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Syntheses and Reactions of Hydrazine and Diazene Complexes of Tungsten. The First Example of Monodentate Coordination of NH=NH[†]

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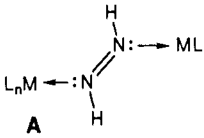
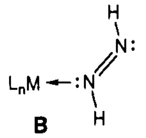
Abstract: Reaction of *trans,trans*-$W(H)(CO)_2(NO)(PR_3)_2$ (**2a**, R = Ph; **2b**, R = Cy) with triflic acid gives *trans,trans*-$W(\eta^1\text{-}OSO_2CF_3)(CO)_2(NO)(PR_3)_2$ (**3a**, R = Ph; **3b**, R = Cy) and dihydrogen in excellent yield. The weakly coordinated triflato ligands of **3a** and **3b** are cleanly displaced by hydrazine to give yellow tungsten–hydrazine coordination complexes [*trans,trans*-$W(NH_2NH_2)(CO)_2(NO)(PR_3)_2^+$][$SO_3CF_3^-$] (**4a**, R = Ph; **4b**, R = Cy). Reaction of **4a** and **4b** with $Pb(OAc)_4$ at −78 °C results in selective oxidation of the hydrazine ligands to give [*trans,trans*-$W(NH{=}NH)(CO)_2(NO)(PR_3)_2^+$][$SO_3CF_3^-$] (**5a**, R = Ph; **5b**, R = Cy). By using $^{15}N_2H_4$, the isotopically labeled derivatives [*trans,trans*-$W(^{15}NH_2{}^{15}NH_2)(CO)_2(NO)(PPh_3)_2^+$][$SO_3CF_3^-$] ([$^{15}N_2$]**4a**) and [*trans,trans*-$W(^{15}NH{=}^{15}NH)(CO)_2(NO)(PPh_3)_2^+$][$SO_3CF_3^-$] ([$^{15}N_2$]**5a**) have been prepared. The magnitudes of the $^3J_{HH}$ (27.0 Hz) and the two $^1J_{NH}$ (−46.0, −65.0 Hz) exhibited by the NH=NH ligand suggest that diazene is coordinated to tungsten (i) via a single nitrogen atom and (ii) with *trans*-NH=NH geometry. Variable-temperature ^1H NMR data for **5a** and **5b** also support the *trans*-NH=NH assignment. Although **5a** undergoes slow decomposition in solution, exchange of the noninnocent triflate anion with sodium tetraphenylborate results in a more robust salt, [*trans,trans*-$W(NH{=}NH)(CO)_2(NO)(PPh_3)_2^+$][$BPh_4^-$] (**5c**). Nucleophilic displacement of NH=NH from **5a** by bromide ion at 0 °C gives N_2 and N_2H_4, the known products of the bimolecular disproportionation of diazene. In the presence of excess diphenylacetylene, bromide displacement of NH=NH from **5a** gives *cis*-stilbene and N_2 in addition to hydrazine.

Introduction

One of the most fundamental hydrides of nitrogen, NH=NH (1,2-diazene), is also one of the most reactive.[1] Although it was suggested as early as 1892 to be a reactive intermediate in the decomposition of azoformic acid,[2] diazene was first observed and characterized in the gas phase by Foner and Hudson in 1958.[3] Interest in diazene stems from its ability to stereoselectively reduce some unsaturated organic substrates (presumably via the cis isomer),[4] as well as its possible relevance in inorganic and bioinorganic N_2-reducing systems.[5,6] In the condensed phase, diazene undergoes a bimolecular decomposition above −150 °C to give, predominately, N_2 and N_2H_4,[7] but its stability is greatly enhanced when its lone pairs are coordinated to transition metals. Several moderately stable bimetallic diazene complexes (**A**) have been prepared by the oxidation of coordinated hydrazine (giving NH=NH ligated via both nitrogen lone pairs).[8] Herein we reported the synthesis and characterization of the first example of a monodentate diazene complex (**B**) and its reactivity with bromide ion to effect displacement of the NH=NH ligand.[9]



