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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

PREPARATION AND PROPERTIES OF DIAZENIDO, HYDRAZIDO(2-), AND HYDRIDO-HYDRAZIDO(2-) COMPLEXES OF TUNGSTEN. X-RAY PHOTOELECTRON SPECTROSCOPY OF DINITROGEN AND HYDRAZIDO(2-) COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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To cite this Article George, T. Adrian and Kwarcinski, Michael E.(1995) 'PREPARATION AND PROPERTIES OF DIAZENIDO, HYDRAZIDO(2-), AND HYDRIDO-HYDRAZIDO(2-) COMPLEXES OF TUNGSTEN. X-RAY PHOTOELECTRON SPECTROSCOPY OF DINITROGEN AND HYDRAZIDO(2-) COMPLEXES OF MOLYBDENUM AND TUNGSTEN', *Journal of Coordination Chemistry*, 35: 3, 349 – 357

To link to this Article: DOI: 10.1080/00958979508024047

URL: <http://dx.doi.org/10.1080/00958979508024047>

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PREPARATION AND PROPERTIES OF DIAZENIDO, HYDRAZIDO(2-), AND HYDRIDO-HYDRAZIDO(2-) COMPLEXES OF TUNGSTEN. X-RAY PHOTOELECTRON SPECTROSCOPY OF DINITROGEN AND HYDRAZIDO(2-) COMPLEXES OF MOLYBDENUM AND TUNGSTEN

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(Received November 21, 1994; in final form February 12, 1995)

Reactions of HBr with *trans*-[W(N₂)₂(dppe)(PPh₂Me)₂] (1) (dppe = Ph₂CH₂CH₂PPh₂) result in protonation of coordinated N₂ but no formation of ammonia or hydrazine. The tungsten-containing product depends upon the reaction conditions: (i) in MeOH, the product formed is [WBr(NNH₂)(dppe)(PPh₂Me)₂]HBr₂ (2) which converts to the hydride, [WBr₂(H)(NNH₂)(dppe)(PPh₂Me)]Br (3), with loss of phosphine in THF or CH₂Cl₂, (ii) in THF or CH₂Cl₂, the hydride (3) is formed directly. Reaction of 2 with Na₂CO₃ in MeOH results in the loss of HBr and the formation of the diazenido complex [WBr(NNH)(dppe)(PPh₂Me)₂] which reacts further with Na₂CO₃ in benzene under N₂ to lose HBr and form a mixture of 1 and *trans*-[W(N₂)₂(dppe)₂]. The reaction of 1 with aqueous HF forms [WF(NNH₂)(dppe)(PPh₂Me)₂]BF₄. The X-ray photoelectron spectra of *trans*-[M(N₂)₂(dppe)₂], [MBr(NNH₂)(dppe)₂]Br (M = Mo, W), [WC1(NNH₂)(dppe)₂]Cl, [WC1(N)(dppe)₂]Cl and [WC1(NH)(dppe)₂] are reported. In all of these complexes, nitrogen is in a highly reduced form.

KEYWORDS: dinitrogen complexes, tungsten, X-ray photoelectron spectra

INTRODUCTION

The reactions of acids with bis(dinitrogen) complexes of molybdenum and tungsten frequently lead to (i) significantly different yields of ammonia¹ and (ii) different complexes containing nitrogen-hydride ligands,² depending upon the acid, the solvent, co-ligands and the metal. Recently, we reported the reactions of *trans*-[Mo(N₂)₂(dppe)(PPh₂Me)₂] with HBr which yielded under various conditions [MoBr(NNH₂)(dppe)(PPh₂Me)₂]Br, [MoBr₂(NNH₂)(dppe)(PPh₂Me)], [MoBr₃(NNH₂)(dppe)], and ammonia and hydrazine.³ In this paper we report the results of similar reactions with *trans*-[W(N₂)₂(dppe)(PPh₂Me)₂]⁴ which have led to the isolation of diazenido, hydrazido(2-), and hydride-hydrazido(2-) complexes of tungsten. In addition we report the X-ray photoelectron spectral data for a number of dinitrogen, hydrazido(2-), nitrido, and imido complexes of molybdenum and tungsten.

