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Synthesis of Tungsten (1-Pyridinio)imido Complexes: Facile N−N Bond Cleavage To Form Pyridine from Coordinated Dinitrogen[1]

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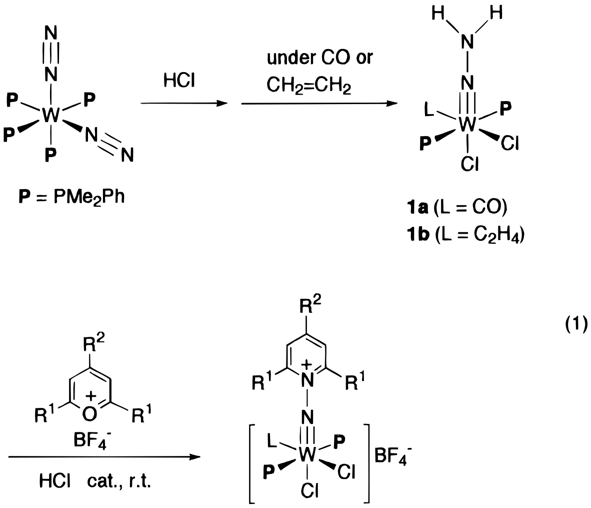
Direct chemical transformation of molecular nitrogen into organo-nitrogen compounds under mild conditions is a fascinating and challenging goal in the chemistry of nitrogen fixation.[2] Protonation of the coordinated nitrogen in molybdenum or tungsten complexes of the type $[M(N_2)_2(PR_3)_4]$ (M = Mo or W, PR_3 = tertiary phosphine) and subsequent nucleophilic attack of the resultant hydrazido(2−) ligand on organic carbonyl groups provides a versatile and convenient route to a variety of diazoalkane[3] and organohydrazido[4] ligands, which are expected to be key intermediates for organic synthesis utilizing molecular nitrogen as the nitrogen source. Recently we have synthesized several molybdenum and tungsten complexes containing heterocyclic ligands such as (1-pyrrolyl)imido[4d,e] and (phthalimidin-2-yl)imido[4f] from the above dinitrogen complexes by using this method. Interestingly, these ligands can be liberated from the metal as nitrogenous heterocycles such as pyrrole, 1-aminopyrrole, and 2-aminophthalimidine. The success in the preparation of these important heterocycles from molecular nitrogen prompted us to extend the scope of this synthetic process. Now we report that ligating dinitrogen in a tungsten complex can be transformed into a novel (1-pyridinio)imido ligand, which further undergoes the facile N−N bond cleavage to form pyridine under mild conditions.



1a (L = CO)
1b (L = C_2H_4)

2a (L = CO, $R^1 = R^2$ = Me): 92%
2b (L = C_2H_4, $R^1 = R^2$ = Me): 93%
2c (L = CO, R^1 = COOEt, R^2 = Ph): 60%
2d (L = C_2H_4, R^1 = COOEt, R^2 = Ph): 78%

Among several hydrazido complexes, tungsten hydrazido complexes $[WCl_2(NNH_2)(L)(PMe_2Ph)_2]$ (**1a**, L = CO; **1b**, L = C_2H_4),[5] which are readily obtained from the dinitrogen complex $[W(N_2)_2(PMe_2Ph)_4]$ through the protonation by hydrochloric acid and the subsequent exchange of one of the phosphine ligands by CO or ethylene, have been found to be suitable for constructing a pyridine ring from ligating dinitrogen. Thus, the reaction of **1a** with 2,4,6-trimethylpyrylium tetrafluoroborate in THF at room temperature for 8 h in the presence of hydrochloric acid led to clean formation of a novel (1-pyridinio)imido complex $[WCl_2(NNC_5H_2Me_3)(CO)(PMe_2Ph)_2][BF_4]$ (**2a**), which was isolated as blue crystals by recrystallization from CH_2Cl_2−ether (eq 1). Addition of hydrochloric acid was not essential but significantly promoted the reaction.[6] By a similar procedure, complexes **2b**−**2d** were obtained in high yields.

The (1-pyridinio)imido complexes **2a**−**2d** were unambiguously characterized by spectroscopic measurements[7] as well as X-ray analysis of $[WCl_2(NNC_5H_2Me_3)(CO)(PMe_2Ph)_2][OTf]$ (**2a′**, OTf = OSO_2CF_3), the OTf analogue of **2a**.[8] An ORTEP drawing is shown in Figure 1, which clearly confirms the structure of the (1-pyridinio)imido ligand. The W−N−N linkage is almost linear (170.2(5)°). The pyridine ring is

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(1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 49. Part 48: see ref 4e.