A



B

Experimental Section

General Considerations. Reactions were carried out using standard high-vacuum and Schlenk techniques using dry, air-free solvents. ^1H NMR spectra were recorded at 500 MHz using the Chicago-built 500-MHz spectromcter or a General Electric Ω-500 spectrometer and referenced to residual proton peaks of the solvent ($CDCl_3$, δ 7.24; CD_2Cl_2, δ 5.32). Simulations of second-order spectra were performed iteratively using the simulation program NMCSIM (Nicolet Magnetics Corp.). ^{31}P NMR spectra were recorded in CH_2Cl_2 solution using a Nicolet Magnetic Corp. 200-MHz spectrometer (^{31}P = 81.0 MHz) or a General Electric Ω-500 spectrometer (^{31}P = 202.4 MHz) and referenced

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[†] Dedicated to the memory of Professor Gerhard L. Closs, beloved colleague and friend.

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to external 85% phosphoric acid (δ 0). ^{15}N NMR spectra were recorded in CD_2Cl_2 solution using a General Electric Ω-500 spectrometer (^{15}N = 50.7 MHz) and referenced to external 80% formamide in DMSO-d_6 (δ 108.0). Infrared spectra were recorded on a Nicolet 20SXB spectrometer in a Fluorolube-S30 mull with CaF_2 plates. Quantitative GC data were obtained on a Hewlett-Packard 5890 instrument with an integrator. $W(H)(CO)_2(NO)(PPh_3)_2$ (**2a**) was prepared according to the literature procedure.[10] $W(ClAlCl_3)(CO)_4(NO)$ was prepared from $W(CO)_6$ and $[NO][AlCl_4]$ by a protocol analogous to the literature procedure for the Mo derivative.[11] Hydrazine (98%), trifluoromethanesulfonic acid (HOTf), and lead tetraacetate were purchased from Aldrich Chemical Co. $^{15}NH_2{}^{15}NH_2$ was prepared by the Soxhlet extraction of $^{15}N_2H_4{\cdot}H_2SO_4$ (95% ^{15}N; Cambridge Isotopes) with liquid ammonia. Tricyclohexylphosphine (PCy_3) was used as purchased from Strem Chemical Co.

***trans,trans*-$W(Cl)(CO)_2(NO)(PCy_3)_2$ (1).** A 200-mL round-bottomed flask fitted with a needle-valve adapter was charged with 2.50 g (5.05 mmol) of *trans*-$W(ClAlCl_3)(NO)(CO)_4$, 4.40 g (15.3 mmol) of PCy_3, and 120 mL of toluene. The mixture was stirred under argon at 90 °C for 30 min, at which time the toluene phase was orange and homogeneous and a viscous tar had collected on the bottom of the flask. The flask was opened to the atmosphere, and the hot solution was filtered through Celite. The orange filtrate was reduced in volume to 25 mL, during which time the product began precipitating as yellow-orange microcrystals. The precipitation was completed by addition of hot EtOH (60 mL), the microcrystalline powder was collected on a frit and washed with hot EtOH (50 mL) and petroleum ether (50 mL), and the yellow product was air-dried to give 3.12 g (71% yield). **1** obtained in this fashion was generally suitable for subsequent preparations but could be conveniently recrystallized from CH_2Cl_2/Et_2O. Solvated ether was removed by heating in vacuo at 60 °C overnight; however, the sample was still solvated with 0.14 equiv of CH_2Cl_2 (^{1}H NMR integration). Anal. Calcd for $C_{38.14}H_{66.28}NO_3P_2Cl_{1.28}W$: C, 52.17; H, 7.61; N, 1.59. Found: C, 52.21; H, 7.69; N, 1.70. IR: ν(CO) 1921 (vs), 2015 (w); ν(NO) 1612 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 2.23 (m, 6 H, *Cy*), 2.07 (m, 12 H, *Cy*), 1.87 (m, 12 H, *Cy*), 1.72 (br s, 6 H, *Cy*), 1.56 (m, 12 H, *Cy*), 1.30 (br s, 18 H, *Cy*). $^{31}P\{^1H\}$ NMR (202.4 MHz, CH_2Cl_2, 20 °C): δ 20.9 (s, J_{PW} = 266 Hz).

