

## Reactions at Metal-Bound Nitrogen Atoms. Formation of Chloroimido Complexes from Tungsten Phosphoraniminato Complexes

Joseph D. Lichtenhan, Joseph W. Ziller, and  
Nancy M. Doherty\*

Department of Chemistry, University of California,  
Irvine, California 92717

Received April 1, 1992

### Introduction

The chemistry of transition-metal phosphoraniminato complexes ( $L_nMNP R_3$ ) has not seen extensive development. In fact, only recently has the first review article describing this interesting class of molecules appeared.<sup>1</sup> The phosphoraniminato ligand,  $NPR_3^-$  in its closed-shell form, can be viewed as an analogue of the organoimido ligand,  $NR_2^-$ , capable of donating up to six electrons to a metal center with changes in its steric and electronic properties possible by variation of the R groups. However, the phosphoraniminato ligand differs from the organoimido ligand in that it has a possible reactive site within the ligand at the nitrogen-phosphorus bond. Inspired by the potential reactivity of the phosphoraniminato ligand and our interest in reactions at metal-bound nitrogen atoms, we have initiated studies on the chemistry of transition-metal phosphoraniminato complexes.<sup>2,3</sup>

We recently reported the reaction of  $W(NSiMe_3)Cl_2(PMe_3)_3$ <sup>4</sup> with excess chlorine gas, which produced the orange phosphoraniminato complex  $W(NPMe_3)Cl_5$  (**1a**) in high yield.<sup>2</sup> During the course of that work, we noted that the formation of **1a** in the presence of excess  $Cl_2$  was occasionally accompanied by the formation of an unknown red compound. We therefore set out to identify this new compound and determine its method of formation. This report describes the unusual reaction that we have uncovered in which tungsten phosphoraniminato complexes ( $W\equiv NPR_3$ ) plus oxygen atom sources produce tungsten chloroimido derivatives ( $W\equiv NCl$ ).

### Experimental Section

**General Procedures.** All reactions and manipulations were performed under standard anhydrous and anaerobic conditions using appropriately dried reagent grade solvents and chemicals.<sup>5</sup>  $W(NPMe_3)Cl_5$  (**1a**),<sup>2</sup>  $W(NPPh_3)Cl_5$  (**1b**),<sup>2</sup> and  $[W(NCl)Cl_4]_2$ <sup>6</sup> were prepared using known procedures. Pyridine *N*-oxide (Aldrich) and triphenylphosphine oxide (Aldrich) were sublimed before use; trimethylphosphine oxide (Aldrich) was used as received. NMR spectra were recorded on General Electric OMEGA500, GN500, and QE300 and Bruker WM250 spectrometers at ambient temperatures in  $CD_2Cl_2$  solution. Chemical shifts are reported relative to the residual solvent signal in ppm downfield from  $\delta = 0$  for  $SiMe_4$  (<sup>1</sup>H, <sup>13</sup>C) or for external 85%  $H_3PO_4$  (<sup>31</sup>P); coupling constants are reported in hertz. Infrared spectra were recorded on a Mattson Galaxy 5030 FT-IR spectrometer as Nujol mulls and are reported in  $cm^{-1}$ . Elemental analyses were carried out by Galbraith Laboratories and Desert Analytics.

**Chlorine Gas.** Chlorine (Matheson, high-purity grade) was used without purification and transferred via rubber vacuum tubing into a glass vacuum line. A sample of chlorine handled in this manner was

Table I. Crystallographic data for  $W(NCl)Cl_4(OPMe_3)$  (**2a**) and  $W(NCl)Cl_4(OPPh_3)$  (**2b**)<sup>a</sup>

	<b>2a</b>	<b>2b</b>
formula	$C_3H_9Cl_5NOPW$	$C_{18}H_{15}Cl_5NOPW$
fw	467.2	653.4
crystal system	orthorhombic	monoclinic
space group	<i>Pbca</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> , Å	12.4040 (11)	18.2831 (21)
<i>b</i> , Å	12.5231 (15)	10.9083 (10)
<i>c</i> , Å	16.049 (2)	22.1815 (24)
$\beta$ , deg	90	90.554 (9)
<i>V</i> , Å <sup>3</sup>	2493.1 (5)	4423.6 (8)
<i>Z</i>	8	8
<i>T</i> , °C	-90	-90
scan method	Wyckoff	Wyckoff
$\lambda$ , Å	0.710 73	0.710 73
$D_{calcd}$ , g $cm^{-3}$	2.489	1.962
$\mu$ , $mm^{-1}$	10.640	6.026
$R(F_o)^b$	0.041	0.044
$R_w(F_o)^c$	0.052	0.046