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(6) Complex **2a** was obtained in 54% from a reaction without hydrochloric acid.

(7) Selected spectroscopic data for **2a**−**2d** are as follows. **2a**: blue crystals. ^{1}H NMR (CD_2Cl_2): δ 1.98 (s, 6 H), 2.01 (t, J = 4.5 Hz, 6 H), 2.16 (t, J = 4.3 Hz, 6 H), 2.36 (s, 3 H), 7.06 (br, 2 H), 7.15−7.21 (m, 6 H), 7.34−7.42 (m, 4 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −12.8 (s, J_{W-P} = 271 Hz). IR (KBr) 1972 (s), 1642 (s), 1561 (m), 1483 (m) cm^{-1}. **2b**: orange crystals. ^{1}H NMR (CD_2Cl_2): δ 1.85 (br, 6 H), 2.10 (t, J = 4.5 Hz, 12 H), 2.36 (s, 3 H), 2.47−2.59 (m, 4 H), 6.99 (br, 2 H), 7.15−7.26 (m, 6 H), 7.30−7.38 (m, 4 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −10.5 (s, J_{W-P} = 219 Hz). IR (KBr): 1640 (s), 1561 (m), 1483 (m) cm^{-1}. **2c**: green crystals. ^{1}H NMR (CD_2Cl_2): δ 1.48 (t, J = 7.1 Hz, 6 H), 2.07 (t, J = 4.6 Hz, 6 H), 2.12 (t, J = 4.3 Hz, 6 H), 4.56 (br, 4 H), 7.15−7.30 (m, 6 H), 7.51−7.75 (m, 8 H), 7.94 (d, J = 7.2 Hz, 2 H), 8.03 (br, 1 H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −12.3 (s, J_{W-P} = 269 Hz). IR (KBr): 1991 (s), 1744 (s), 1613 (s), 1593 (m) cm^{-1}. **2d**: green crystals. ^{1}H NMR (CD_2Cl_2): δ 1.41 (br t, J = 6.2 Hz, 3 H), 1.58 (t, J = 6.9 Hz, 3 H), 2.08 (t, J = 4.5 Hz, 6 H), 2.15 (t, J = 4.7 Hz, 6 H), 2.28 (br, 2 H), 2.38 (br, 2 H), 4.39 (br, 2 H), 4.70 (br, 2 H), 7.18−7.28 (m, 6 H), 7.51−7.94 (m, 11 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −9.7 (s, J_{W-P} = 217 Hz). IR (KBr): 1715 (s), 1613 (s), 1593 (m) cm^{-1}.

(8) Crystallographic data for **2a′**: $C_{26}H_{33}O_4N_2Cl_2F_3P_2SW$, M = 843.32, monoclinic, space group $P2_1/n$, a = 8.823(4) Å, b = 34.939(5) Å, c = 10.729(3) Å, β = 93.58(3)°, V = 3301(1) Å^3, Z = 4, D_{calcd} = 1.697 g cm^{-3}, μ(Mo Kα) = 38.75 cm^{-1}, R = 0.041, R_w = 0.027, GOF = 1.33 for 3753 unique reflections with $I > 3\sigma(I)$.