***trans,trans*-$W(H)(CO)_2(NO)(PCy_3)_2$ (2b).** A 2.5-g (2.89 mmol) sample of **1**, 5.28 g (18.83 mmol) of PCy_3, and 0.25 g (11.54 mmol) of lithium borohydride were added to a 250-mL flask attached to a needle-valve adapter. To this mixture was added 180 mL of THF, and the solution was warmed to near reflux for 20 min under argon, during which time the reaction mixture turned deep orange and became homogeneous. The flask was then opened to the air, and the solution was filtered through Celite. The filtrate volume was reduced to 15 mL on a rotary evaporator, and 100 mL of hot EtOH was added to the solution to give a precipitate. The precipitate was filtered, and the bright-yellow solids were washed with hot EtOH (3 × 20 mL) and petroleum ether (15 mL) to give 2.16 g (90% yield) of **2b**. Anal. Calcd for $C_{38}H_{67}NO_3P_2W$: C, 54.87; H, 8.12; N, 1.68. Found: C, 54.84; H, 8.40; N, 1.87. IR: ν(CO) 1896 (vs), 1993 (w); ν(NO) 1580 (s); ν(WH) 1680 (s) cm^{-1} [Note: ν(NO) and ν(WH) are strongly coupled modes].[10] ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 2.07–2.03 (m, 6 H, *Cy*), 1.98–1.96 (m, 12 H, *Cy*), 1.85 (br s, 12 H, *Cy*), 1.72 (br s, 6 H, *Cy*), 1.50–1.45 (m, 12 H, *Cy*), 1.28–1.27 (m, 18 H, *Cy*), –1.71 (t, 1 H, W-*H*, $^2J_{PH}$ = 24.1 Hz). $^{31}P\{^1H\}$ NMR (202.4 MHz, CH_2Cl_2, 20 °C): δ 34.2 (s, J_{PW} = 274 Hz).

***trans,trans*-$W(\eta^1\text{-}OSO_2CF_3)(CO)_2(NO)(PPh_3)_2$ (3a).** A 2.99-g (3.76 mmol) sample of **2a** was dissolved in 60 mL of methylene chloride. The solution was stirred and cooled to –78 °C, and then 0.35 mL (1.05 equiv) of trifluoromethanesulfonic acid was added via syringe. The orange solution was allowed to slowly warm to ambient temperature, during which time gas evolution (H_2) was evident. The resulting yellow solution was filtered, and the product was precipitated from the filtrate as lemon-yellow microcrystals by addition of Et_2O/petroleum ether (100 mL of a 1:1 mixture). The precipitate was washed with petroleum ether (20 mL) and dried in air to yield 3.10 g (88%) of **3a**. Anal. Calcd for $C_{39}H_{30}NO_6F_3P_2SW$: C, 49.65; H, 3.20; N, 1.48. Found: C, 48.30; H, 2.99; N, 1.23. IR: ν(CO) 1944 (vs), 2057 (w); ν(NO) 1657 (s); $\nu(OSO_2CF_3)$ 1340 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.58–7.52 (m, 12 H, *Ph*), 7.50–7.40 (m, 18 H, *Ph*). $^{31}P\{^1H\}$ NMR (81.0 MHz, CH_2Cl_2, 20 °C): δ 24.5 (s, J_{PW} = 292 Hz). ***trans,trans*-$W(\eta^1\text{-}OSO_2CF_3)(CO)_2(NO)(PCy_3)_2$ (3b)** was analogously prepared from triflic acid and **2b** in 84% yield. Anal. Calcd for $C_{39}H_{66}NO_6F_3P_2SW$: C, 47.81; H, 6.79; N, 1.53. Found: C, 48.85; H, 7.26; N, 1.36. IR: ν(CO) 1931 (vs), 2025 (w); ν(NO) 1626 (s); $\nu(OSO_2CF_3)$ 1339 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 2.33–2.30 (m, 6 H, *Cy*), 2.00–1.98 (m, 12 H, *Cy*), 1.89–1.88 (m, 12 H, *Cy*), 1.74 (br s, 6 H, *Cy*), 1.60–1.58 (m, 12 H, *Cy*), 1.34–1.30 (m, 18 H, *Cy*). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 20 °C): δ 30.2 (s, J_{PW} = 272 Hz).

