

Synthesis and Structures of Tungsten (1-Pyridinio)imido Complexes and Their Facile N–N Bond Cleavage¹

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The tungsten (1-pyridinio)imido complexes $[\text{WX}_2(\text{NNC}_5\text{H}_4\text{OMe})(\text{L})(\text{PMe}_2\text{Ph})_2]^+$, $[\text{WX}_2(\text{NNC}_5\text{H}_2\text{Me}_3)(\text{L})(\text{PMe}_2\text{Ph})_2]^+$, and $[\text{WCl}_2\{\text{NNC}_5\text{H}_2(\text{COOEt})_2\text{Ph}\}(\text{L})(\text{PMe}_2\text{Ph})_2]^+$ ($\text{X} = \text{Cl}, \text{Br}$; $\text{L} = \text{CO}, \text{C}_2\text{H}_4, \text{PMe}_2\text{Ph}$) were synthesized by the reaction of the salts of pyrylium cations with the hydrazido complexes $[\text{WX}_2(\text{NNH}_2)(\text{L})(\text{PMe}_2\text{Ph})_2]$, which were derived from the dinitrogen complex *cis*- $[\text{W}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$. The complexes obtained were characterized by spectroscopic measurements as well as crystallographic studies of *cis,mer*- $[\text{WBr}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$, *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{ClO}_4]$, *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_2\text{Me}_3-2,4,6)(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{OTf}]$ ($\text{OTf} = \text{OSO}_2\text{CF}_3$), and *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2][\text{ClO}_4]$, which revealed that the N–N bond distances of these (1-pyridinio)imido complexes are shorter than those of the trialkyl- or unsubstituted hydrazidium complexes so far reported. The (1-pyridinio)imido complexes with a π -acidic ligand (CO or C_2H_4) underwent smooth N–N bond cleavage on reaction with cobaltocene under ambient conditions to liberate the pyridines in moderate to high yields. In some reactions that were conducted in the presence of $\text{HNEt}_3\text{-Cl}$, the corresponding imido (NH) complexes were recovered as the metal products. The (1-pyridinio)imido complexes also reacted with KOH in MeOH to give the pyridines and ammonia in high yields. These reactions provide the first examples of N–N bond cleavage of well-defined hydrazidium complexes and accomplish the synthesis of pyridines from molecular nitrogen under mild conditions.

Introduction

Great efforts have been directed toward the activation and chemical transformation of dinitrogen assisted by transition metal complexes with the intention not only of understanding the biological dinitrogen reduction mechanisms but also of developing a new nitrogen fixation process under mild conditions.^{2,3} Incorporation of dinitrogen directly into organic substrates by using transition metal dinitrogen complexes is one of the most fascinating goals in the chemistry of nitrogen fixation. In this context, we have continuously been investigating the conversion of ligating dinitrogen into organonitrogen ligands.

Previously, we have shown that facile transformations of coordinated dinitrogen in molybdenum or tungsten complexes of the type $[\text{M}(\text{N}_2)_2(\text{PR}_3)_4]$ ($\text{M} = \text{Mo}, \text{W}$; PR_3 = tertiary phosphine) into various diazoalkane ligands⁴ ($\text{N}_2\text{CR}^1\text{R}^2$) are realized by the two-step process:⁵ the protonation of the dinitrogen complexes leading to the hydrazido(2–) complexes

followed by the condensation reaction of the resultant complexes with organic carbonyl compounds ($\text{R}^1\text{R}^2\text{C}=\text{O}$). This condensation reaction provides a versatile method for the C–N bond formation at the coordinated dinitrogen and enjoys wide applicability. The diazoalkane ligands thus formed can be transformed into nitrogenous compounds, such as amines,^{5b} azines,^{3a,5b,6} and pyrazoles.^{5d,e} Furthermore, this condensation method has been extended to the reaction with dialdehydes or their equivalents to synthesize the complexes with five-membered heterocyclic ligands, such as (1-pyrrolyl)imido⁷ and (phthalimidin-2-yl)imido ligands,⁸ from which nitrogen heterocycles, including pyrrole, *N*-aminopyrrole, phthalimidine, and *N*-aminophthalimidine, are released in good yields. These results stimulated us to investigate the construction of a pyridine ring, another important nitrogen heterocyclic system, by the reaction

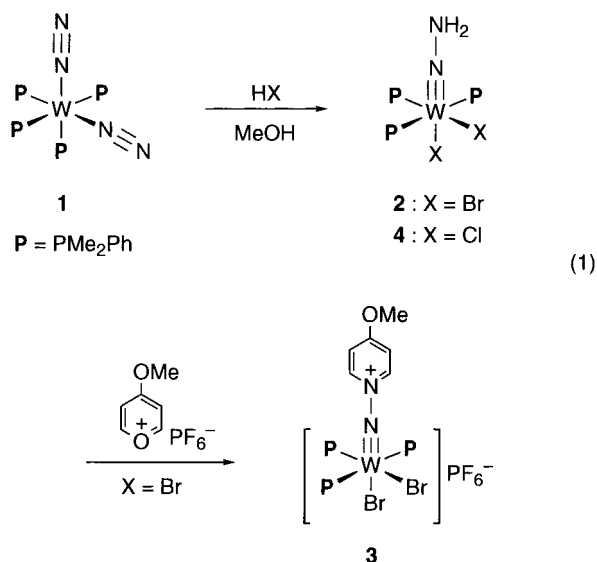
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of hydrazido(2-) complexes with the salts of pyrylium cations. Herein, we describe the synthesis of (1-pyridinio)imido complexes of tungsten from the dinitrogen complex *cis*-[W(N₂)₂(PMe₂Ph)₄] (**1**) by way of the hydrazido(2-) complexes and the formation of pyridines via the N–N bond cleavage. A part of this work has been reported as a preliminary communication.⁹

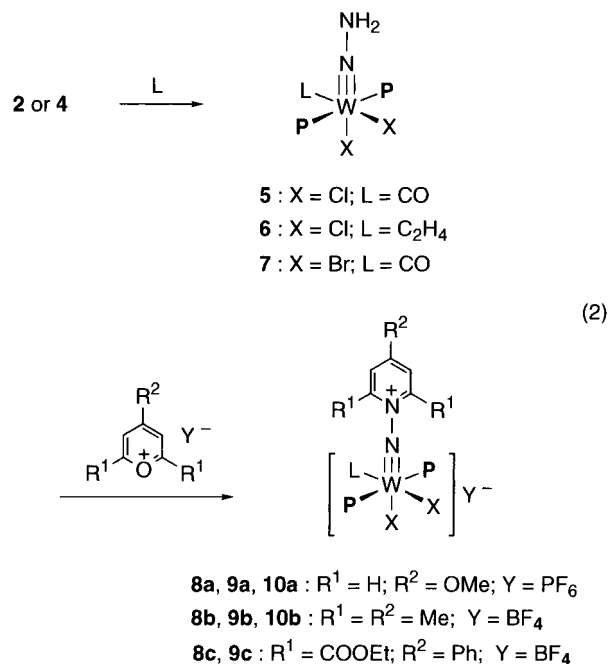
Results and Discussion

Synthesis of Tungsten (1-Pyridinio)imido Complexes from the Dinitrogen Complex 1. When the hydrazido(2-) complex *cis,mer*-[WBr₂(NNH₂)(PMe₂Ph)₃] (**2**),¹⁰ which is readily derived from complex **1** by protonation with hydrobromic acid, was allowed to react with 4-methoxyppyrylium hexafluorophosphate at room temperature, the corresponding (1-pyridinio)imido complex *cis,mer*-[WBr₂(NNC₅H₄OMe-4)(PMe₂Ph)₃][PF₆] (**3**) was isolated in moderate yield after recrystallization (eq 1). However, complex **2** failed to give any isolable product in reactions with the salts of 2,6-disubstituted pyrylium cations, and attempts to synthesize the chloro analogue of **3** from *cis,mer*-[WCl₂(NNH₂)(PMe₂Ph)₃] (**4**) were also unsuccessful.



