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Nitrogen–Nitrogen Bond Cleavage Reactions. Generation of Ammonia and Amines from Substituted Hydrazido(2–) Complexes of Tungsten

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Dinitrogen coordinated to molybdenum and tungsten is smoothly converted into ammonia in reactions with acid in either the presence[2–4] or the absence of an added reducing agent.[5–9] Only one nitrogen hydride intermediate has been unambiguously characterized during these reactions:[10] the hydrazido(2–) (NNH_2) moiety. On the basis of experimental data, this same hydrazido(2–) ligand has been proposed to arise during biological nitrogen fixation.[7,10–12] The detection and characterization of intermediates beyond the hydrazido(2–) stage and following nitrogen–nitrogen bond cleavage are complicated by (i) the difficulty of monitoring the formation of new N–H bonds in acidic solution, (ii) the difficulty in distinguishing between ammonia formed from each of the two nitrogen atoms, and (iii) the generation of paramagnetic complexes. In an effort to distinguish between the two nitrogen atoms and provide better monitoring capability alkyl- and aryl-substituted hydrazido(2–) complexes have been prepared and their reactions with acid studied. Some time ago, aryldiazo (RNN)[13] and organohydrazido(2–) (RR′NN)[14] complexes of transition metals were studied as models for nitrogen fixation principally because the unsubstituted analogues were not available at that time. These were not satisfactory models because, with few exceptions they uniformly failed to yield an amine and ammonia in subsequent reactions.[15] We wish to report what we believe are the first examples of the generation of both an amine and ammonia from organohydrazido(2–) metal complexes that are strict analogues of the corresponding unsubstituted hydrazido(2–) complexes prepared from N_2 complexes which afford ammonia. These results have been achieved by reacting the diorganohydrazido(2–) complexes $[WCl_2(NNR_2)(PMe_2Ph)_3]$ (**1**, R = Me; **2**, R = Ph) and $[WCl_2(NNPh_2)(dppe)(PMe_2Ph)]$ (**3**; dppe = $Ph_2PCH_2CH_2PPh_2$) with acid.

The complexes $[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Br, Cl, I) are known to react with acid to form ammonia, or ammonia and hydrazine.[10b] However until recently organohydrazido(2–) complexes of molybdenum and tungsten of this type containing monodentate phosphines were unknown.[19] Complexes **1** and **2** were prepared using a two-step procedure beginning with WCl_6 (Scheme I).[20] In the first step, the tungsten(VI) hydrazido(2–) complex was isolated in almost quantitative yield and used without further purification. These hydrazido(2–) complexes have not been characterized. In the second step, reduction to the tungsten(IV) hydrazido(2–) complex was carried out with excess 1% sodium amalgam in the presence of PMe_2Ph (3 mol). Extended reduction times resulted in significantly diminished yields of **1–3**. To prepare the mixed phosphine complex **3**, $[WCl_3(NNPh_2)(dppe)]$ (**4**) was synthesized first by reducing a mixture of dppe (1 mol) and $[W(NNPh_2)Cl_4]$ with zinc (5 min) and then **4** was reduced with excess 1% Na/Hg in the presence of PMe_2Ph (1 mol, 0.5 h). Complexes **1–3** are air-stable in the solid state.

Scheme I

$$WCl_6 + Ph_2NNH_2{\cdot}HCl \rightarrow [W(NNPh_2)Cl_4] + 3HCl$$

$$[W(NNPh_2)Cl_4] + 3PMe_2Ph + 2Na/Hg \rightarrow [WCl_2(NNPh_2)(PMe_2Ph)_3] + 2NaCl$$

In a typical acid reaction, **1** dissolved in CH_2Cl_2 was treated with excess HCl (1 M in Et_2O). The solution was allowed to stir at room temperature for 48 h. After this time, water was added and the mixture stirred for 1 h. The aqueous phase was analyzed for ammonia, and the organic phase, for amine and organohydrazine. For reactions with water, water was added in place of HCl. Results are shown in Table I. Three points are worthy of note. First, no substituted hydrazine was formed. Considering

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(15) There are two notable exceptions. First, the reduction of the aryldiimide complex $[Pt(NHNC_6H_4F\text{-}p)Cl(PEt_3)_2]BF_4$ with H_2 over Pt or with aqueous $Na_2S_2O_4$ afforded ammonia and *p*-fluoroaniline.[16] Second, the *N*-piperidino complex $[MoBr(N\overline{NCH_2CH_2CH_2CH_2CH_2})(dppe)_2]Br$, which was prepared from *trans*-$[Mo(N_2)_2(dppe)_2]$, reacted with HBr to yield piperidine and the imido complex $[MoBr(NH)(dppe)_2]Br$.[17] No yield data were given in a third example; the reaction of $[MoO(NNMe_2)L_2]$ (L = C_9H_6NO, quinolin-8-olate) with anhydrous hydrogen halide produced Me_2NH, Me_2NNH_2, and ammonia.[18]