<sup>a</sup> Data collection and structure solution and refinement were performed using previously described procedures.<sup>2</sup> <sup>b</sup>  $R(F_o) = \sum |F_o| - |F_c| / \sum |F_o|$ . <sup>c</sup>  $R_w(F_o) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , where  $w^{-1} = \sigma^2|F_o| + g|F_o|^2$ .

expanded into an evacuated glass IR cell with NaCl windows. The IR spectrum showed the series of bands characteristic of HCl in the gas phase ( $\nu = 2886 \text{ cm}^{-1}$ ).<sup>7</sup>

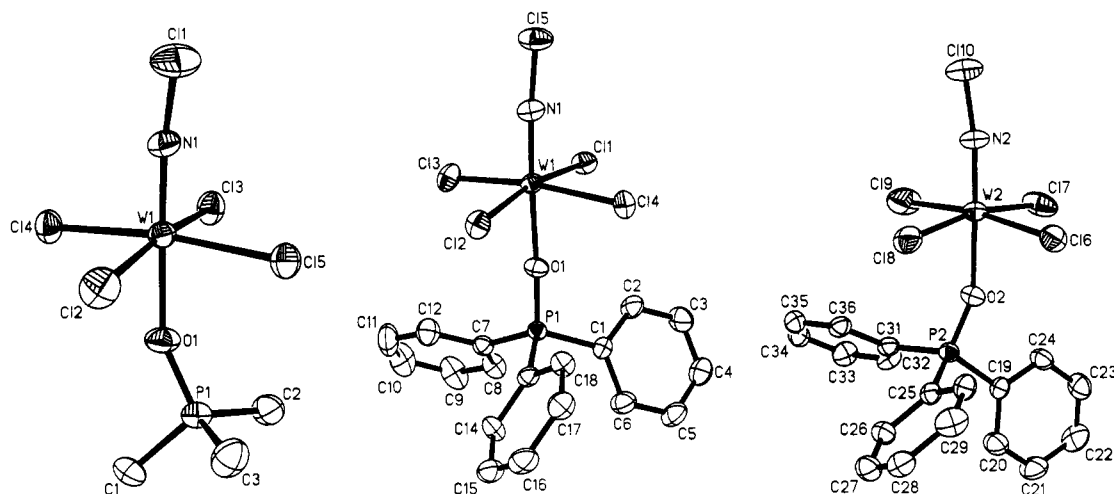
**$W(NCl)Cl_4(OPMe_3)$  (**2a**).** (a) A large excess of  $Cl_2$  was vacuum-transferred onto a sample of **1a** (150 mg, isolated from the reaction of  $W(NSiMe_3)Cl_2(PMe_3)_3$  and  $Cl_2$  and still contaminated with a small amount of the  $PCl_2Me_3$  byproduct of this reaction)<sup>2</sup> in dichloromethane at  $-196^\circ C$ . The mixture was warmed to room temperature and allowed to react for 3 h. During this time, all of the sparingly soluble orange **1a** dissolved and a reaction occurred producing a red solution. The solvent was removed under reduced pressure, yielding a red solid, which was recrystallized from a mixture of dichloromethane and pentane and identified as **2a** by NMR spectroscopy. (b) A mixture of **1a** (13 mg, 0.029 mmol) and pyridine *N*-oxide (5 mg, 0.053 mmol) in  $CD_2Cl_2$  was sealed in an NMR tube and allowed to react at room temperature. After 2 h, the NMR spectra of this deep red solution showed a complex mixture, including **2a**,  $W(NCl)Cl_4(ONC_5H_5)$  (see below), pyridine *N*-oxide, and pyridine, as well as at least two unidentified pyridine-containing species. After 2 days, the NMR spectrum of the red solution had simplified, showing **2a** as the major product; unreacted pyridine *N*-oxide, some free  $P(O)Me_3$ , and one unidentified pyridine-containing species were also observed. (c) A mixture of  $[W(NCl)Cl_4]_2$  (1.026 g, 2.74 mmol of W) and  $P(O)Me_3$  (0.259 g, 2.81 mmol) in dichloromethane (25 mL) was stirred for 10 h at room temperature. The solvent volume was reduced to a minimum, producing a red crystalline solid, which was collected by filtration, washed with pentane, and dried under vacuum, yielding 1.140 g of **2a** (89%).