Interestingly, the hydrazido(2-) complexes with a sterically small π -acceptor ligand *cis,trans*-[WX₂(NNH₂)(L)(PMe₂Ph)₂] (**5**, X = Cl, L = CO; **6**, X = Cl, L = C₂H₄; **7**, X = Br, L = CO),¹⁰ which can be prepared by the ligand substitution reaction of **2** or **4** with L,¹¹ reacted smoothly even with the salts of 2,6-disubstituted pyrylium cations to form the corresponding (1-pyridinio)imido complexes. Thus, reactions of **5**, **6**, and **7** with various salts of substituted pyrylium cations in the presence of a small amount of hydrochloric or hydrobromic acid afforded the corresponding (1-pyridinio)imido complexes **8** (X = Cl, L = CO), **9** (X = Cl, L = C₂H₄), and **10** (X = Br, L = CO),

respectively, in high yields (eq 2). Addition of the acid was not essential for this reaction but appreciably improved the yields.



For example, the yield of complex **8b** was increased from 54% to 92% by conducting the reaction in the presence of a catalytic amount of hydrochloric acid. The hydrazido(2-) complex with dppe ligands *trans*-[Wf(NNH₂)(dppe)₂]⁺ (dppe = Ph₂PCH₂CH₂PPh₂) failed to react with all the salts of pyrylium cations examined. This result is in contrast to our previous observation that the same complex readily reacts with 2,5-dimethoxytetrahydrofuran in the presence of an acid catalyst to give the (1-pyrrolyl)imido complex.⁷

In agreement with the formation of (1-pyridinio)imido ligands, complexes **3**, **8**, **9**, and **10** exhibited strong IR absorptions at 1613–1642 cm⁻¹ characteristic of a pyridinium skeleton. Their ¹H NMR and ³¹P{¹H} NMR spectra were also consistent with the formulation. The ¹H NMR spectra of complexes **8b**, **8c**, **9b**, and **9c** showed significant temperature dependence, revealing their dynamic behavior. At 20 °C in CD₂Cl₂, complex **8b** exhibited a set of singlets at δ 1.98 (6H), 2.36 (3H), and 7.06 (2H) attributable to the 2,6-Me₂, 4-Me, and pyridine ring protons, respectively. Upon cooling to -40 °C or below, the singlet signal at δ 1.98 split into two singlets (δ 1.83, 1.91). Similarly, the OCH₂ signal of complex **8c** and the 2,6-Me₂ signal of **9b** were observed as one broad peak at 20 °C (δ 4.56 for **8c** and δ 1.85 for **9b**), which started to split at 0 °C into two quartets (δ 4.51, 4.62) and two singlets (δ 1.64, 1.98), respectively. Further, the signals due to the 2,6-(COOEt)₂ groups in **9c** appeared as two distinct sets of signals (δ 1.41 (br t, 3H), 1.58 (t, 3H), 4.39 (br, 2H), 4.70 (br, 2H)) even at room temperature. In contrast, the ¹H NMR spectrum of complex **9a**, which has a substituent only at the 4-position of the pyridine ring, did not show pronounced temperature dependence over the range of 20 to -40 °C. Considering that the complexes with the larger steric congestion between the substituents on the pyridine ring and the equatorial ancillary ligands show the higher coalescence temperatures, it is obvious that these ¹H NMR behaviors are due to the sterically restricted rotation around the W–N–N axis.

Crystal Structures of (1-Pyridinio)imido Complexes. The molecular structures of the (1-pyridinio)imido complexes were

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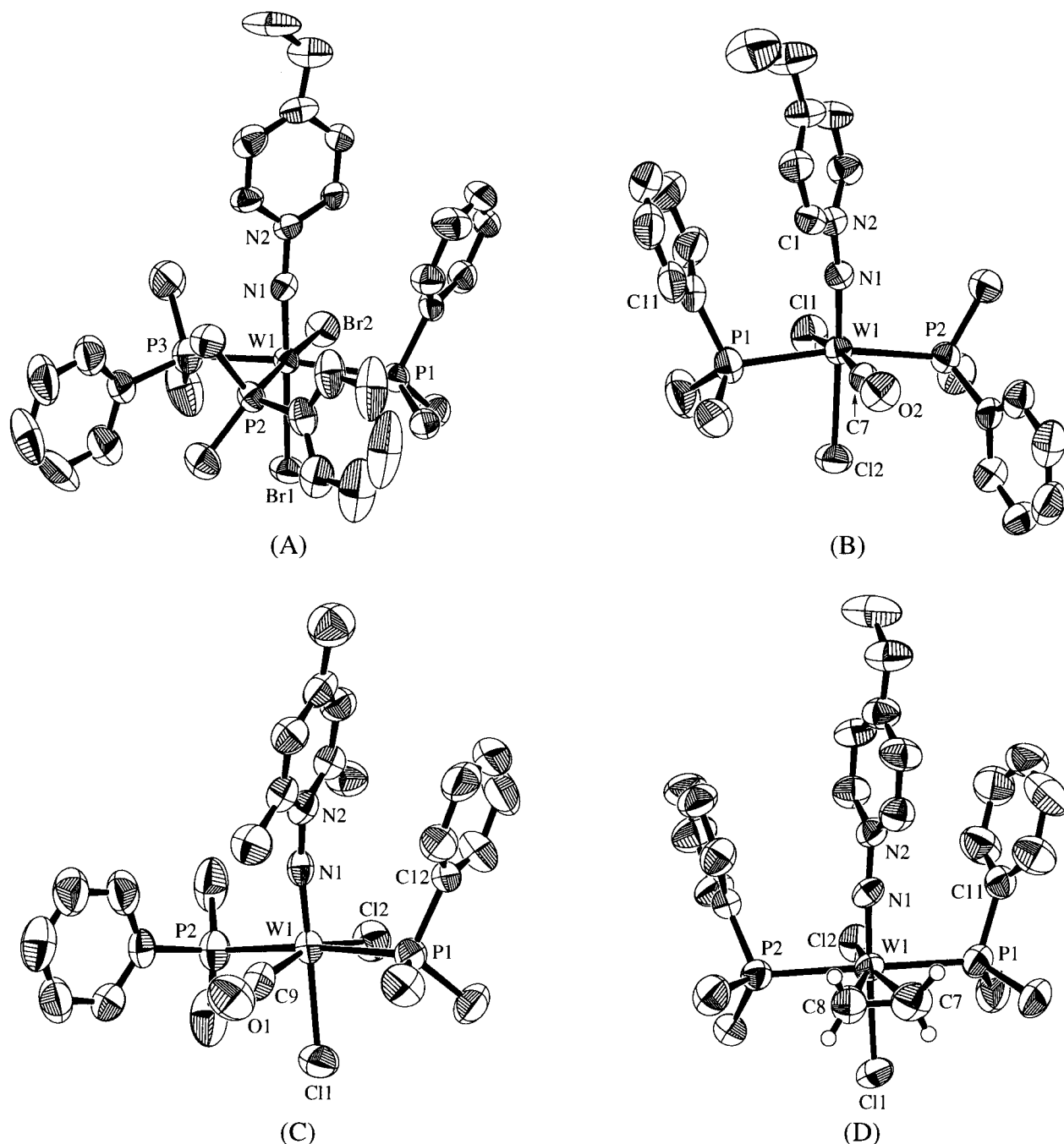


Figure 1. ORTEP drawings for the cationic part of **3** (A), **8a'** (B), **8b'** (C), and **9a'·0.5(CH₂Cl₂)** (D) (hydrogen atoms except for the ethylene protons of **9a'·0.5(CH₂Cl₂)** are omitted for clarity).