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(20) Dichloromethane (40 mL) was added to a mixture of WCl_6 (2.5 g, 6.3 mmol) and $Ph_2NNH_2{\cdot}HCl$ (1.4 g, 6.3 mmol), and that was cooled at −78 °C. After 5 min of stirring, solvent was removed in vacuo. The solid was redissolved in CH_2Cl_2 (5 mL) and $[W(NNPh_2)Cl_4]$ (**5**) was precipitated by adding pentane (40 mL), collected by filtration, and dried in vacuo. To a mixture of **5** (2.0 g, 3.9 mmol), PMe_2Ph (1.66 g, 12 mmol), and THF (50 mL) was added 1% Na/Hg (1.1 g, 47 mmol of Na). The mixture was stirred for 0.75 h. The solution was decanted and filtered through Celite. Solvent was removed and the solid dissolved in CH_2Cl_2 (10 mL). After filtration, **2** was precipitated by adding pentane (40 mL), collected by filtration, washed with pentane (3 × 10 mL), and dried in vacuo. Yield: 68%. Anal. Calcd for $C_{36}H_{43}Cl_2N_2P_3$: C, 50.79; H, 5.09; N, 3.29. Found: C, 50.68; H, 5.17; N, 3.31. **2**: ^{31}P NMR (C_6D_6) δ −15.7 (s, 2, J_{PW} = 293 Hz), −16.2 (s, 1, J_{PW} = 390 Hz). **3**: ^{31}P NMR (C_6D_6) δ −13.3 (s, 1, J_{PW} = 380 Hz), −14.3 (s, 2, J_{PW} = 296 Hz). $[WCl_2(NN(Me)Ph)(PMe_2Ph)_3]$: ^{31}P NMR (C_6D_6) δ −15.9 (s, 2, J_{PW} = 353 Hz), −16.2 (s, 1, J_{PW} = 304 Hz).

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Table I. Yields[a] of Nitrogen-Containing Products from Reactions of Diorganohydrazido(2–) Complexes in CH_2Cl_2 at 23 °C for 48 h

			mol of product	
compd	R	acid (mol)	R_2NH[b]	NH_3[c]
1	Ph	HCl (20)	0.62	0.20
1	Ph	H_2O[d]	0.98	0.30
2	Me	HCl (20)	0.62	0.25
2	Me	H_2O[d]	0	*e*

[a] Mol/mol of W complex. [b] Diphenylamine was determined by HPLC using a reverse-phase C_{18} column with MeOH as solvent. Dimethylamine was determined colorimetrically using the pyrocatechol–silver oxide method: Pesez, M.; Bartos, J. Clinical and Biochemical Analysis. *Colorimetric and Fluorimetric Analysis of Organic Compounds and Drugs*; Marcel Dekker: New York, 1974; Vol. 1, p 159. [c] Ammonia was determined by the indophenol method: Weatherburn, M. W. *Anal. Chem.* **1974**, *39*, 971. [d] Very large excess. [e] Trace of ammonia.

the ancestry of the hydrazido(2–) ligand in **1** and **2**, simple cleavage of the metal–nitrogen bond might have been expected. Obviously the reduction step (Scheme I) results in a weakening of the N–N bond and a strengthening of the W–N bond, respectively (vide infra). Second, when water was used in place of HCl in reaction with **2**, *the yield of diphenylamine was essentially quantitative.* Although the yield of ammonia also increased, more than half of the remaining nitrogen is unaccounted for. Two electrons are required to produce 1 mol of Ph_2NH from 1 mol of **2**. Thus, tungsten is oxidized from W(IV) to W(VI), with an imido–W(VI) complex as a possible product following N–N bond cleavage (eq 1). No further redox chemistry is necessary for the formation

$$[WCl_2(NNPh_2)(PMe_2Ph)_3] + 3HCl \rightarrow [Ph_2NH_2]Cl + \{[WCl_3(NH)(PMe_2Ph)_2]Cl\} + PMe_2Ph \quad (1)$$

of ammonia. It is interesting but perhaps not surprising that more amine and ammonia were formed when water was used in place of HCl. In the presence of water, coordination of water and subsequent formation of a W=O bond will result in a more stable tungsten(VI) complex (hence facilitating oxidation of tungsten) than would be the case if only chloride ions were available for coordination. Third, although yields of amine and ammonia were similar for **1** and **2** when HCl was used, this was not true for reaction with water. Indeed, no ammonia, dimethylamine, or dimethylhydrazine was formed when **1** was reacted with water.