<sup>1</sup>H NMR: 1.97 (d,  $J_{PH} = 13$ ). <sup>13</sup>C{<sup>1</sup>H} NMR: 16.5 (d,  $J_{PC} = 71$ ). <sup>31</sup>P{<sup>1</sup>H} NMR: 69.6. IR: 1410, 1309, 1297, 1190, 1086, 955, 869, 858, 766, 755, 679, 463, 419, 318. Anal. Calcd. for  $C_3H_9Cl_5NOPW$ : C, 7.71; H, 1.94; N, 3.00. Found: C, 7.97; H, 1.99; N, 2.99. Crystals of **2a** for X-ray diffraction experiments were obtained by vapor diffusion of pentane into a dichloromethane solution of the compound.

**$W(NCl)Cl_4(OPPh_3)$  (**2b**).** Procedure b above was followed to react 20 mg of **1b** (0.03 mmol) and 2 mg of pyridine *N*-oxide (0.02 mmol) in  $CD_2Cl_2$ . After 1 day at room temperature, NMR spectra showed signals for **2b** as the major product; some unreacted **1b**, free  $P(O)Ph_3$ , and unidentified pyridine-containing species were also observed. Procedure c above was followed to react 0.508 g of  $[W(NCl)Cl_4]_2$  (1.35 mmol of W) and 0.396 g of  $P(O)Ph_3$  (1.42 mmol) in benzene (20 mL), yielding 0.762 g of **2b** (86%). <sup>1</sup>H NMR: 7.92 (dd,  $J_{PH} = 13$ ,  $J_{HH} = 8$ , 6 H), 7.72 (t,  $J_{HH} = 8$ , 3 H), 7.58 (td,  $J_{HH} = 8$ ,  $J_{PH} = 3$ , 6 H). <sup>13</sup>C{<sup>1</sup>H} NMR: 134.3 (s), 133.8 (d,  $J_{PC} = 14$ ), 129.4 (d,  $J_{PC} = 13$ ). <sup>31</sup>P{<sup>1</sup>H} NMR: 49.5. IR: 1588, 1435, 1204, 1136, 1086, 1025, 998, 748, 727, 690, 538, 468, 460, 445, 422, 327. Anal. Calcd. for  $C_{18}H_{15}Cl_5NOPW$ : C, 33.09; H, 2.31; N, 2.14. Found: C, 33.45; H, 2.24; N, 1.93. Crystals of **2b** for X-ray diffraction experiments were obtained by vapor diffusion of pentane into a dichloromethane solution of the compound.

(7) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: Princeton, NJ, 1950; Vol. 1, pp 53-57.

- Dehnicke, K.; Strähle, J. *Polyhedron* **1989**, *8*, 707-726.
- Lichtenhan, J. D.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1992**, *31*, 2893-2900.
- Schomber, B. M.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1991**, *30*, 4488-4490.
- Lichtenhan, J. D.; Critchlow, S. C.; Doherty, N. M. *Inorg. Chem.* **1990**, *29*, 439-442.
- Shriver, D. F. *The Manipulation of Air Sensitive Compounds*; Kreiger: Malabar, FL, 1982. *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.
- Görge, A.; Dehnicke, K.; Fenske, D. *Z. Naturforsch.* **1988**, *43B*, 677-681.



**Figure 1.** ORTEP drawings of (left)  $W(NCl)Cl_4(OPMe_3)$  (**2a**) and (middle, right) the two crystallographically independent molecules of  $W(NCl)Cl_4(OPPh_3)$  (**2b**) with 50% probability thermal ellipsoids.

**Related Reactions.  $[W(NCl)Cl_4]_2$  and Pyridine *N*-Oxide.** A mixture of  $[W(NCl)Cl_4]_2$  (20 mg, 0.05 mmol of W) and pyridine *N*-oxide (7 mg, 0.07 mmol) in  $CD_2Cl_2$  was sealed in an NMR tube. NMR signals consistent with formation of  $W(NCl)Cl_4(ONC_5H_5)$  were immediately observed.  $^1H$  NMR: 8.81 (d,  $J_{HH} = 7$  Hz, 2 H), 8.07 (t,  $J_{HH} = 8$  Hz, 1 H), 7.81 (t,  $J_{HH} = 7$  Hz, 2 H).