Table 1. Bond Lengths (Å) and Angles (deg) of **3**

W(1)–N(1)	1.747(7)	W(1)–N(1)–N(2)	170.3(6)
W(1)–P(1)	2.539(2)	P(1)–W(1)–N(1)	97.8(2)
W(1)–P(2)	2.492(2)	P(2)–W(1)–N(1)	92.8(2)
W(1)–P(3)	2.525(3)	P(3)–W(1)–N(1)	93.6(2)
W(1)–Br(1)	2.565(1)	Br(1)–W(1)–N(1)	178.8(2)
W(1)–Br(2)	2.666(1)	Br(2)–W(1)–N(1)	91.3(2)
N(1)–N(2)	1.379(9)		

unambiguously determined by X-ray analysis of complexes **3**, *cis,trans*-[WCl₂(NNC₅H₄OMe)(CO)(PMe₂Ph)₂][ClO₄] (**8a'**, the [ClO₄][−] analogue of **8a**), *cis,trans*-[WCl₂(NNC₅H₂Me₃)(CO)(PMe₂Ph)₂][OTf] (**8b'**, the [OTf][−] analogue of **8b**; OTf = OSO₂CF₃), and *cis,trans*-[WCl₂(NNC₅H₄OMe)(C₂H₄)(PMe₂Ph)₂][ClO₄]·0.5CH₂Cl₂ (**9a'**·0.5CH₂Cl₂, the [ClO₄][−] analogue of **9a**). Their ORTEP drawings are shown in Figure 1, and selected bond distances and angles are listed in Tables 1–4. It is clearly

Table 2. Bond Lengths (Å) and Angles (deg) of **8a'**

W(1)–N(1)	1.750(4)	W(1)–N(1)–N(2)	168.8(3)
W(1)–P(1)	2.519(1)	P(1)–W(1)–N(1)	93.8(1)
W(1)–P(2)	2.516(1)	P(2)–W(1)–N(1)	98.9(1)
W(1)–Cl(1)	2.457(1)	Cl(1)–W(1)–N(1)	101.0(1)
W(1)–Cl(2)	2.417(1)	Cl(2)–W(1)–N(1)	169.3(1)
W(1)–C(7)	1.987(6)	C(7)–W(1)–N(1)	89.1(2)
N(1)–N(2)	1.363(4)		

confirmed that in each case the terminal nitrogen atom in complex **2**, **5**, or **6** is incorporated into the respective pyridine ring with retention of the stereochemistry around the tungsten center. The W–N–N linkages are essentially linear (168.8(3)–172.8(6)°), and the N–N bond distances are in the range of 1.363(4)–1.383(8) Å. It should be pointed out that the (1-pyridinio)imido complexes can be regarded as hydrazidium complexes (MNNR₃⁺), only a limited number of which have

Table 3. Bond Lengths (Å) and Angles (deg) of **8b'**

W(1)–N(1)	1.744(7)	W(1)–N(1)–N(2)	170.2(5)
W(1)–P(1)	2.532(2)	P(1)–W(1)–N(1)	91.8(2)
W(1)–P(2)	2.529(2)	P(2)–W(1)–N(1)	94.8(2)
W(1)–Cl(1)	2.445(2)	Cl(1)–W(1)–N(1)	170.8(2)
W(1)–Cl(2)	2.451(3)	Cl(2)–W(1)–N(1)	102.3(2)
W(1)–C(9)	2.021(9)	C(9)–W(1)–N(1)	96.2(3)
N(1)–N(2)	1.383(8)		

Table 4. Bond Lengths (Å) and Angles (deg) of **9a'**·0.5CH₂Cl₂

W(1)–N(1)	1.738(6)	W(1)–N(1)–N(2)	172.8(6)
W(1)–P(1)	2.541(2)	P(1)–W(1)–N(1)	93.1(2)
W(1)–P(2)	2.551(2)	P(2)–W(1)–N(1)	93.9(2)
W(1)–Cl(1)	2.436(2)	Cl(1)–W(1)–N(1)	178.1(2)
W(1)–Cl(2)	2.468(3)	Cl(2)–W(1)–N(1)	94.8(2)
W(1)–C(7)	2.22(1)	C(7)–W(1)–C(8)	37.5(4)
W(1)–C(8)	2.19(1)		
N(1)–N(2)	1.373(8)		

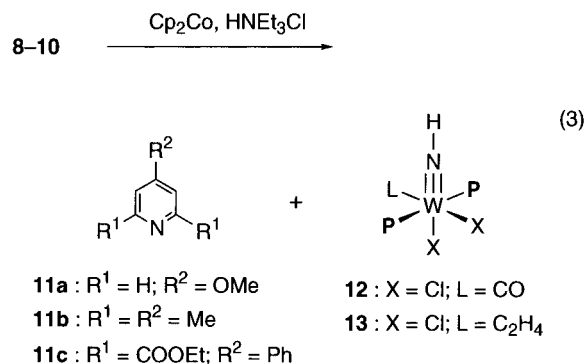
been synthesized so far.^{12–16} The N–N bond distances found for the (1-pyridinio)imido complexes **3**, **8a'**, **8b'**, and **9a'** are shorter than those in crystallographically determined trialkyl- or unsubstituted hydrazidium complexes, including [WCl(NNH₃)(PMe₃)₄]₂ (1.396(20) Å),¹² [Cp*MoMe₃(NNMe₃)]-[OTf] (Cp* = η⁵-C₅Me₅, 1.426(5) Å),¹³ and [Cp*TaS(S'Bu)(NNMe₂Bu)] (1.46(1) Å),¹⁴ but are similar to those found in titanium (1-pyridinio)imido complexes, such as [CpTiCl₂(NNC₅H₅)](PF₆) (Cp = η⁵-C₅H₅, 1.363(3) Å).¹⁶

In the (2,4,6-trimethyl-1-pyridinio)imido complex **8b'**, the pyridine ring takes the conformation coplanar to the Cl(2)–W(1)–C(9)–O(1) axis, by which steric congestion between the 2,6-disubstituted pyridine ring and the phosphine ligands is minimized. This conformation is in good agreement with the dynamic behavior observed in the ¹H NMR spectrum of **8b** (vide supra). Interestingly, one of the phenyl groups of the phosphine ligands in each of **8a'**, **8b'**, and **9a'** is oriented in almost parallel with the pyridine ring (dihedral angles 4.6–16.6°), and the distances between the atoms of these rings are considerably short (C(1)···C(11) in **8a'**, 3.382(6) Å; N(2)···C(12) in **8b'**, 3.45(1) Å; N(2)···C(11) in **9a'**, 3.48(1) Å). These features indicate that the positively charged pyridinium moiety in each complex has an attractive interaction with the π-electrons of the phenyl group located nearby.

N–N Bond Cleavage of (1-Pyridinio)imido Complexes: Reduction with Cobaltocene. Having a series of (1-pyridinio)imido complexes in hand, we have investigated their N–N bond cleavage reactions in detail. In the chemistry of reducing dinitrogen to ammonia at transition metal centers, the N–N bond cleavage of NH_x–NH_y type ligands has been attracting considerable attention,^{2,17} and the NNH₃⁺ ligand has been proposed as one of the intermediates for such processes.¹⁸ Actually,

Henderson and co-workers reported that the Mo(II) organohydrazido(2–) complex [Mo{NN(CH₂)₄CH₂}(dppe)₂] reacts with HBr in a nitrile (NCR) solution to give piperidine and the imido complex *trans*-[MoBr(NH)(dppe)₂]Br and proposed that the hydrazidium complex *trans*-[Mo{NNH(CH₂)₄CH₂}(NCR)-(dppe)₂]⁺ is an intermediate for the N–N bond cleavage on the basis of kinetic measurements.¹⁹ However, none of the isolated and characterized trialkyl- or unsubstituted hydrazidium complexes has been reported to undergo the N–N bond cleavage.^{12,13} For example, the N–N bond in [Cp*MoMe₃(NNMe₃)](OTf) was not cleaved by reduction with Zn/Hg or cobaltocene.¹³ It is hence of great interest to shed light upon the reactivities of the N–N bond in the (1-pyridinio)imido complexes, a special type of hydrazidium complexes. Further, fission of the N–N bond accomplishes the synthesis of pyridines from coordinated dinitrogen. Therefore, development of a mild and efficient method for such a N–N bond cleavage is desirable from the viewpoint of organic synthesis utilizing molecular nitrogen.