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EXPERIMENTAL

All reactions were performed using standard inert atmosphere (dinitrogen) or vacuum line techniques.⁵ All chemicals were purchased from commercial sources and stored and handled in a dry box unless otherwise noted. All solvents were dried by refluxing over an appropriate drying agent⁶ and were freshly distilled under dry dinitrogen immediately prior to use. ¹H and ³¹P{¹H} NMR spectra were obtained on either a Varian VXR 200 (200.05 and 80.891 MHz), or G.E. Omega 300 (300.52 and 121.65 MHz) or 500 (500.096 and 202.453 MHz) spectrometers. Chemical shifts were referenced to PPh₃ (-5.5 ppm vs 85% H₃PO₄ = 0.0 ppm) and Me₄Si (¹H). Phosphorus atom assignments are: Ph₂P_aCH₂CH₂P_aPh₂, P_xPh₂Me for the "P₄" complexes (**1,2,4,5** and chloro analogues of **2** and **4**) and Ph₂P_aCH₂CH₂P_bPh₂, P_xPh₂Me for the "P₃" complex **3** and the chloro analogue. IR spectra were obtained on an Analect RFX-65 FTIR spectrometer. [WCl(N)(dppe)₂] and [WCl(NH)(dppe)₂]Cl were prepared according to a literature procedure.⁷ Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville TN.

Synthesis of trans-[W(N₂)₂(dppe)(PPh₂Me)₂] (1)

WCl₆ (1.0 g, 2.5 mmol) was added to a Schlenk flask containing THF (100 mL), diphenylmethylphosphine (1.5 g, 7.5 mmol), 1% sodium amalgam (200 g, 0.087 mol) and a stirring bar. The mixture was allowed to stir under dinitrogen for *ca.* 10 min until it began to assume an orange color. Dppe (0.70 g, 1.7 mmol) was added and the mixture stirred for at least 24 h. The dark brown-orange solution was decanted and filtered through THF-saturated Celite. The Celite was washed with THF. The volume of the combined filtrate was reduced to *ca.* 15 mL under vacuum and diethyl ether (75 mL) was added. The red-orange solid was filtered off, washed with diethyl ether (3 × 10 mL) and pentane (10 mL), and dried in *vacuo* (24 h). The yield of product was 1.50 g (1.44 mmol, 85%). IR (KBr): ν(NN) 1990 (w), 1925 (vs) cm⁻¹. ³¹P NMR (C₆D₆): δ 42.7 (*dd*, J_{P_aP_x} *trans* = 158 Hz, J_{P_aP_x} *cis* = 49.0 Hz, P_a), 4.4 (*dd*, P_x). ¹H NMR (C₆D₆): δ 7.1 (*m*, 40, Ph), 2.1 (*d*, 4, J_{P_aH} = 17.3 Hz, CH₂), 1.6 (*d*, 6, J_{P_xH} = 5.7 Hz, CH₃).

Synthesis of [WBr(NNH₂)(dppe)(PPh₂Me)₂][HBr₂] (2)

Bromotrimethylsilane (1.0 mL, 7.6 mmol) was added to a suspension of **1** (1.0 g, 0.96 mmol) in methanol (100 mL). The mixture was stirred until all solid dissolved (at least 10 h). Solvent was removed and the apricot colored residue dried in *vacuo* (24 h). The residue was triturated with diethyl ether (30 mL, 0.5 h). The product was filtered off, washed with diethyl ether (3 × 10 mL) and pentane (10 mL) and dried in *vacuo* (24 h). The yield was 0.94 g (0.75 mmol, 78%). Anal. *Calcd* (found) for C₅₂H₅₃Br₃N₂P₄W: C, 49.83 (49.71); H, 4.26 (4.58); N, 2.23 (2.38); Br, 19.12 (19.05). IR (KBr): ν(NH) 3443 (w) 3286 (w) 2780 (w,b) cm⁻¹. ³¹P NMR (CD₃OD): δ 25.7 (*dd*, J_{P_aP_x} *trans* = 151 Hz, J_{P_aP_x} *cis* = 16.0 Hz, P_a), -14.9 (*dd*, P_x). ¹H NMR (CD₂Cl₂): δ 7.4 (*m*, Ph), 6.0 (*s*, 2, NH₂), 3.0 (*m*, 2, CH₂), 2.4 (*m*, 2, CH₂), 1.5 (*d*, 6, J_{P_xH} = 9.0 Hz, CH₃). This same complex could be prepared by condensing HBr (at least 3 mol) onto **1** at -196°C and working up the product as described below for the reaction of **1** with anhydrous HCl.