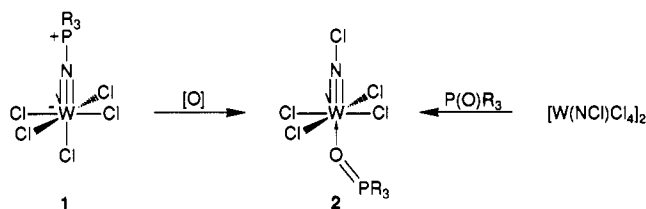
**$[W(NCl)Cl_4]_2$  and Pyridine.** A mixture of  $[W(NCl)Cl_4]_2$  (38 mg, 0.10 mmol of W) and pyridine (8  $\mu$ L, 0.10 mmol) in  $CD_2Cl_2$  was sealed in an NMR tube. NMR signals consistent with formation of  $W(NCl)Cl_4(NC_5H_5)$  as the major product were immediately observed.  $^1H$  NMR: 9.54 (dd,  $J_{HH} = 7$  and 1, 2 H), 8.11 (tt,  $J_{HH} = 7$  and 1, 1 H), 7.68 (t,  $J_{HH} = 7, 2$  H).

## Results and Discussion

$W(NPMe_3)Cl_5$  (**1a**) reacts with excess chlorine gas in dichloromethane solution in glass apparatus to produce the chloroimido complex  $W(NCl)Cl_4(OPMe_3)$  (**2a**). Compound **2a** was identified by comparison of its NMR and IR spectra to those of an authentic sample (see below). An oxygen atom is needed to convert **1a** to **2a**, indicating that some impurity must be responsible for the reaction. Consistent with this, formation of **2a** from **1a** plus excess chlorine requires anywhere from hours to days, depending upon the source and handling of the chlorine gas. Furthermore, experiments using flame-treated glassware and multiply-distilled semiconductor-purity chlorine produce negligible amounts, if any, of the chloroimido product. Oxygen ( $O_2$ ) and water are common oxygen-containing impurities in many reagents, but neither appears to be directly responsible for the conversion of **1a** to **2a**. Mixtures of **1a** and  $O_2$  gas in  $CD_2Cl_2$  produce no detectable **2a** after 1 week at room temperature, and **1a** is decomposed by  $H_2O$  to an unidentified white solid.

An IR spectrum of the chlorine used in the reactions shows the series of bands characteristic of HCl in the gas phase.<sup>7</sup> HCl is not a typical impurity in commercial  $Cl_2$ ,<sup>8</sup> suggesting that it may be formed by the reaction of  $Cl_2$  with water absorbed on the walls of the transfer apparatus and of the IR cell. The reaction of  $H_2O$  with  $Cl_2$  would also be expected to produce HOCl, which might possibly be in equilibrium with  $Cl_2O$ ,<sup>9</sup> both of which are potential reactive sources of an oxygen atom. Although we have not been able to establish which of these species, if either, is responsible

## Scheme I



for the conversion of **1a** to **2a**, the possible presence of these impurities prompted us to examine whether other oxidizing oxygen atom sources might also perform this chemistry. This is the case for pyridine *N*-oxide, which reacts with both **1a** and the triphenylphosphoraninato complex  $W(NPPh_3)Cl_5$  (**1b**) to produce the chloroimido complexes **2a** and  $W(NCl)Cl_4(OPPh_3)$  (**2b**) in reasonable yields (Scheme I).  $^1H$  and  $^{31}P$  NMR monitorings of these reactions indicate that they are quite complex at intermediate stages. This is in part because both the pyridine *N*-oxide reagent and the pyridine byproduct can potentially react with tungsten chloroimido species present in solution. We have observed fast coordination of these ligands to the tungsten center of the base-free chloroimido dimer  $[W(NCl)Cl_4]_2$ ,<sup>6</sup> producing  $W(NCl)Cl_4(ONC_5H_5)$  and  $W(NCl)Cl_4(NC_5H_5)$ . However, in the formation of **2** from **1** plus pyridine *N*-oxide, only  $W(NCl)Cl_4(ONC_5H_5)$  is unequivocally detected at intermediate stages of the reaction.

