)	N–P–Cl(3)	110.1(7)
N–P–Cl(4)	109.8(4)	Cl(3)–P–Cl(4)	110.0(2)
N–P–Cl(4A)	109.8(4)	Cl(3)–P–Cl(4A)	110.0(2)
Cl(4)–P–Cl(4A)	107.2(2)	W–N–P	156.2(11)
W–Cl(7)–Ga	124.4(2)		

The X-ray analysis showed that in the solid state $[Cl_4WNPCl_3][GaCl_4]$ (**4**) consists of molecules in which a $GaCl_4$ unit is weakly coordinated to the tungsten atom of a $WCl_4(N{=}PCl_3)$ moiety. The molecular structure is shown in Figure 3. The intensity collection parameters are included in Table 1 and the fractional atomic coordinates, bond angles, and bond lengths are presented in Tables 8–10, respectively.

The X-ray structural analyses revealed that the *trans* chlorine is abstracted by $GaCl_3$, which is to be expected as the trans influence of the phosphoraniminate ligand should make this more facile to remove. This is apparent from a consideration of the W–Cl bond lengths in **1** where the W–Cl bond trans to the

Table 10. Bond Lengths (Å) for **4** with Estimated Standard Deviations in Parentheses

W–N	1.748(17)	W–Cl(1)	2.286(3)
W–Cl(2)	2.268(3)	W–Cl(7)	2.704(4)
W–Cl(1A)	2.286(3)	W–Cl(2A)	2.268(3)
Ga–Cl(5)	2.146(3)	Ga–Cl(7)	2.257(3)
Ga–Cl(6)	2.151(6)	Ga–Cl(5A)	2.146(3)
P–N	1.616(14)	P–Cl(3)	1.911(8)
P–Cl(4)	1.937(3)	P–Cl(4A)	1.937(3)

phosphoraniminato ligand (2.377(7) Å) is longer than that for the equatorial W–Cl bonds (average 2.284 (6) Å). The weakly coordinated ion pair nature of **4** in the solid state is supported by a consideration of the W–Cl(7) and Ga–Cl(7) bond lengths. The W–Cl(7) bond (2.704(4) Å) is dramatically lengthened in comparison to those in the equatorial position (2.268(3) and 2.286(3) Å). Furthermore, the W–Cl(7) bond is also significantly longer than the analogous W–Cl bond trans to the phosphoraniminate ligand in **1**, which possesses a length of 2.377(7) Å. Although the Ga–Cl(7) bond (2.257(3) Å) is significantly longer than the other Ga–Cl bonds (average 2.148(6) Å), the degree to which it is lengthened (0.11 Å) is not as dramatic as for the W–Cl(7) bond (0.33 Å) relative to the W–Cl bond trans to the phosphoraniminate ligand in **1**. The formation of the weakly coordinated ion pair may reflect the difficulty in forming a cationic tungsten(VI) species by chloride abstraction from an already electron poor transition metal center. The W–N bond length in **4** (1.748(17) Å) is similar to that in **1** (1.773(17) Å) whereas the WNP bond angle is dramatically smaller (156.2(11)° in **4** compared to 176.2(12)° in **1**). The P–N bond length in **4** (1.616(14) Å) is slightly longer than in **1** (1.576(18) Å). These changes are consistent with a more dominant contribution from the resonance form **III** to the structure of **4** which would be expected to relieve the electron deficiency at the tungsten center.

Summary

A series of halogenated (phosphoraniminato)tungsten(VI) complexes have been synthesized via the reaction of WCl_6 with phosphoranimines. In addition an interesting species, **4**, which formally contains the tungsten analogue of the cation $[Cl_3PNPCl_3]^+$ has been prepared via chloride ion abstraction. We are now exploring the synthesis of related compounds involving other transition elements and the use of these and **1**, **2**, and **4** in cyclocondensation reactions and as precursors to solid-state materials.

Acknowledgment. This work was supported by the Natural Science and Engineering Research Council of Canada (NSERC).

Supplementary Material Available: Tables of anisotropic thermal parameters for **1**, **3**, and **4** and hydrogen atom coordinates for **3** (4 pages). Ordering information is given on any current masthead page. A listing of observed and calculated structure factors is available upon request.