Synthesis of [W(H)Br₂(NNH₂)(dppe)(PPh₂Me)]Br (3)

Complex 2 (0.20 g, 0.16 mmol) was dissolved in CH₂Cl₂ (20 mL). The solution was stirred (at least 3 h) and filtered. Pentane (50 mL) was added to precipitate a yellow-tan solid which was filtered off, washed with diethyl ether (10 mL) and pentane (10 mL) and dried in *vacuo* (24 h). The yield was 0.13 g (0.12 mmol, 77%). Anal. *Calcd* (found) for C₃₉H₄₀Br₃N₂P₃W: C, 44.47 (44.64); H, 3.83 (4.11); N, 2.66 (2.22). IR (KBr): ν (WH) 1928 (w); ν (NH) 3286 (w) cm⁻¹. ³¹P NMR (CD₂Cl₂): δ 32.8 (*dd*, 1, J_{PaPb} = 29.6 Hz, J_{PaPx} = 167 Hz, P_a), 52.3 (*dd*, 1, J_{PaPx} = 19.6 Hz, P_b), -1.5 (*dd*, 1, P_x). ¹H NMR (CD₂Cl₂): δ 8.7 (*ddd*, 1, J_{PaH} = 14.3 Hz, J_{PbH} = 75.3 Hz, J_{PxH} = 71.5 Hz, J_{WH} = 23 Hz, WH), 7.6 (m, Ph), 7.0 (*t*, 2, NNH₂), 3.4 (m, 2, CH₂), 3.1 (m, 2, CH₂), 2.7 (*d*, 1.3, J_{PH} = 10.1 Hz, CH₃), 2.5 (*d*, 1.7, J_{PH} = 14.1 Hz, CH₃). Complex 3 was also prepared by reacting 1 with HBr in either THF or CH₂Cl₂ solution.

Synthesis of [WBr(NNH)(dppe)(PPh₂Me)] (4)

Methanol (20 mL) was added to a mixture of 2 (0.20 g, 0.16 mmol) and Na₂CO₃ (0.20 g, 1.9 mmol) and the mixture was stirred (at least 1 h). The yellow solid was filtered off, washed with water (5 × 15 mL), methanol (3 × 10 mL), diethyl ether (2 × 10 mL), and pentane (10 mL), and dried in *vacuo* (24 h). The yield was 0.11 g (0.10 mmol, 63%). Anal. *Calcd* (found) for C₅₂H₅₁BrN₂P₄W: C, 57.21 (57.72); H, 4.71 (4.79); N, 2.57 (1.89); Br, 7.32 (7.32). IR (KBr): ν (NH) 3309 (w); ν (NN) 1861 (m) cm⁻¹. ³¹P NMR (C₆D₆): δ 33.8 (*dd*, J_{PaPx} *trans* = 141 Hz, J_{PaPx} *cis* = 12.2 Hz, P_a), -11.2 (*dd*, P_x). ¹H NMR (C₆D₆): δ 7.2 (m, Ph and NH), 2.5 (m, 4, CH₂), 1.7 (*d*, 6, J_{PH} = 8.0 Hz, CH₃).