The N–N bond cleavage of a hydrazidium complex (MN–NR₃⁺) to give the corresponding amine (NR₃) and a cationic nitrido complex (MN⁺) has to formally accompany a two-electron oxidation of the metal center. Therefore, we envisaged that reduction of the tungsten(IV) center of complexes **3**, **8**, **9**, and **10** might cause such reactions. In fact, when complex **8b** was allowed to react with cobaltocene (2.5 equiv) and HNEt₃·Cl (1.5 equiv) in THF at room temperature, a smooth reaction took place within 1 h to form 2,4,6-trimethylpyridine (**11b**) in 87% yield, along with a cobaltocenium salt (eq 3). The tungsten fragment was recovered as the imido complex *cis,trans*-[WCl₂(NH)(CO)(PMe₂Ph)₂] (**12**)¹⁰ in 53% yield, which was characterized crystallographically.



The molecular structure of complex **12** is depicted in Figure 2, and selected bond distances and angles are listed in Table 5. The metrical features found for **12** are similar to those reported for related tungsten imido complexes, such as [WCl₂(NCH₂–CH=CH₂)(CO)(PPh₂Me)₂]²⁰ and [WCl₂(NPh)(PMe₃)₃].²¹ It should be pointed out that pyridine **11b** was also obtained in high yield by the reduction conducted in the absence of HNEt₃·Cl, but in this case no characterizable tungsten complex except for a trace amount of **12** was recovered. Therefore, HNEt₃·Cl is not essential for the reductive N–N bond cleavage of **8b** but plays a role in protonating the resultant tungsten complex to give the stable imido complex **12**.

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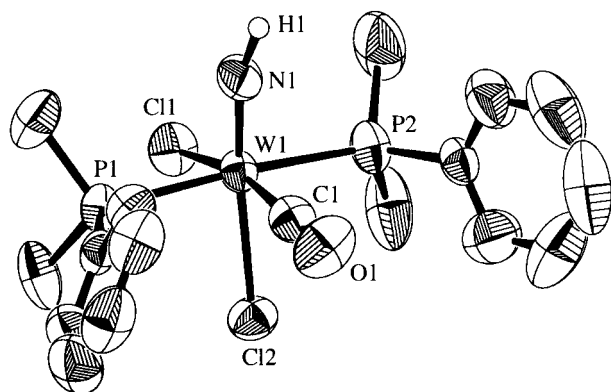


Figure 2. An ORTEP drawing for **12** (hydrogen atoms except for the NH proton are omitted for clarity).

Table 5. Bond Lengths (Å) and Angles (deg) of **12**

W(1)–N(1)	1.740(3)	P(1)–W(1)–N(1)	93.9(1)
W(1)–P(1)	2.509(1)	P(2)–W(1)–N(1)	93.8(1)
W(1)–P(2)	2.510(1)	Cl(1)–W(1)–N(1)	105.9(1)
W(1)–Cl(1)	2.472(1)	Cl(2)–W(1)–N(1)	165.8(1)
W(1)–Cl(2)	2.509(1)	C(1)–W(1)–N(1)	89.1(2)
W(1)–C(1)	1.990(5)		

Table 6. Reductive N–N Bond Cleavage of (1-Pyridinio)imido Complexes with Cobaltocene^a

complex	pyridine, yield (%)	W product, yield (%)	E_p (V) ^b
3	0 ^c	0	–1.10
8a	11a , 49	— ^d	–0.95
8b	11b , 87	12 , 53	–0.77
8b^e	11b , 87	12 , trace	
8c	11c , 62	12 , 27	nd
9a^f	11a , 25	— ^d	nd
9b^f	11b , 88	13 , 53	–0.80
9b	11b , 88	13 , 25 ^g	
9c^f	11c , 52	13 , 23	nd
10a	11a , 36	— ^d	–0.96
10b	11b , 89	14 , 47	–0.80

^a Reaction conditions: (1-pyridinio)imido complex (0.066–0.11 mmol); Cp₂Co (2.5 equiv); HNEt₃Cl (1.5 equiv); THF (3 mL); room temperature; under N₂; 1 h. ^b Peak potentials for irreversible reduction waves vs SCE in CH₂Cl₂/0.1 M [Bu₄N][BF₄]. Scan rate = 200 mV·s^{–1}.

^c No reaction. ^d Uncharacterized solids were obtained. ^e In the absence of HNEt₃Cl. ^f Under an ethylene atmosphere. ^g A small amount of the imido complex *cis,mer*-[WCl₂(NH)(PMe₂Ph)₃], which was characterized by preliminary crystallographic analysis, was isolated as a by-product.

Treatment of **9b** with cobaltocene and HNEt₃Cl under an ethylene atmosphere also produced **11b** and the imido complex *cis,trans*-[WCl₂(NH)(C₂H₄)(PMe₂Ph)₂] (**13**)¹⁰ in 88% and 53% yields, respectively. An analogous reaction of **9b** under a nitrogen atmosphere resulted in the formation of **13** in much lower yield (25%), although the yield of **11b** was the same. Further results for the cobaltocene reduction of (1-pyridinio)imido complexes are summarized in Table 6. In the reactions of (4-methoxy-1-pyridinio)imido complexes **8a**, **9a**, and **10a**, the tungsten species recovered were paramagnetic and could not be characterized, while complex **10b** underwent partial halogen exchange on the tungsten center to give [WBrCl(NH)(CO)(PMe₂Ph)₂] (**14**) as the metal product.

These findings clearly show that the N–N bonds in complexes **8**–**10** are cleaved under very mild conditions despite their relatively short N–N bond distances (vide supra), although the yields of pyridines **11** vary with the substituents on the pyridine rings. The reactions provide the first examples of the

Table 7. Reaction of (1-Pyridinio)imido Complexes with KOH^a

complex	pyridine, yield (%)	yield of NH ₃ (%)
3	11a , 82	92
8a'	11a , 85	94
8b	11b , 84	94
9a'	11a , 88	100
9b	11b , 96	100
10a	11a , 82	87
10b	11b , 77	85

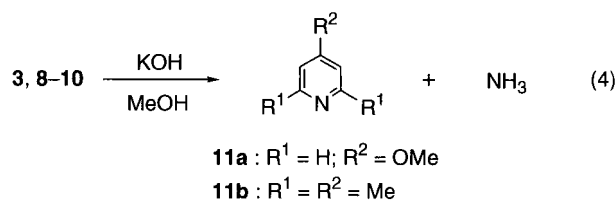
^a Reaction conditions: (1-pyridinio)imido complex, (0.070–0.10 mmol); KOH (10 equiv); MeOH (3 mL); room temperature; 1 h.