[*trans,trans*-$W(NH_2NH_2)(CO)_2(NO)(PPh_3)_2{}^+][SO_3CF_3{}^-]$ (4a). To 4.00 g (3.19 mmol) of **3a** in a 100 mL round-bottomed flask attached to a swivel-frit assembly was added 80 mL of methylene chloride. The contents of the flask were stirred and cooled to –78 °C, and then 145 μL (4.53 mmol) of hydrazine (98%) was added via syringe to the stirred suspension. The yellow mixture was slowly warmed until it began to turn orange, at which point it was filtered through a Celite pad. The volume of the filtrate was reduced in vacuo to about 20 mL, taking care *not* to warm the solution by using a water bath. Petroleum ether (30 mL) was vacuum-transferred into the flask to complete the precipitation of the salt, the mixture was filtered, and the residual solvent was removed in vacuo. The product was washed with a 10-mL portion of toluene (which served to wash away an orange impurity) and then with petroleum ether (30 mL) and was dried in vacuo to yield 3.01 g of a yellow-orange powder. Recrystallization of this crude product (from CH_2Cl_2/Et_2O or CH_2Cl_2/toluene) gave 2.40 g (58%) of an analytically pure, bright-yellow powder. (*NOTE: The recrystallization removes a flaky white CH_2Cl_2 insoluble impurity, possibly $[N_2H_5{}^+][OTf^-]$, and is essential for successful oxidation of **4** to **5** as detailed below.*) Anal. Calcd for $C_{39}H_{36}N_3O_3F_6P_3W$: C, 47.99; H, 3.51; N, 4.31. Found: C, 47.75; H, 3.31; N, 4.33. IR: ν(CO) 1965 (vs), 2045 (w); ν(NO) 1658 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.58–7.47 (m, 30 H, *Ph*), 3.73 (br, 2 H, NH_2), δ 2.27 (br, 2 H, NH_2). $^{31}P\{^1H\}$ NMR (202.4 MHz, CH_2Cl_2, 20 °C): δ 23.6 (s, J_{PW} = 283 Hz). **[$^{15}N_2$]4a** was prepared analogously to **4a** except that $^{15}N_2H_4$ was used. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 7.58–7.47 (m, 30 H, *Ph*), 3.73 (br d, 2 H, $|^1J_{NH}|$ = 69 Hz, $^{15}NH_2$), 2.27 (br d, 2 H, $|^1J_{NH}|$ = 63 Hz, $^{15}NH_2$). **[*trans,trans*-$W(NH_2NH_2)(CO)_2(NO)(PCy_3)_2{}^+][SO_3CF_3{}^-]$ (4b)** was prepared from **3b** in 54% yield by a procedure analogous to that for **4a**. Anal. Calcd for $C_{39}H_{70}N_3O_6F_3P_2SW$: C, 46.29; H, 6.97; N, 4.15. Found: C, 46.58; H, 7.31; N, 4.21. IR: ν(CO) 1927 (vs), 2033 (w); ν(NO) 1647 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, 20 °C): δ 2.34–2.31 (m, 6 H, *Cy*), 1.94–1.90 (m, 18 H, *Cy*), 1.78 (br s, 6 H, *Cy*), 1.63–1.60 (m, 6 H, *Cy*), 1.38–1.30 (m, 12 H, *Cy*), 1.34–1.30 (m, 18 H, *Cy*), 3.73 (br, 2 H, NH_2), 2.27 (br, 2 H, NH_2). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$, 20 °C): δ 25.0 (s, J_{PW} = 259 Hz).