Reaction of 4 with Na₂CO₃ in Benzene

Benzene was added to the solid first isolated from the reaction of 2 with Na₂CO₃ (see previous experiment) which was a mixture of 4, Na₂CO₃, NaHCO₃, and NaBr. The suspension was stirred (2 h). The yellow suspension became orange. The solid was filtered off and pentane was added to the filtrate to precipitate an orange solid. IR and ³¹P NMR spectral data indicated that this solid was a mixture of 1 and *trans*-[W(N₂)₂(dppe)₂].

Reactions of trans-[W(N₂)₂(dppe)(PPh₂Me)] with HCl

(i) Anhydrous HCl (0.67 mmol) was condensed onto 1 (0.100 g, 0.096 mmol) at 10⁻⁵ torr and -196°C in a 50 mL round-bottom flask which contained a stirring bar. The reaction flask was allowed to warm up, allowing the HCl to melt, then vaporize. As the HCl melted, the surface of the solid was exposed by moving the stirring bar with an external magnet. The flask was again cooled to -196°C and then allowed to warm with stirring. This cycle was repeated three times to produce a tan solid. HCl was removed in *vacuo*. The solid was triturated with diethyl ether (15 mL, 0.5 h) and filtered off. The solid was washed with diethyl ether (10 mL) and pentane (2 × 10 mL) and dried in *vacuo* (24 h). The yield of product was 0.090 g (0.080 mmol, 83%). ³¹P NMR (CH₃OH): δ 27.8 (*dd*, J_{PaPx} *trans* = 142 Hz, J_{PaPx} *cis* = 15.5 Hz, P_a), -11.0 (*dd*, P_x). ¹H NMR (CD₂Cl₂): δ 9.6 (*ddd*, 1, WH), 7.5 (m,

Ph and NNH_2), 3.4 (*m*, 2, CH_2), 3.1 (*d*, 2, CH_2), 2.6 (*d*, 3, CH_3). By analogy with 2 this complex is formulated as $[\text{WCl}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2][\text{HCl}_2]$.

(ii) Anhydrous HCl, 1 M in diethyl ether (1.2 mL, 1.2 mmol) was added to a suspension of 1 (0.15 g, 0.14 mmol) in methanol (30 mL). The mixture was stirred until all solid dissolved (48 h). Solvent was reduced to ca. 5 mL in *vacuo* and diethyl ether (60 mL) was added to precipitate a tan solid which was filtered off, washed with pentane (3×10 mL) and dried in *vacuo*. The yield of product was 0.062 g (0.067 mmol, 45%). IR (KBr): $\nu(\text{WH})$ 1903 (w) cm^{-1} . ^{31}P NMR (CH_3OH): δ 36.2 (dd, 1, $J_{\text{PaPb}} = 25.9$ Hz, $J_{\text{PaPx}} = 178$ Hz P_a), 57.5 (dd, 1, $J_{\text{PbPx}} = 23.5$ Hz, P_b), 6.5 (dd, 1, P_x). ^1H NMR (CD_2Cl_2): δ 9.6 (ddd, 1, WH). By analogy with 3, this complex is formulated as $[\text{W}(\text{H})\text{Cl}_2(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})]\text{Cl}$.

(iii) Chlorotrimethylsilane (0.5 mL, 3.4 mmol) was added to a stirred suspension of 1 (0.500 g, 0.481 mmol) in methanol (40 mL). The mixture was stirred (18 h) during which time a brown solution formed. Solvent was removed in *vacuo*. Diethyl ether (20 mL) was added to the residue. The sides of the flask were scraped clean and the suspension was stirred (0.5 h). The solid was filtered off, washed with diethyl ether (10 mL) and pentane (3×10 mL) and dried in *vacuo* (24 h). The yield of product was 0.44 g. ^{31}P NMR (CH_3OH) indicated that this solid was *ca* an equimolar mixture of the two hydrazido(2-) complexes reported above.