The crystal structures of **1** (Figure 1) and **2** have been determined.[21,22] Although the two complexes appear to be isostructural, common groups are orientated identically, and the N–N bond lengths are similar and are on the long side for hydrazido(2–) complexes, there are significant differences in W–N, W–P, and W–Cl bond lengths. For example, the W–N distance is notably shorter in the $NNPh_2$ complex than in **1**. The corresponding trans W–Cl(2) distance is also significantly shorter in the $NNPh_2$ complex. This is counterintuitive since a short W–N multiple bond would be expected to cause a correspondingly long W–Cl distance; the opposite is observed. All W–P bond lengths are shorter in **1** than in **2**. Regardless of these structural differences, **1** and **2** react similarly with HCl. However, there is a very large difference in the reactivities of **1** and **2** with water, which suggests that the mechanisms of the HCl and water reactions with **1** and **2** are different. The cyclic voltammograms of **1** and **2** are essentially the same in THF (0.2 M $[NBu^n_4][BF_4]$ electrolyte). Both show a reversible one-electron oxidation wave at ca. –0.54 V and an irreversible reduction wave at ca. –2.5 V vs the ferrocenium/ferrocene couple (=0.00 V).

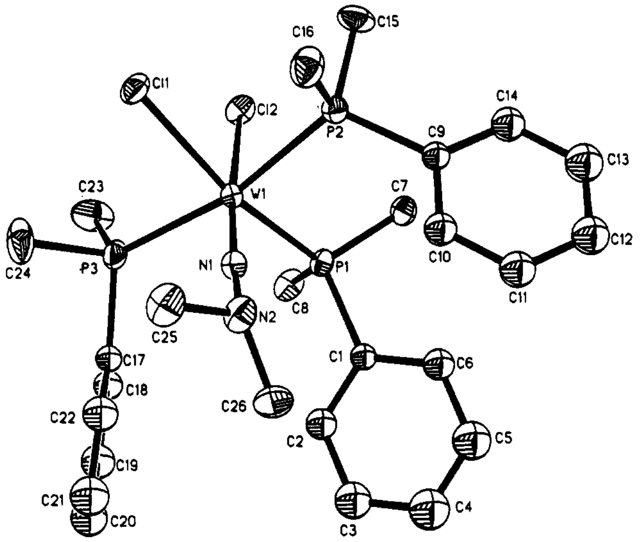

Figure 1. ORTEP view of the structure of $[WCl_2(NNMe_2)(PMe_2Ph)_3]$ (**1**). Selected bond lengths (Å) and angles (deg): W–N1 = 1.851(5); N1–N2 = 1.385(8); N2–C25 = 1.436(10); N2–C26 = 1.483(9); W–Cl1 = 2.481(2); W–Cl2 = 2.625(2); W–P1 = 2.391(2); W2–P2 = 2.422(2); W–P3 = 2.442(2); Cl2–W–N1 = 175.2(2); W–N1–N2 = 173.8(4); N1–N2–C25 = 112.4(5); N1–N2–C26 = 121.5(5); C25–N2–C26 = 114.4(6).

Work in progress includes attempting to characterize the final tungsten-containing product and identifying intermediates especially following fission of the nitrogen–nitrogen bond together with parallel studies of the analogous molybdenum hydrazido(2–) complexes.

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Supplementary Material Available: Tables of crystal data and experimental details, bond lengths, bond angles, anisotropic temperature factors, and positional parameters and isothermal temperature factors (18 pages). Ordering information is given on any current masthead page.[23]

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(21) Crystal data for $C_{26}H_{39}Cl_2N_2P_3W$ (**1**): brown, monoclinic, $P2_1/a$; a = 17.554(4) Å, b = 10.400(2) Å, c = 16.634(3) Å, β = 97.59(1)°; V = 3010.1(15) Å^3 for Z = 4 and fw = 727.3; D(calcd) = 1.603 Mg/m^3, μ(Mo Kα) = 4.192 mm^{-1} (T = 193 K). A total of 3931 reflections with a maximum 2θ = 45.0° were collected, of which 3237 reflections with $F > 6.0\sigma(F)$ were used in the refinement; R = 3.84; R_w = 4.89.

(22) Selected bond lengths (Å) and angles (deg) for **2** using the same atom labeling as for **1**: W–N1 = 1.761(8); N1–N2 = 1.36(1); N2–C25 = 1.44(1); N2–C26 = 1.41(1); W–Cl1 = 2.497(3); W–Cl2 = 2.486(3); W–P1 = 2.481(3); W–P2 = 2.517(3); W–P3 = 2.506(3); Cl2–W–N1 = 174.9(3); W–N1–N2 = 178.0(6); N(1)–N(2)–C(25) = 119.4(7); N1–N2–C26 = 118.8(8); C25–N2–C26 = 121.3(8). Crystal data for $C_{36}H_{43}Cl_2N_2P_3W$ (**2**): deep red, monoclinic, $P2_1/n$; a = 10.236(2) Å, b = 18.495(4) Å, c = 18.979(6) Å, β = 90.89(2)°; V = 3593(3) Å^3 for Z = 4 and fw = 851.43; D(calcd) = 1.574 g cm^{-3}, μ(Mo Kα) = 3.59 mm^{-1} (T = 193 K). A total of 5187 reflections with a maximum 2θ = 45.0° were collected, of which 3770 reflections with $F > 6.0\sigma(F)$ were used in the refinement; R = 0.043; R_w = 0.056.

(23) Full details of the structures of both **1** and **2** will be submitted by the same authors to *Inorganic Chemistry* in a full paper.