[*trans,trans*-$W(NH{=}NH)(CO)_2(NO)(PPh_3)_2{}^+][SO_3CF_3{}^-]$ (5a). A 0.50-g (0.51 mmol) sample of **4a** was placed in a 50-mL two-necked flask attached to a swivel-frit assembly and fitted with a solids-addition side arm containing 250 mg (0.56 mmol) of $Pb(OAc)_4$. The system was evacuated, and then 15 mL of CH_2Cl_2 was transferred at –78 °C into the flask. The $Pb(OAc)_4$ was added in small portions to the cold, stirred suspension, giving an orange solution and a white precipitate. The cold solution was filtered, and the volume of the filtrate was reduced in vacuo to approximately 5 mL. Care was taken *not* to warm the solution by using a water bath so that the solution remained cold during solvent evaporation. A 15-mL portion of petroleum ether was transferred into the flask at –78 °C, causing an orange powder to precipitate. The mixture was filtered, and the solids were washed with 10 mL of petroleum ether to yield 0.21 g (42%) of product. Anal. Calcd for $C_{39}H_{34}N_3O_3F_6P_3W$: C, 48.09; H, 3.31; N, 4.31. Found: C, 47.01; H, 3.19; N, 4.02. IR: ν(CO) 1969 (vs), 2052 (w); ν(NO) 1670 (s) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ 14.48 (br dt, 1 H, W—NH═N*H*, $^3J_{HH}$ = 27.0 Hz, $^4J_{PH}$ = 2.4 Hz), 14.15 (br d, 1 H, W—N*H*═NH, $^3J_{HH}$ = 27.0 Hz), 7.50 (br m, 30 H, P*Ph*$_3$). $^{31}P\{^1H\}$ NMR (202.4 MHz, CH_2Cl_2, 20 °C): δ 26.5 (s, J_{PW} = 286 Hz). **[$^{15}N_2$]5a** was analogously prepared by the $Pb(OAc)_4$ oxidation of **[$^{15}N_2$]4a**. ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ 14.48 (m, 1 H, W—^{15}NH═^{15}N*H*, $^1J_{NH}$ ≈ –46.0 Hz, $^2J_{NH}$ = –3.7 Hz, $^4J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 27.0 Hz), 14.15 (m, 1 H, W—^{15}N*H*═^{15}NH, $^1J_{NH}$ = –65.0 Hz, $^2J_{NH}$ = 1.6 Hz, $^3J_{PH}$ = 0 Hz, $^3J_{HH}$ = 27.0 Hz), 7.50 (br m, 30 H, P*Ph*$_3$). $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2, 20 °C): δ 26.5 (dd, $^2J_{PN}$ = 3.1 Hz, $^3J_{PN}$ = 1.8 Hz, J_{PW} = 286 Hz). ^{15}N NMR (50.7 MHz, CD_2Cl_2, 20 °C): δ 563.9 (dd, W—^{15}NH═^{15}*N*H, $^1J_{NN}$ = 14.7 Hz, $^1J_{NH}$ = –46.0 Hz), 450.1 (dd, W—^{15}*N*H═^{15}NH, $^1J_{NN}$ = 14.7 Hz, $^1J_{NH}$ = –65.0 Hz). **[*trans,trans*-$W(NH{=}NH)(CO)_2(NO)(PCy_3)_2{}^+][SO_3CF_3{}^-]$ (5b)** was prepared from **4b** in 38% yield by a procedure analogous to that used for **5a**. IR: ν(CO) 1934 (vs), 2030 (w); ν(NO) 1655 (s) cm^{-1}. ^{1}H NMR (500 MHz, CD_2Cl_2, 20 °C): δ 16.06 (dt, 1 H, W—NH═N*H*, $^3J_{HH}$ = 28.0 Hz, $^4J_{PH}$ = 2.7 Hz), 14.99 (d, 1 H, W—N*H*═NH, $^3J_{HH}$ = 28.0 Hz), 2.13–2.11 (m, 6 H, *Cy*), 2.05–1.92 (m, 12 H, *Cy*), 1.85–1.83

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(m, 12 H, *Cy*), 1.75 (br s, 6 H, *Cy*), 1.50–1.46 (m, 12 H, *Cy*), 1.33–1.29 (m, 18 H, *Cy*). $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2, 20 °C): δ 27.1 (s, J_{PW} = 260 Hz).