N–N bond cleavage of well-characterized hydrazidium complexes. Further, they demonstrate the synthesis of pyridines using molecular nitrogen as the nitrogen source under ambient conditions in a well-defined manner. Very recently, we have also observed that titanium (1-pyridinio)imido complexes, such as [Cp*TiCl₂(NNC₅H₃Me₂-2,6)] and [Cp*Ti(NNC₅H₃Me₂-2,6)-(terpy)][OTf]₂ (terpy = 2,2':6',2''-terpyridine) undergo the N–N bond fission on treatment with sodium amalgam and cobaltocene, respectively,¹⁶ although the (1-pyridinio)imido ligands in these titanium complexes are not derived from molecular nitrogen.

As shown in Table 6, complex **3** failed to react with cobaltocene. To account for the low reactivity of **3**, cyclic voltammograms of some of the (1-pyridinio)imido complexes were measured. The data obtained are also listed in Table 6. Complexes **8b**, **9b**, and **10b**, which produced pyridine **11b** in high yield on treatment with cobaltocene, showed irreversible reduction waves at –0.77, –0.80, and –0.80 V (E_p vs SCE), respectively. On the other hand, complex **3** had a much more negative E_p value of –1.10 V. Since the redox potential for the cobaltocene/cobaltocenium couple is reported to be –0.80 to –0.98 V vs SCE,²² it is reasonable to conclude that the N–N bond cleavage of the (1-pyridinio)imido complexes is initiated by direct electron transfer from cobaltocene, which does not occur in the case of complex **3**. It is still not clear whether the N–N bond cleavage proceeds on a W(III) or W(II) center. The reaction of complex **3** with sodium, which is a stronger reducing agent than cobaltocene, was also investigated, but the formation of 4-methoxypyridine could not be observed. Complexes **8a** and **10a** exhibited reduction waves with more negative E_p potentials (–0.95 to –0.96 V) than those of **8b** and **10b**. We consider that both the lower susceptibility to reduction and the higher coordination ability of 4-methoxypyridine (**11a**) than those of **11b** are responsible for the low yield of **11a** from complexes **8a**, **9a**, and **10a**.

Reaction of (1-Pyridinio)imido Complexes with KOH. We have already revealed that organonitrogen ligands derived from the coordinated dinitrogen of molybdenum or tungsten complexes can be liberated by treatment with KOH through the rupture of the M–N (M = Mo, W) and/or N–N bond.^{5d,e,6,7b,c,8} Reactions of complexes **3**, **8**, **9**, and **10** with KOH in MeOH were also found to produce the corresponding pyridine **11** concomitantly with NH₃ under ambient conditions (eq 4). The tungsten species formed could not be characterized. As summarized in Table 7, the yields of pyridines **11** and ammonia were very high irrespective of the ancillary ligands on the tungsten center. The selective formation of **11** through the N–N bond cleavage is in sharp contrast to the reaction of the (1-pyrrolyl)imido complex [WBr₂(NNC₄H₄)(CO)(PMe₂Ph)₂] with KOH in alcohols, where the W–N bond is selectively cleaved.^{4b}

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Thermal Decomposition of (1-Pyridinio)imido Complexes.

Finally, pyrolysis of the (1-pyridinio)imido complexes was examined. Complex **3** with three PMe_2Ph ligands is of relatively low thermal stability and decomposed completely on refluxing in benzene for 2 h to give **11a** in 40% yield and an unidentified tungsten species. In contrast, carbonyl and ethylene complexes **8a**, **8b**, **9a**, **9b**, **10a**, and **10b** are thermally stable and showed almost no change in refluxing benzene, probably because of their low tendency to dissociate PMe_2Ph ligands. Such difference in thermal stability provides, in addition to steric reasons, an explanation why the hydrazido complexes with a π -acceptor ligand **5**, **6**, and **7** act as suitable starting materials for the synthesis of (1-pyridinio)imido complexes in comparison with complexes **2** and **4**.

Experimental Section

General Procedure. All reactions were carried out under a dry nitrogen atmosphere unless otherwise noted. Solvents were dried by usual methods and distilled before use. The tungsten hydrazido(2-) complexes *cis,mer*- $[\text{WX}_2(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]$ (**2**, $\text{X} = \text{Br}$; **4**, $\text{X} = \text{Cl}$)²³ and *cis,trans*- $[\text{WX}_2(\text{NNH}_2)(\text{L})(\text{PMe}_2\text{Ph})_2]$ (**5**, $\text{X} = \text{Cl}$, $\text{L} = \text{CO}$; **6**, $\text{X} = \text{Cl}$, $\text{L} = \text{C}_2\text{H}_4$; **7**, $\text{X} = \text{Br}$, $\text{L} = \text{CO}$)¹¹ 2,4,6-trimethylpyrylium tetrafluoroborate,²⁴ 2,4,6-trimethylpyrylium triflate,²⁴ 2,6-diethoxycarbonyl-4-phenylpyrylium tetrafluoroborate,²⁵ 4-methoxyppyrylium hexafluorophosphate,²⁶ and 4-methoxyppyrylium perchlorate²⁶ were prepared according to the literature methods. Other reagents were commercially obtained and used without further purification.

Caution! Perchlorate salts are potentially explosive and should be handled in small quantities.

NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^1H , 270 MHz; ^{31}P , 109 MHz), and IR spectra were recorded on a Shimadzu FTIR-8100M spectrophotometer. Amounts of the solvent molecules in the crystals were determined not only by elemental analyses but also by ^1H NMR spectroscopy. Quantitative GC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector, using a 25 m $\times$ 0.25 mm CBP10 fused silica capillary column. Electrochemical measurements were made with Hokuto Denko instrumentation (HA-501 potentiostat and a HB-105 function generator), by using a glassy carbon working electrode; potentials were measured in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{Bu}_4\text{N}][\text{BF}_4]$ vs an SCE. GC-MS analyses (70 eV) were carried out on a Shimadzu GC-MS QP-2000 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of *cis,mer*- $[\text{WBr}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$ (3**).** Hydrazido(2-) complex **2** (114.4 mg, 0.13 mmol) and 4-methoxyppyrylium hexafluorophosphate (33.9 mg, 0.13 mmol) were dissolved in THF (2 mL), and the mixture was stirred for 2 h at room temperature. The resulting reaction mixture was evaporated under vacuum to give a dark red oil. Recrystallization from $\text{ClCH}_2\text{CH}_2\text{Cl}/\text{MeOH}/\text{ether}$ afforded brown crystals of **3**, which were collected, washed with ether, and dried in vacuo (58.6 mg, 43% yield). ^1H NMR (CD_2Cl_2) δ 1.79 (t, 6H, $J = 3.9 \text{ Hz}$), 1.90 (d, 6H, $J = 8.6 \text{ Hz}$), 2.06 (t, 6H, $J = 3.9 \text{ Hz}$), 4.01 (s, 3H), 6.72 (d, 2H, $J = 7.4 \text{ Hz}$), 7.01 (d, 2H, $J = 7.4 \text{ Hz}$), 7.23–7.74 (m, 15H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ -31.6 (s with ^{183}W satellites, $J_{\text{WP}} = 284 \text{ Hz}$, P(trans)), -27.3 (s with ^{183}W satellites, J_{WP}

= 370 Hz, P(unique)). IR (KBr) 1634 (s) cm^{-1} . Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{Br}_2\text{F}_6\text{N}_2\text{O}_4\text{PW}$: C, 35.11; H, 3.93; N, 2.73. Found: C, 35.03; H, 4.06; N, 2.81.