Synthesis of $[\text{WF}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2][\text{BF}_4]$ (5)

48% aqueous HF (0.6 mL, 14 mmol) was added to a stirred suspension of 1 (0.256 g, 0.246 mmol) in methanol (25 mL) in a borosilicate glass Schlenk flask. After 48 h, a gold-brown solution resulted. Solvent was removed in *vacuo* and the residue was triturated with diethyl ether (20 mL, 0.5 h, 0°C). The tan solid was filtered off and washed with diethyl ether (10 mL) and pentane (10 mL) and dried in *vacuo* (24 h). The borosilicate reaction flask was noticeably etched. The yield of product was 0.16 g (0.143 mmol, 58%). IR (KBr): $\nu(\text{NH})$ 3332 (w), 3260 (w) cm^{-1} ; $\nu(\text{BF})$ 1058 (s), 1026 (s) cm^{-1} . ^{31}P NMR (CD_3OD): δ 30.4 (ddd, $J_{\text{PaPx trans}} = 168$ Hz, $J_{\text{PaPx cis}} = 14.7$ Hz, $J_{\text{PaF}} = 40.4$ Hz, P_a), -5.5 (ddd, $J_{\text{PxP}} = 43.8$ Hz, P_x). ^1H NMR (CD_2Cl_2): δ 7.2 (m, Ph), 4.9 (br s, 2, NNH_2), 2.4 (*d*, 4, $J_{\text{PH}} = 14.8$ Hz, CH_2), 1.4 (*d*, 6, $J_{\text{PH}} = 7.4$ Hz, CH_3). ^{19}F NMR (CD_3OD): δ 155.1 (*m*, 1, WF), 146.0 (*s*, 4, BF_4).

Synthesis of $[\text{WCl}(\text{NNH})(\text{dppe})(\text{PPh}_2\text{Me})_2]$

This complex was prepared according to the procedure for 4. IR (KBr): $\nu(\text{NN})$ 1860 (*m*) cm^{-1} . ^{31}P NMR (C_6D_6): δ 37.0 (complex *d*, $J_{\text{PaPx trans}} = 129$ Hz, P_a), -7.0 (complex *d*, P_x).

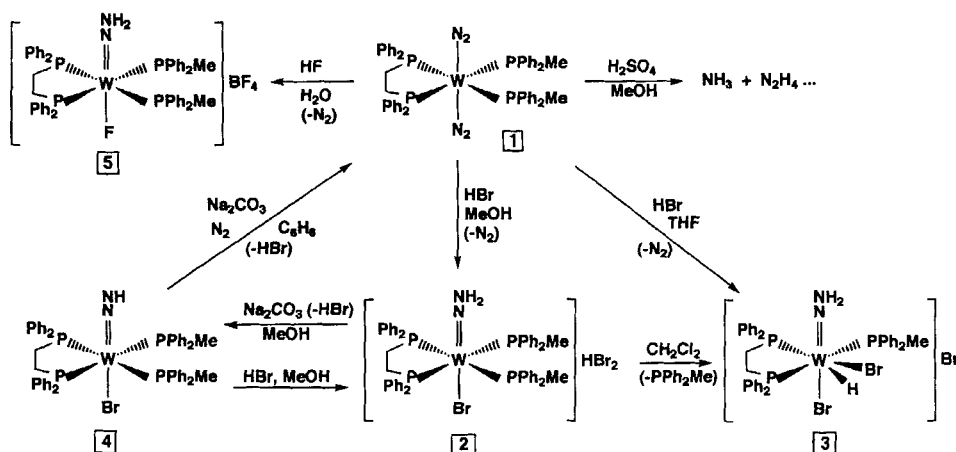
XPS Studies

Photoelectric kinetic energy was measured by a Physical Electronics (Phi) Model 15-255G double-pass CMA in conjunction with an associated pulse count technique. X-rays were generated by a Phi Model 04-548 Mg (1253.6 eV) source. Satisfactory spectra were obtained by signal averaging the pulse-count data. The N(1s) signal required up to 1000 scans, the metal atom signals typically required

200 scans while the C(1s) signal was satisfactory upon averaging ten scans. Upon signal averaging, the data were handled by the program Curvefit.⁸ Technical support was provided by C.L. Berrie, B.P. Hearty, and K. Wulser.