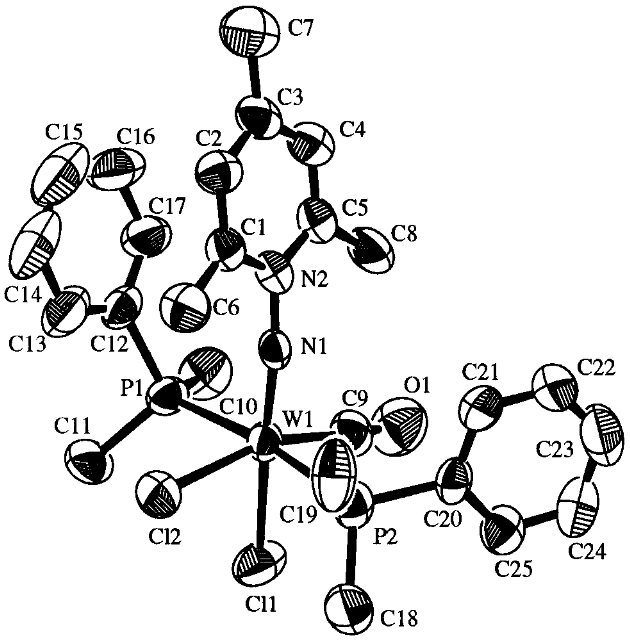


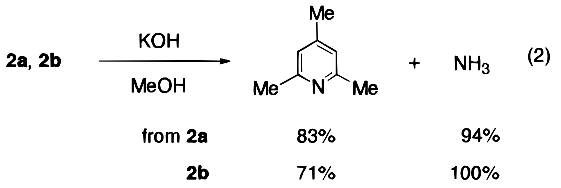
Figure 1. ORTEP drawing for the cationic part of **2a′** (hydrogen atoms are omitted). Selected bond distances (Å) and angles (deg): W(1)–N(1), 1.744(7); N(1)–N(2), 1.383(8); N(2)–C(1), 1.398(10); N(2)–C(5), 1.366(10); W(1)–N(1)–N(2), 170.2(5); N(1)–N(2)–C(1), 118.2(7); N(1)–N(2)–C(5), 119.9(7); C(1)–N(2)–C(5), 121.9(8).

oriented coplanar with the Cl–W–CO axis to minimize steric congestion between the methyl substituents on the pyridine ring and phosphine ligands. One of the phenyl groups of the phosphines is positioned in nearly parallel with the pyridine ring. The short distances between the rings (for example, N(2)···C(12), 3.45(1) Å; N(2)···C(17), 3.46(1) Å; C(5)···C(17), 3.53(1) Å) strongly suggest that there exists an attractive interaction between them.

(1-Pyridinio)imido complexes (**2**) can be regarded as rare examples of hydrazidium (NNR_3^+) complexes.[9–12] Despite its high reactivity (vide infra), the N–N bond in **2a′** (1.383(8) Å) is shorter than those in crystallographically characterized hydrazidium complexes such as $[WCl(NNH_3)(PMe_3)_4]Cl_2$ (1.396(20) Å),[9] $[Cp^*MoMe_3(NNMe_3)][OTf]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (1.426(5) Å),[10] and $[Cp^*TaS(S^tBu)(NNMe_2{}^tBu)]$ (1.46(1) Å).[11]

The ^1H NMR spectrum of **2a** in CD_2Cl_2 at 20 °C showed a set of singlets at δ 2.03 (6H), 2.39 (3H), and 7.11 (2H) assignable to the 2,6-Me_2, 4-Me, and aromatic CH of the pyridine ring, respectively. Upon cooling to −40 °C or below, the 2,6-Me_2 signal split into two singlets (δ 1.84, 1.98) owing to sterically restricted rotation around the N–N bond, which is in good agreement with the solid state structure. Complexes **2b**–**2d** exhibited broadened ^1H NMR signals even at room temperature. For example, the OCH_2 protons of **2c** appear as a broad signal (δ 4.56) at 20 °C and start to split into two quartets (δ 4.52, 4.57) at 0 °C.

The hydrazidium (NNH_3^+) ligand has been considered as one of the precursors to N–N bond cleavage in the reduction of dinitrogen to ammonia at metal centers.[13] However, the N–N bond cleavage of isolated and characterized hydrazidium complexes has never been reported so far.[9–11] Quite interestingly, the N–N bond in **2a** was readily cleaved upon treatment with KOH (10 equiv) in MeOH at room temperature for 1 h, and GC analysis of the volatile products collected by means of a cold trap revealed the formation of 2,4,6-trimethylpyridine in a high yield (eq 2).[14] In a separate run, it was confirmed that the nitrogen atom directly bound to the tungsten was almost completely converted into ammonia. Similar reaction of **2b** also gave 2,4,6-trimethylpyridine and ammonia in good yields. These results are in a sharp contrast to the fact that a related (1-pyrrolyl)imido complex $[WBr_2(NNC_4H_4)(CO)(PMe_2Ph)_2]$ undergoes a similar base-promoted reaction to afford 1-aminopyrrole through the selective W–N bond cleavage.[3e]



Furthermore, complex **2a** exhibited an irreversible reduction wave at −0.77 V in the cyclic voltammogram (E_p vs SCE, in CH_2Cl_2–0.1 M NBu_4BF_4), and in accordance with the electrochemical property, it quickly reacted with cobaltocene (2 equiv) in THF at room temperature to give 2,4,6-trimethylpyridine (53%) concurrently with cobaltocenium tetrafluoroborate. Although we must await further study to elucidate the mechanism of the N–N bond fission, it is noteworthy that the above reactions accomplish the synthesis of a pyridine derivative from dinitrogen under mild conditions.

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Supporting Information Available: Listings of details of the X-ray structure determination and tables of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **2a′** (6 pages). Ordering information is given on any current masthead page.

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(14) The yield of 2,4,6-trimethylpyridine determined by direct GC analysis of the reaction solution was essentially quantitative (95–100%).