Preparation of *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{PF}_6]$ (8a**).** Hydrazido(2-) complex **5** (297.4 mg, 0.50 mmol) and 4-methoxyppyrylium hexafluorophosphate (129.0 mg, 0.50 mmol) were dissolved in THF (5 mL). The mixture was stirred for 8 h at room temperature, and the resulting solution was evaporated under vacuum to give a dark green oil. The residual oil was dissolved in CH_2Cl_2 , and the solution was filtered and diluted with MeOH. Layering the $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution with ether afforded blue crystals of **8a**, which were collected, washed with ether, and dried in vacuo (216.7 mg, 52% yield). ^1H NMR (CD_2Cl_2) δ 2.05 (t, 6H, $J = 4.5 \text{ Hz}$), 2.25 (t, 6H, $J = 4.3 \text{ Hz}$), 4.01 (s, 3H), 6.65–6.75 (m, 4H), 7.31–7.38 (m, 6H), 7.65–7.70 (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ -12.9 (s with ^{183}W satellites, $J_{\text{WP}} = 271 \text{ Hz}$). IR (KBr) 1966 (s), 1628 (s) cm^{-1} . Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{Cl}_2\text{F}_6\text{N}_2\text{O}_3\text{P}_2\text{W}$: C, 33.40; H, 3.53; N, 3.39. Found: C, 33.31; H, 3.59; N, 3.16. The corresponding perchlorate salt *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{ClO}_4]$ (**8a'**), which was used for the crystallographic study, was obtained similarly from **5** and 4-methoxyppyrylium perchlorate as blue crystals in 60% yield.

Preparation of *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_2\text{Me}_3\text{-2,4,6})(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{BF}_4]$ (8b**).** Hydrazido(2-) complex **5** (117.8 mg, 0.20 mmol) and 2,4,6-trimethylpyrylium tetrafluoroborate (42.1 mg, 0.20 mmol) were dissolved in THF (5 mL), and 37% aqueous hydrochloric acid (5 drops) was added to the solution. The mixture was stirred for 8 h at room temperature, and then $\text{Na}[\text{BF}_4]$ (110 mg, 1.0 mmol) was added to the resultant blue solution. The mixture was stirred for further 2 h at room temperature, and the solvent was evaporated to give a blue oil. The residual oil was dissolved in CH_2Cl_2 , and the solution was filtered and diluted with MeOH. Layering the $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution with ether afforded blue crystals of **8b**, which were collected, washed with ether, and dried in vacuo (143.7 mg, 92% yield). ^1H NMR (CD_2Cl_2) δ 1.98 (s, 6H), 2.01 (t, 6H, $J = 4.3 \text{ Hz}$), 2.16 (t, 6H, $J = 4.3 \text{ Hz}$), 2.36 (s, 3H), 7.06 (br, 2H), 7.15–7.21 (m, 6H), 7.34–7.42 (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ -12.8 (s with ^{183}W satellites, $J_{\text{WP}} = 271 \text{ Hz}$). IR (KBr) 1972 (s), 1642 (s) cm^{-1} . Anal. Calcd for $\text{C}_{25}\text{H}_{33}\text{BCl}_2\text{F}_4\text{N}_2\text{OP}_2\text{W}$: C, 38.44; H, 4.26; N, 3.59. Found: C, 38.37; H, 4.19; N, 3.44. The corresponding triflate salt *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_2\text{Me}_3\text{-2,4,6})(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{OTf}]$ (**8b'**), which was used for the crystallographic study, was obtained similarly from **5** and 2,4,6-trimethylpyrylium triflate as blue crystals in 77% yield.

Preparation of *cis,trans*- $[\text{WCl}_2\{\text{NNC}_5\text{H}_2(\text{COOEt})\text{-2,6-Ph-4}\}(\text{CO})(\text{PMe}_2\text{Ph})_2][\text{BF}_4]$ (8c**).** Hydrazido(2-) complex **5** (117.8 mg, 0.20 mmol) and 2,6-diethoxycarbonyl-4-phenylpyrylium tetrafluoroborate (77.6 mg, 0.20 mmol) were dissolved in THF (5 mL), and 37% aqueous hydrochloric acid (5 drops) was added to the solution. The mixture was stirred for 1 h at room temperature, during which period of time a green solid precipitated. Addition of hexane to the mixture deposited an additional quantity of the product. The precipitate was filtered, washed with hexane, and recrystallized from $\text{CH}_2\text{Cl}_2/\text{ether}$ to afford green crystals of **8c**, which were collected, washed with ether, and dried in vacuo (115.1 mg, 60% yield). ^1H NMR (CD_2Cl_2) δ 1.48 (t, 6H, $J = 7.1 \text{ Hz}$), 2.07 (t, 6H, $J = 4.6 \text{ Hz}$), 2.12 (t, 6H, $J = 4.3 \text{ Hz}$), 4.56 (br, 4H), 7.15–7.30 (m, 6H), 7.51–7.75 (m, 8H), 7.94 (d, 2H, $J = 7.2 \text{ Hz}$), 8.03 (br, 1H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ -12.3 (s with ^{183}W satellites, $J_{\text{WP}} = 269 \text{ Hz}$). IR (KBr) 1991 (s), 1744 (s), 1613 (s) cm^{-1} . Anal. Calcd for $\text{C}_{34}\text{H}_{39}\text{BCl}_2\text{F}_4\text{N}_2\text{O}_5\text{P}_2\text{W}$: C, 42.57; H, 4.10; N, 2.92. Found: C, 42.79; H, 4.14; N, 2.86.

Preparation of *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2][\text{PF}_6] \cdot 0.5(\text{CH}_2\text{Cl}_2)$ (9a**·0.5(CH_2Cl_2)).** Complex **9a**·0.5(CH_2Cl_2) was prepared from complex **6** and 4-methoxyppyrylium hexafluorophosphate by a similar procedure to that described for complex **8a** and isolated as orange crystals in 74% yield. ^1H NMR (CDCl_3) δ 2.10–2.15 (m, 12H), 2.40–2.45 (m, 2H), 2.85–2.87 (m, 2H), 4.04 (s, 3H), 6.73 (d, 2H, $J = 6.3 \text{ Hz}$), 7.29 (d, 2H, $J = 6.3 \text{ Hz}$), 7.14–7.30 (m, 6H), 7.51–7.54 (m, 4H). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ -11.4 (s with ^{183}W satellites, $J_{\text{WP}} = 219 \text{ Hz}$). IR (KBr) 1632 (s) cm^{-1} . Anal. Calcd for $\text{C}_{24.5}\text{H}_{34}\text{Cl}_3\text{F}_6\text{N}_2\text{O}_3\text{P}_2\text{W}$: C, 33.84; H, 3.94; N, 3.22. Found: C, 33.75; H, 4.05; N, 3.01. The corresponding perchlorate salt *cis,trans*- $[\text{WCl}_2(\text{NNC}_5\text{H}_4\text{OMe-4})(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2][\text{ClO}_4] \cdot 0.5(\text{CH}_2\text{Cl}_2)$ (**9a'**·0.5(CH_2Cl_2)), which

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was used for the crystallographic study, was obtained similarly from **6** and 4-methoxyppyrylium perchlorate as orange crystals in 84% yield.

Preparation of *cis,trans*-[WCl₂(NNC₅H₂Me₃-2,4,6)(C₂H₄(PMe₂Ph)₂)]-[BF₄] (9b**).** Complex **9b** was prepared from complex **6** and 2,4,6-trimethylpyrylium tetrafluoroborate by a similar procedure to that described for complex **8b** and isolated as orange crystals in 93% yield. ¹H NMR (CD₂Cl₂) δ 1.85 (br, 6H), 2.10 (t, 12H, *J* = 4.5 Hz), 2.36 (s, 3H), 2.47–2.59 (m, 4H), 6.99 (br, 2H), 7.15–7.26 (m, 6H), 7.30–7.38 (m, 4H). ³¹P{¹H} NMR (CD₂Cl₂) δ –10.5 (s with ¹⁸³W satellites, *J*_{WP} = 219 Hz). IR (KBr) 1640 (s) cm^{–1}. Anal. Calcd for C₂₆H₃₇B-Cl₂F₄N₂P₂W: C, 39.98; H, 4.77; N, 3.59. Found: C, 39.74; H, 4.72; N, 3.54.