RESULTS AND DISCUSSION

An improved method for the high yield one-pot synthesis of *trans*-[W(N₂)₂(dppe)(PPh₂Me)₂] was developed based upon the sodium amalgam reduction of WCl₆ in THF under N₂.⁹ This synthesis involves having PPh₂Me present (three equivalents added) in the reaction mixture before the addition of dppe (see Experimental). It is important to use less than the stoichiometric amount of dppe in order to minimize the amount of *trans*-[W(N₂)₂(dppe)₂] formed which is difficult to separate from the desired product. The other coproduct *trans*-[W(N₂)₂(PPh₂Me)₄], is more soluble and thus more easily removed. *Trans*-[W(N₂)₂(dppe)(PPh₂Me)₂] reacted with sulfuric acid in methanol to produce ammonia and hydrazine; 0.37 and 0.10 moles per mole of **1**, respectively. Reactions with HBr produced no ammonia or hydrazine but instead formed two different types of hydrazido(2-) complexes as shown in Scheme 1.



Scheme 1 Summary of reactions of [W(N₂)₂(PPh₂Me)₂] with acids.

The reactions of **1** with HBr were solvent dependent. The reaction of **1** with either anhydrous HBr, followed by washing the product with diethyl ether, or HBr, generated *in situ* from the reaction of Me₃SiBr with methanol, resulted in the formation of a complex **2** that analyzed for [WBr(NNH₂)(dppe)(PPh₂Me)₂]Br with an "extra HBr" present. There are three possible structures that fit this formulation for which there is precedent in the literature: [WBr(NNH₂)(dppe)(PPh₂Me)₂] [HBr₂]^{2c}, [WBr(NNH₃)(dppe)(PPh₂Me)₂]Br₂,^{2b,c} and [WBr(H)(NNH₂)(dppe)(PPh₂Me)₂]Br₂.^{10,11} The latter hydride complex can be eliminated as a possibility due to the absence of a hydride resonance in the ¹H NMR spectrum. Chemical evidence supports **2** being a hydrazido(2-) complex with the [HBr₂]⁻ counterion.

Thus treatment of **2** with Et_3N , which yielded $[\text{Et}_3\text{NH}]\text{Br}$, caused no change in the ^{31}P NMR spectrum of **2** and by inference, no change in the nitrogen hydride ligand.

Upon dissolving **2** in either THF or CH_2Cl_2 a change in the ^{31}P NMR spectrum was observed. Three new doublets of doublets of equal relative intensity and a signal due to free PPh_2Me began to appear in the spectrum as the original pair of doublet of doublets due to **2** began to decrease in intensity. Eventually, a single new species **3** was present together with PPh_2Me . The IR spectrum of **3** displayed a peak of weak intensity at 1928 cm^{-1} that can be attributed to a metal hydride stretch. The ^1H NMR spectrum supported the presence of a single hydride with a resonance that appeared as a double doublet of doublets with accompanying ^{183}W satellites centered around δ 8.7. Phosphorus-hydride coupling constants are similar to those reported for other hydrazido(2-) hydride complexes.^{2c,d,10,11} Formulation of **3** as $[\text{WBr}_2(\text{H})(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})]\text{Br}$ is supported by elemental analysis and the appearance of the intact cation in the FAB mass spectrum. In the FAB mass spectrum, the parent ion shows an isotopic pattern extremely close to the calculated pattern. Complex **3** was prepared independently by the reaction of **1** with HBr in either THF or CH_2Cl_2 ; in both cases $[\text{HPPh}_2\text{Me}]\text{Br}$ was a coproduct. Selective phosphorus-decoupled ^1H NMR spectra enabled J_{PH} to be determined for each phosphorus atom. The NMR data are not inconsistent with a distorted octahedral geometry with P_a , P_b , P_x and a Br occupying the equatorial plane (as noted in the structure⁸ of $[\text{WBrCl}(\text{H})(\text{NNH}_2)(\text{PMe}_2\text{Ph})_3]^+$) and the hydride ligand occupying either an edge or a face which includes P_a and Br. Thus the hydride is transoid to P_b and P_x which display the larger J_{PH} . A further feature of the ^1H NMR spectrum was the appearance of two separate resonances at 2.70 and 2.50 ppm of unequal intensity with different $J(\text{PH})$ for the single Me group of the one PPh_2Me ligand. These data suggest that at room temperature there are two orientations for PPh_2Me of slightly different energies which provides two different environments for the Me group.