[*trans,trans*-W(NH=NH)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][BPh$_4$$^-$] (5c). A 0.40-g (0.41 mmol) sample of **5a** and 0.154 g (0.45 mmol) of $NaBPh_4$ were combined in a 25-mL round-bottomed flask fitted to a swivel-frit assembly. Tetrahydrofuran (10 mL) was vacuum-transferred onto the solids at −78 °C. The reaction mixture was stirred at dry ice temperature for 15 min, and then the solvent was removed in vacuo. The residue was redissolved in 10 mL of methylene chloride, the solution was filtered, and the volume of the filtrate was reduced to about 5 mL. Slow addition of diethyl ether (15 mL) caused a dark-orange solid to precipitate. The product was collected by filtration and was washed with 10 mL of petroleum ether to yield 0.32 g (72%). Anal. Calcd for $C_{62}H_{52}O_3N_3BP_2W$: C, 65.11; H, 4.58; N, 3.67. Found: C, 65.21; H, 4.68; N, 3.42. IR: ν(CO) 1958 (vs), 2052 (w); ν(NO) 1665 (s) cm^{-1}. ^1H NMR (500 MHz, CD_2Cl_2, 20 °C): δ 12.37 (d, 1 H, W—NH=N*H*, $^3J_{HH}$ = 28.1 Hz), 11.13 (d, W—N*H*=NH, 1H, $^3J_{HH}$ = 28.1 Hz), 7.62–7.22 (m, 30 H, P*Ph*$_3$), 7.20–6.75 (m, 20 H, B*Ph*$_4$). $^{31}P\{^1H\}$ NMR (202.4 MHz, CH_2Cl_2, 20 °C): δ 23.7 (s, J_{PW} = 285 Hz).

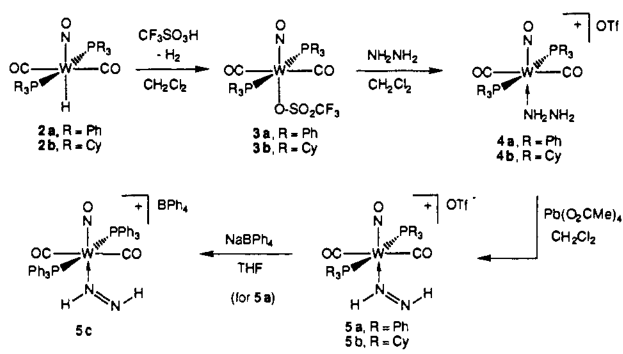
Quantification of N_2H_4 Produced in the Reaction of 5a with Tetra-*n*-butylammonium bromide. The procedure followed is adapted from Snell et al.[12a] and Watt and Chrisp.[12b] As reagent, 0.40 g of *p*-(dimethylamino)-benzaldehyde (Ehrlich's reagent) was added to 20 mL of 95% EtOH and 2.0 mL of concentrated HCl and was fully dissolved after 10 min. A 10-mL aliquot of an aqueous hydrazine solution and 10 mL of the reagent were then placed in a 25-mL volumetric flask, and this was diluted to the mark with 1:11 HCl. A reagent blank (using H_2O in place of the hydrazine solution) was prepared in a similar manner. The color was allowed to develop for 15 min, and the UV–vis spectrum of the sample against the reagent blank was then recorded at 458 nm.

The standards used for the concentrations of hydrazine were prepared by dissolving hydrazine sulfate in water and diluting, to obtain concentrations on the order of 0.1–0.7 ppm (mg/L) in hydrazine. A typical procedure is as follows: 0.771 g of $N_2H_4{\cdot}H_2SO_4$ was placed in a volumetric flask, and water was added to make 500 mL of solution. A 2.0-mL aliquot of this solution was then diluted with water to again make 500 mL of solution. A 10-mL aliquot of this solution was used in preparing 25 mL of sample, as detailed above. The resulting concentration of this solution was 0.608 ppm, and the UV–vis spectrum shows A = 0.248 at 457.5 nm.