Preparation of *cis,trans*-[WCl₂{NNC₅H₂(COOEt)-2,6-Ph-4}-(C₂H₄(PMe₂Ph)₂)]-[BF₄] (9c**).** Complex **9c** was prepared from complex **6** and 2,6-diethoxycarbonyl-4-phenylpyrylium tetrafluoroborate by a similar procedure to that described for complex **8c** and isolated as green crystals in 78% yield. ¹H NMR (CD₂Cl₂) δ 1.41 (br t, 3H, *J* = 6.2 Hz), 1.58 (t, 3H, *J* = 6.9 Hz), 2.08 (t, 6H, *J* = 4.5 Hz), 2.15 (t, 6H, *J* = 4.7 Hz), 2.28 (br, 2H), 2.38 (br, 2H), 4.39 (br, 2H), 4.70 (br, 2H), 7.18–7.28 (m, 6H), 7.51–7.94 (m, 11H). ³¹P{¹H} NMR (CD₂Cl₂) δ –9.7 (s with ¹⁸³W satellites, *J*_{WP} = 217 Hz). IR (KBr) 1715 (s), 1613 (s) cm^{–1}. Anal. Calcd for C₃₅H₄₃BCl₂F₄N₂O₄P₂W: C, 43.82; H, 4.52; N, 2.92. Found: C, 43.76; H, 4.54; N, 2.83.

Preparation of *cis,trans*-[WBr₂(NNC₅H₄OMe-4)(CO)(PMe₂Ph)₂]-[PF₆] (10a**).** Hydrazido(2–) complex **7** (135.6 mg, 0.20 mmol) and 4-methoxyppyrylium hexafluorophosphate (51.6 mg, 0.20 mmol) were dissolved in THF (2 mL), and 47% aqueous hydrobromic acid (2 drops) was added to the solution. The mixture was stirred for 21 h at room temperature. K[PF₆] (368 mg, 2.0 mmol) was added to the resultant blue solution, and the mixture was stirred for 2 h further. The blue oil obtained by evaporation of the solvent was dissolved in CH₂Cl₂, and the solution was filtered. Addition of MeOH and ether to the CH₂Cl₂ solution afforded blue crystals of **10a**, which were collected, washed with ether, and dried in vacuo (84.3 mg, 46% yield). ¹H NMR (CD₂Cl₂) δ 2.14 (t, 6H, *J* = 4.6 Hz), 2.31 (t, 6H, *J* = 4.3 Hz), 4.00 (s, 3H), 6.69 (d, 2H, *J* = 7.6 Hz), 6.77 (d, 2H, *J* = 7.6 Hz), 7.26–7.32 (m, 6H), 7.56–7.68 (m, 4H). ³¹P{¹H} NMR (CD₂Cl₂) δ –20.5 (s with ¹⁸³W satellites, *J*_{WP} = 268 Hz). IR (KBr) 1991 (s), 1626 (s) cm^{–1}. Anal. Calcd for C₂₃H₂₉Br₂F₆N₂O₂P₃W: C, 30.16; H, 3.19; N, 3.06. Found: C, 30.17; H, 3.13; N, 2.96.

Preparation of *cis,trans*-[WBr₂(NNC₅H₂Me₃-2,4,6)(CO)(PMe₂Ph)₂]-[BF₄] (10b**).** Hydrazido(2–) complex **7** (136.0 mg, 0.20 mmol) and 2,4,6-trimethylpyrylium tetrafluoroborate (41.9 mg, 0.20 mmol) were dissolved in THF (3 mL) and 47% aqueous hydrobromic acid (2 drops) was added to the solution. The mixture was stirred for 14 h at room temperature, and then Na[BF₄] (220 mg, 2.0 mmol) was added to the resultant blue solution. The mixture was stirred for 2 h further at room temperature, filtered, and evaporated to dryness to give a blue oil. The residual oil was dissolved in CH₂Cl₂, and the solution was filtered and diluted with MeOH. Layering this CH₂Cl₂/MeOH solution with ether afforded blue crystals of **10b**, which were collected, washed with ether, and dried in vacuo (133.3 mg, 77% yield). ¹H NMR (CD₂Cl₂) δ 1.98 (s, 6H), 2.14 (t, 6H, *J* = 4.6 Hz), 2.28 (t, 6H, *J* = 4.3 Hz), 2.34 (s, 3H), 7.20–7.24 (m, 8H), 7.41–7.48 (m, 4H). ³¹P{¹H} NMR (CD₂Cl₂) δ –21.0 (s with ¹⁸³W satellites, *J*_{WP} = 268 Hz). IR (KBr) 1977 (s), 1626 (s) cm^{–1}. Anal. Calcd for C₂₅H₃₃BBR₂F₄N₂OP₂W: C, 34.52; H, 3.82; N, 3.22. Found: C, 34.41; H, 3.88; N, 3.01.

Reduction of (1-Pyridinio)imido Complexes **8a, **9a**, and **10a** with Cobaltocene.** The following account is a representative procedure. Complex **8a** (82.2 mg, 0.099 mmol), cobaltocene (47.0 mg, 0.25 mmol), and HNEt₃Cl (20.6 mg, 0.15 mmol) were dissolved in THF (3 mL) under a nitrogen atmosphere, and the mixture was stirred for 1 h at room temperature. The volatile products were collected by means of a cold trap, and their GC and GC–MS analyses indicated that 4-methoxyppyridine was formed in 49% yield. The tungsten species was recovered as an unidentified red solid.

A similar reaction of **9a** under an ethylene atmosphere and a reaction of **10a** under a nitrogen atmosphere gave 4-methoxyppyridine in 25% and 36% yields, respectively.

Reduction of the (1-Pyridinio)imido Complexes **8b and **9b** with Cobaltocene.** Complex **8b** (55.0 mg, 0.070 mmol), cobaltocene (33.5

mg, 0.18 mmol), and HNEt₃Cl (14.5 mg, 0.11 mmol) were dissolved in THF (3 mL), and the mixture was stirred for 1 h at room temperature. Then, the volatile materials formed were collected by means of a cold trap. Their GC and GC–MS analyses indicated that 2,4,6-trimethylpyridine was formed in 87% yield. The residual solid was recrystallized from THF/hexane to give *cis,trans*-[WCl₂(NH)(CO)(PMe₂Ph)₂] (**12**) as brown crystals, which were collected, washed with hexane, and dried in vacuo (21.2 mg, 53% yield). ¹H NMR (CD₂Cl₂) δ 1.93 (t, 6H, *J* = 4.1 Hz), 1.98 (t, 6H, *J* = 4.1 Hz), 7.37–7.46 (m, 6H), 7.62–7.69 (m, 4H). NH signal could not be found. ³¹P{¹H} NMR (CD₂Cl₂) δ –10.0 (s with ¹⁸³W satellites, *J*_{WP} = 292 Hz). IR (KBr) 3245 (s), 1975 (s) cm^{–1}. Anal. Calcd for C₁₇H₂₃Cl₂NOP₂W: C, 35.57; H, 4.04; N, 2.44. Found: C, 35.97; H, 4.05; N, 2.37.

Reduction of **9b** by a similar procedure under an ethylene atmosphere afforded 2,4,6-trimethylpyridine as a volatile product (88% yield) and *cis,trans*-[WCl₂(NH)(C₂H₄)(PMe₂Ph)₂] (**13**) as a pale green solid (53% yield). **13**: ¹H NMR (CD₂Cl₂) δ 1.57–1.60 (m, 2H), 1.73–1.74 (m, 2H), 1.96 (t, 6H, *J* = 4.5 Hz), 2.05 (t, 6H, *J* = 4.3 Hz), 5.53 (s, 1H), 7.36–7.43 (m, 6H), 7.53–7.60 (m, 4H). ³¹P{¹H} NMR (CD₂Cl₂) δ –7.6 (s with ¹⁸³W satellites, *J*_{WP} = 236 Hz). IR (KBr) 3206 (s) cm^{–1}. Anal. Calcd for C₁₈H₂₇Cl₂NP₂W: C, 37.66; H, 4.74; N, 2.44. Found: C, 37.79; H, 4.74; N, 2.39.