Complex **2** was stabilized with respect to conversion into **3** in solvents with a high dielectric constant such as methanol and ethanol. In less polar solvents such as THF and CH_2Cl_2 where ion pairing is more likely to occur, **2** was converted into **3**. The corresponding reactions of **1** with HCl produced the same results except that even in methanol some of the hydride hydrazido(2-) complex was formed. The reaction of **1** with aqueous HF in methanol produced $[\text{WF}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2][\text{BF}_4]$ which showed no evidence for loss of phosphine ligand or formation of a hydride (see Scheme 1).

Stirring a mixture of solid **2** and Na_2CO_3 in methanol (see Scheme 1), in which neither substance has any noticeable solubility, resulted in the formation of the corresponding diazenido complex $[\text{WBr}(\text{NNH})(\text{dppe})(\text{PPh}_2\text{Me})_2]$ (**4**).¹² The chloride analogue of **4** was prepared similarly. Complex **4**, in benzene solution, was deprotonated by Na_2CO_3 under dinitrogen to yield the starting bis(dinitrogen) complex **1** in low yield (see Scheme 1). A coproduct in this latter reaction was *trans*- $[\text{W}(\text{N}_2)_2(\text{dppe})_2]$. Although stable in benzene solution, **4** decomposed slowly in THF and CH_2Cl_2 solutions to generate free PPh_2Me and a complex containing only three coordinated phosphorus atoms together with resonances of less intensity due to other species. Loss of PPh_2Me from **4** would generate a complex such as $[\text{WBr}(\text{NNH})(\text{dppe})(\text{PPh}_2\text{Me})]$ that would produce three sets of resonances like those observed in the ^{31}P nmr spectrum. The sixth coordination site is likely to be occupied by a solvent molecule. After five days in THF, only two singlets were

observed in the ^{31}P nmr spectrum, one due to free PPh_2Me and the other due to a tungsten complex containing either one or, more likely (*vide supra*), two dppe ligands. The resonance due to this complex does not correspond to any reported $\{\text{W}(\text{dppe})_2\}$ -containing complex. Reaction of **4** with HBr in methanol regenerated **2** whereas in THF or CH_2Cl_2 solution a mixture of **2** and **3** was formed.

Comparison between Reactivity of Molybdenum and Tungsten Analogues^{13,14}

Both *trans*- $[\text{M}(\text{N}_2)_2(\text{dppe})(\text{PPh}_2\text{Me})_2]$ ($\text{M} = \text{Mo}, \text{W}$) reacted with HBF_4 , which in the current work was formed as the result of HF reaction with the borosilicate glass, to form $[\text{MF}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2]\text{BF}_4$ that did not react further with acid. *trans*- $[\text{M}(\text{N}_2)_2(\text{dppe})(\text{PPh}_2\text{Me})_2]$ reacted with HBr to initially form a hydrazido(2-) complex of the form $[\text{MBr}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2]^+$ which eventually formed the stable hydride hydrazido(2-) complex with the loss of one PPh_2Me in THF and CH_2Cl_2 solution when $\text{M} = \text{W}$. In THF solution $[\text{MoBr}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2]^+$ reacted further with the loss of two PPh_2Me ligands and the formation of $[\text{MoBr}_3(\text{NNH}_2)(\text{dppe})]$, a Mo(V) complex.³ It was suggested that a putative hydride was formed from which a hydrogen atom was lost to account for the oxidation of molybdenum from IV to V. In CH_2Cl_2 solution $[\text{MoBr}(\text{NNH}_2)(\text{dppe})(\text{PPh}_2\text{Me})_2]^+$ reacted further to produce ammonia, hydrazine, and N_2 in yields of 0.39, 0.44, and 1.39 mol/mol of Mo, respectively, for a 100% nitrogen atom balance. The major difference between the two systems rests with the formation of the stable W(VI) hydride hydrazido(2-) complex which effectively ties up all the tungsten valence electrons.