A 100-mg (0.103 mmol) sample of **5a** and 36 mg (0.11 mmol, 1.1 equiv) of [Bu^n$_4$N$^+$][Br$^-$] were weighed in a 25-mL Kjeldahl flask fitted to a needle-valve adapter. CH_2Cl_2 (5 mL) was added by vacuum transfer at −78 °C, and the flask was covered with foil to exclude light. The dry ice bath was replaced with an ice bath, and the solution was stirred for 25 min. After this time, the flask was examined and the solution had changed color from orange to yellow, indicating completion of the displacement reaction. After the flask was opened to air, the methylene chloride solution was placed in a separatory funnel and extracted with H_2O (6 × 10 mL). The aqueous extracts were combined and diluted to make 500 mL of solution. An aliquot (250 mL) of this solution was then diluted to make 500 mL of solution, and a 10-mL aliquot of this solution was used in the colorimetric analysis. The resulting absorbance, at 457.1 nm, was 0.169. This gives a hydrazine concentration of 0.412 ppm when compared to the standards. The calculated theoretical concentration from the reaction ($2NH{=}NH \rightarrow N_2 + N_2H_4$) is 0.658 ppm, resulting in a 62.5% yield of hydrazine (or 0.31 equiv N_2H_4/**5a**).

Displacement of NH=NH from 5a in the Presence of Diphenylacetylene. An 80-mg (0.082 mmol) sample of **5a**, along with 30 mg (0.093 mmol, 1.1 equiv) of [Bu^n$_4$N$^+$][Br$^-$] and 240 mg (1.35 mmol, 16 equiv) of diphenylacetylene, was weighed into a 25-mL flask attached to a needle-valve adapter. Methylene chloride (5 mL) was vacuum-transferred into the flask at −78 °C, and the flask was covered with foil to exclude light. The dry ice bath was replaced with an ice bath, and the solution was stirred for 30 min at 0 °C. After this time, the solution had changed from orange to yellow. Subsequent workup was performed in the air. The products were characterized as *cis*- and *trans*-stilbene by ^1H NMR and by GC (co-injection with authentic samples). Isomeric yields were determined by GC quantification (*n*-dodecane internal standard) with comparison to a solution of known concentration of *cis*- and *trans*-stilbene. The total yield of stilbene was 12%, based on **5a**. The ratio of cis/trans was ~8:1.

Scheme I



Results and Discussion

The tungsten(0) hydrido complexes *trans,trans*-W(H)(CO)$_2$(NO)(PR$_3$)$_2$ (**2a**, R = Ph; **2b**, R = cyclo-C_6H_{11} ≡ Cy) react with triflic acid to give dihydrogen and *trans,trans*-W(η^1-OSO$_2$CF$_3$)(CO)$_2$(NO)(PR$_3$)$_2$ (**3a**, R = Ph; **3b**, R = Cy) in excellent yield (see Scheme I). Hydrazine cleanly displaces the triflato ligands of **3a** and **3b** to afford yellow tungsten–hydrazine coordination complexes [*trans,trans*-W(NH$_2$NH$_2$)(CO)$_2$(NO)(PR$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**4a**, R = Ph; **4b**, R = Cy). In this regard, these complexes, containing weakly coordinating triflato ligands, exhibit reactivity similar to that of the hexafluorophosphato analogue *trans,trans*-W(η^1-FPF$_5$)(CO)$_2$(NO)(PPh$_3$)$_2$ (**3c**), which has been shown to react with methylhydrazine to give [*trans,trans*-W(NH$_2$NHMe)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][PF$_6$$^-$].[13] Hydrazine coordination complexes are well established, with the N_2H_4 ligand exhibiting three distinct modes of binding: monodentate (η^1), bidentate (η^2), and bridging (μ_2).[14] It is probably the steric bulk of the "W(CO)$_2$(NO)(PR$_3$)$_2$" fragment that dictates the η^1 coordination of N_2H_4 in **4a** and **4b**.