Compounds **2a** and **2b** have been prepared independently by addition of the organophosphine oxides to the known chloroimido dimer  $[W(NCl)Cl_4]_2$  (Scheme I). Related reactions of acetonitrile and chloride with  $[W(NCl)Cl_4]_2$ , forming  $W(NCl)Cl_4(NCMe)$ <sup>6</sup> and  $[W(NCl)Cl_5]^-$ , have previously been reported.<sup>6,10</sup> Red crystalline **2a** and **2b** are soluble in aromatic, chlorinated, and coordinating organic solvents and produce NMR, IR, and elemental analysis data consistent with their formulation. X-ray crystal structures (Figure 1) confirm that these complexes contain chloroimido and phosphine oxide ligands, coordinated trans to each other at the octahedral tungsten centers. Important bond distances and angles are summarized in Table II and are typical of those reported for related complexes.<sup>6,10-12</sup>

The tungsten phosphoraninato complexes  $W(NPR_3)Cl_5$  (**1**) are highly oxidized species containing tungsten(VI) and phos-

(8) Typical low-level impurities in gaseous chlorine are Ar,  $O_2$ ,  $N_2$ ,  $CH_4$ , CO, and  $CO_2$ ; *Matheson Gas Products Catalog*; Matheson: East Rutherford, NJ, March 1990; pp 13-14, 81-82.

(9) The gas-phase infrared spectra of  $Cl_2O$  and  $H_2O$  (generated by the gas-phase reaction of  $Cl_2O$  and  $H_2O$  and examined in a mixture with these gases) have been reported: Hedberg, K.; Badger, R. M. *J. Chem. Phys.* **1951**, *19*, 508-509. Hedberg, K. *J. Chem. Phys.* **1951**, *19*, 509. In the IR spectra of our impure  $Cl_2$ , we do not observe sufficiently strong bands for HOCl or  $Cl_2O$  to unequivocally invoke their presence in these samples.

(10) G6rge, A.; Ute, P.-S.; M6ller, U.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43B*, 1633-1638.

(11) G6rge, A.; Dehnicke, K.; Fenske, D. *Z. Naturforsch.* **1989**, *44B*, 117-120. Fenske, D.; Frankenau, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1989**, *579*, 27-34.

(12) For a summary of structure information for transition-metal phosphine oxide complexes see: Goggin, P. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 2, pp 497-501.

**Table II.** Selected Bond Distances (Å) and Angles (deg) for W(NCl)Cl<sub>4</sub>(OPMe<sub>3</sub>) (**2a**) and W(NCl)Cl<sub>4</sub>(OPPh<sub>3</sub>) (**2b**)

	2a		2b	
W–N	1.737 (6)	1.732 (5)	1.731 (5)	
N–Cl	1.608 (6)	1.606 (5)	1.608 (6)	
W–O	2.038 (5)	2.073 (4)	2.072 (4)	
O–P	1.529 (6)	1.511 (4)	1.515 (4)	
W–N–Cl	167.0 (4)	175.8 (4)	172.2 (4)	
W–O–P	151.2 (3)	168.5 (3)	158.4 (3)	

phorus(V) centers. It is therefore surprising to find that these compounds undergo further oxidation by oxygen atom sources, producing tungsten(VI) chloroimido complexes, W(NCl)Cl<sub>4</sub>(OPR<sub>3</sub>) (**2**). This transformation involves net two-electron oxidation of the multiply-bonded nitrogen atom from N<sup>-III</sup> in the phosphoraniminato ligand to N<sup>-I</sup> in the chloroimido ligand. The oxygen atom ends up attached to the phosphorus(V) in an organophosphine oxide. It is also interesting to note that this reaction appears to occur with both nucleophilic (pyridine *N*-oxide)<sup>13</sup> and electrophilic (HOCl or Cl<sub>2</sub>O)<sup>14</sup> sources of the oxygen atom.

In summary, reactions of tungsten phosphoraniminato com-

plexes with oxygen atom reagents produce tungsten chloroimido complexes in reasonable yields. This work demonstrates that interesting and unusual reactivity is possible at the nitrogen–phosphorus bond of the phosphoraniminato ligand and suggests that further exploration of the chemistry of phosphoraniminato complexes will prove fruitful.

**Acknowledgment.** We gratefully acknowledge support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. Susan C. Critchlow for assistance with preliminary X-ray experiments and Donna M. DeCoster for help with NMR and IR spectra. N.M.D. thanks the Alfred P. Sloan Foundation for a Fellowship (1990–2).

**Supplementary Material Available:** X-ray diffraction data for **2a** and **2b**, including tables of structure determination summaries, atomic coordinates, interatomic distances, interatomic angles, anisotropic displacement coefficients, and hydrogen atom coordinates (17 pages). Ordering information is given on any current masthead page.

(13) Fieser, M.; Fieser, L. *Reagents for Organic Synthesis*; Wiley: New York, 1969; Vol. 2, p 353.

(14) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; pp 476–478, 726–727.