X-Ray Photoelectron Spectroscopy Studies

In an effort to determine the relative change in charge distribution as coordinated dinitrogen is protonated the N (1s), Mo ($3d_{5/2}$) and W ($4f_{7/2}$) binding energies (BE) were measured by X-ray photoelectron spectroscopy. These data are shown in Table 1. Both the dinitrogen and hydrazido(2-) complexes show two N(1s) signals. On the basis of studies performed in other laboratories on some of the same complexes the signal near 398 eV is assigned to the outer (β) nitrogen and that near 400 eV to the inner (α) nitrogen.¹⁵⁻¹⁷ Most amines, including ammonia, have N (1s) BEs of 399 ± 1 eV and ammonium salts BEs of 401 ± 1 eV.¹⁸ The data show that both nitrogen atoms in the dinitrogen and hydrazido(2-) complexes are in a highly reduced state. Upon protonation the BE of molybdenum and tungsten increase suggesting greater positive charge. The molybdenum BE further increases upon

Table 1 Binding energies (eV) determined by X-ray photoelectron spectroscopy.^a

Complex	P($2p_{3/2}$)	N α (1s)	N β (1s)	Mo($3d_{5/2}$)	W ($4f_{7/2}$)
$[\text{Mo}(\text{N}_2)_2(\text{dppe})_2]$	130.9	399.6	397.1	227.7	
$[\text{W}(\text{N}_2)_2(\text{dppe})_2]$	131.4	400.0	398.6		30.7
$[\text{MoBr}(\text{NNH}_2)(\text{dppe})_2]\text{Br}$	131.4	400.2	397.9	229.0	
$[\text{WBr}(\text{NNH}_2)(\text{dppe})_2]\text{Br}$	132.0	400.2	398.5		32.6
$[\text{WCl}(\text{NNH}_2)(\text{dppe})_2]\text{Cl}$	131.6	399.9	398.1		32.1
$[\text{WCl}(\text{N})(\text{dppe})_2]$	131.3	398.1			32.0
$[\text{WCl}(\text{NH})(\text{dppe})_2]\text{Cl}$	131.6	398.7			32.9

^aReferenced to the aromatic C (1s) signal at 285.0 eV. ± 0.2 eV.

formation of the molybdenum(V) hydrazido(2-) complex. The net effect of protonating the terminal nitrogen atom (and replacing an N_2 with a halide ion) is to cause an oxidation (increase in BE) of the metal and a small (Mo) or negligible (W) increase in the BEs of the nitrogen atoms. Protonation of the nitride nitrogen, which is highly reduced, to the imide results in an increase in the BEs of the metal, the nitrogen atom, and the phosphorus atoms.

CONCLUSIONS

The reactions reported in this manuscript show that protonation of bis(dinitrogen) complexes of tungsten result in different products depending upon (i) the solvent and (ii) the acid. Furthermore, some of the hydrazido(2-)-containing products are different from those obtained from similar reactions of the analogous molybdenum complex. In the former case, reaction with HBr resulted in the formation of a tungsten(VI) hydride, whereas the corresponding molybdenum reaction resulted in formation of ammonia and hydrazine.

Acknowledgement

We are grateful to the National Institutes of Health (Grant GM-38613) for support of this work. Additional funds were provided by Nebraska NSF-EPSCoR (OSR-9255225). The help of Professor M. A. Langell in obtaining the X-ray photoelectron spectra, Dr. C.J. Pickett in synthesizing the nitride and imide complexes, and Dr. R. Shoemaker in obtaining the selectively-decoupled NMR spectra is greatly appreciated.

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