Reduction of the (1-Pyridinio)imido Complexes **8c and **9c** with Cobaltocene.** Complex **8c** (89.0 mg, 0.093 mmol), cobaltocene (43.8 mg, 0.23 mmol), and HNEt₃Cl (19.0 mg, 0.14 mmol) were dissolved in THF (3 mL), and the mixture was stirred for 1 h at room temperature. Then the solvent was removed under reduced pressure, and the residue was extracted with ether. The ether solution was concentrated under reduced pressure until white-green powder began to precipitate. Addition of hexane to the concentrated extract gave 2,6-diethoxycarbonyl-4-phenylpyridine as a slightly greenish solid, which was collected by filtration, washed with hexane, and dried in vacuo (17.3 mg, 62% yield). The solid insoluble in ether was recrystallized from THF/hexane to give complex **12** (14.4 mg, 27% yield). A similar reaction of **9c** with cobaltocene under an ethylene atmosphere afforded 2,6-diethoxycarbonyl-4-phenylpyridine and complex **13** in 52% and 23% yields, respectively.

Reduction of the (1-Pyridinio)imido Complexes **10b with Cobaltocene.** Complex **10b** (57.3 mg, 0.066 mmol), cobaltocene (30.2 mg, 0.16 mmol), and HNEt₃Cl (13.6 mg, 0.099 mmol) were dissolved in THF (3 mL), and the mixture was stirred for 1 h at room temperature. Then the volatile materials formed were collected by means of a cold trap, and their GC and GC–MS analyses indicated that 2,4,6-trimethylpyridine was formed in 89% yield. The residual solid was recrystallized from THF/hexane to give [WBrCl(NH)(CO)(PMe₂Ph)₂] (**14**) as brown crystals, which were collected, washed with hexane, and dried in vacuo (19.2 mg, 47%). ¹H NMR (CD₂Cl₂) δ 2.03 (t, 6H, *J* = 4.1 Hz), 2.09 (t, 6H, *J* = 4.1 Hz), 7.35–7.44 (m, 6H), 7.61–7.70 (m, 4H). NH signal could not be found. ³¹P{¹H} NMR (CD₂Cl₂) δ –17.4 (s with ¹⁸³W satellites, *J*_{WP} = 290 Hz). IR (KBr) 3250 (s), 1975 (s) cm^{–1}. Anal. Calcd for C₁₇H₂₃BrClNOP₂W: C, 33.01; H, 3.75; N, 2.26. Found: C, 32.71; H, 3.67; N, 2.31.

Reaction of the (1-Pyridinio)imido Complexes with KOH. The following account is a representative procedure. To a suspension of complex **8b** (55.0 mg, 0.070 mmol) in MeOH (3 mL) was added KOH (10 equiv), and the mixture was stirred for 1 h at room temperature. Organic volatile products were collected by means of a cold trap, and their GC–MS and quantitative GC analyses revealed that 2,4,6-trimethylpyridine was formed in 84% yield. In a separate run, the reaction mixture was distilled under reduced pressure, and the distillate was trapped in aqueous H₂SO₄, which was used for the determination of ammonia (94% yield, indophenol method).

Pyrolysis of (1-Pyridinio)imido Complexes. In a typical run, a suspension of complex **3** (28.7 mg, 0.028 mmol) in benzene (2 mL) was refluxed for 2 h. The initial brown suspension gradually changed to a pale brown solution. Organic volatile products were collected by means of a cold trap under vacuum and analyzed by GC and GC–MS, which indicated that 4-methoxyppyridine was formed in 40% yield. The tungsten species formed could not be characterized. Complexes **8a**, **8b**, **9a**, **9b**, **10a**, and **10b** were recovered unchanged after similar treatment.

Table 8. Crystallographic Data for **3**, **8a'**, **8b'**, **9a'**·0.5CH₂Cl₂, and **12**

	3	8a'	8b'	9a' ·0.5CH ₂ Cl ₂	12
formula	C ₃₀ H ₄₀ Br ₂ F ₆ N ₂ O ₄ P ₄ W	C ₂₃ H ₂₉ Cl ₂ N ₂ O ₆ P ₂ W	C ₂₆ H ₃₃ Cl ₂ F ₃ N ₂ O ₄ P ₂ SW	C _{24.5} H ₃₄ Cl ₄ N ₂ O ₅ P ₂ W	C ₁₇ H ₂₃ Cl ₂ NOP ₂ W
formula weight	1026.20	781.65	843.32	824.16	574.08
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>a</i>
<i>a</i> (Å)	9.593(1)	10.068(1)	8.823(4)	20.266(2)	13.0529(8)
<i>b</i> (Å)	30.315(4)	10.756(1)	34.939(5)	10.502(1)	9.985(2)
<i>c</i> (Å)	13.708(2)	14.323(2)	10.729(3)	30.363(2)	18.070(1)
α (deg)	90	98.640(10)	90	90	90
β (deg)	108.66(1)	96.330(9)	93.58(3)	96.012(7)	110.755(4)
γ (deg)	90	96.472(9)	90	90	90
<i>V</i> (Å ³)	3777.0(9)	1510.7(3)	3301(1)	6426.9(10)	2202.2(4)
<i>Z</i>	4	2	4	8	4
<i>d</i> _{calc} (g cm ⁻³)	1.805	1.718	1.697	1.703	1.731
<i>μ</i> _{calc} (cm ⁻¹)	54.10	42.37	38.75	40.66	56.43
<i>R</i> ^a	0.044	0.032	0.041	0.044	0.027
<i>R</i> _w ^b	0.035	0.029	0.027	0.027	0.018

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

Crystallography. Crystals of **3**, **8a'**, **8b'**, **9a'**·0.5(CH₂Cl₂), and **12** suitable for X-ray analyses were sealed in Pyrex glass capillaries under an argon atmosphere and used for data collection. Diffraction data were collected on a Rigaku AFC-7R four-circle automated diffractometer with Mo Kα ($\lambda = 0.71069$ Å) radiation and a graphite monochromator at 20 ± 1 °C, using the ω scan technique ($5 < 2\theta < 55$) for **3**, **8b'**, and **9a'**·0.5(CH₂Cl₂), and the ω - 2θ scan technique ($5 < 2\theta < 55$) for **8a'** and **12**. Accurate cell dimensions of each crystal were determined by least-squares refinement of 25 machine-centered reflections. Empirical absorption correction based on ψ scans and Lorentz-polarization correction were applied. For all crystals, no significant decay was observed for the respective three standard reflections during the data collection. Details of the X-ray diffraction study are summarized in Table 8. The structure solution and refinements were performed by using the TEXSAN program package.²⁷ The structures were solved by a combination of heavy-atom Patterson methods (DIRDIF PATTY²⁷) and Fourier techniques. All non-hydrogen atoms were found from the difference Fourier maps and refined by full-matrix least-squares techniques with anisotropic thermal parameters. The C₂H₄ hydrogens

in **9a'**·0.5(CH₂Cl₂) and the NH hydrogen in **12** were found in the difference Fourier map, while the other hydrogen atoms were placed at the calculated positions. All the hydrogen atoms were included in the refinements with fixed isotropic parameters.

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Supporting Information Available: X-ray crystallographic files in CIF format are available for **3**, **8a'**, **8b'**, **9a'**·0.5CH₂Cl₂, and **12**. Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

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