Lead tetraacetate acts on **4a** and **4b** at low temperature (CH_2Cl_2 solution, −78 °C) to effect oxidation of the coordinated hydrazine ligands, forming [*trans,trans*-W(NH=NH)(CO)$_2$(NO)(PR$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**5a**, R = Ph; **5b**, R = Cy), which can be isolated as yellow-orange, air-sensitive powders in moderate yields (Scheme I). We have had no success in isolating stable diazene complexes in this system when oxidants other than Pb(OAc)$_4$ have been employed; this was also the case in the preparation of [*trans,trans*-W(NH=NMe)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][PF$_6$$^-$] (**6**) from the corresponding methylhydrazine complex.[13] By using $^{15}N_2H_4$, the isotopically labeled derivatives [*trans,trans*-W(^{15}NH$_2$^{15}NH$_2$)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] ([$^{15}N_2$]**4a**) and

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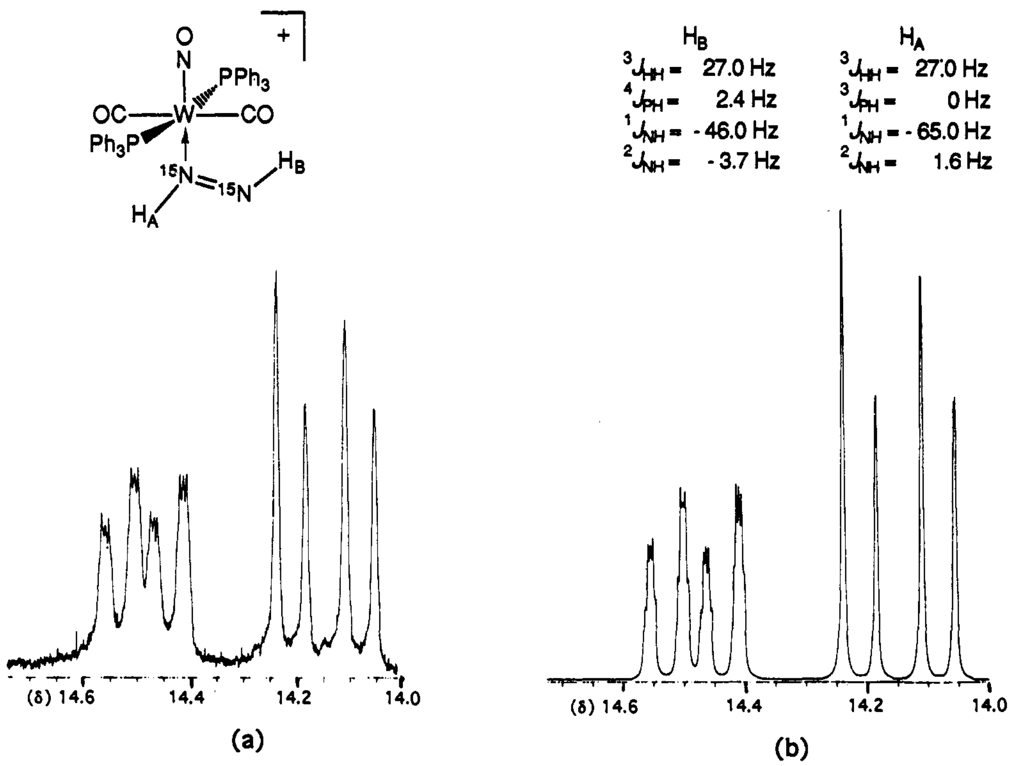

Figure 1. (a) ^{1}H NMR spectrum of the diazenyl protons of [$^{15}N_2$]**5a** (20 °C, 500 MHz, CD_2Cl_2). The isotopic enrichment was 95% ^{15}N. (b) A computer simulation of this complex ABM_2XY spin system. For calculating the simulated spectrum, a value of $^1J_{NN}$ = 14 Hz (measured by ^{15}N NMR) was used, the contribution of ^{183}W (14% abundance, $I = {}^1/_2$) was ignored, and a line width of 1.5 Hz was included. All other pertinent coupling constants are shown in the figure.

[*trans,trans*-W($^{15}NH{=}^{15}NH$)$(CO)_2(NO)(PPh_3)_2{}^+$][$SO_3CF_3{}^-$] ([$^{15}N_2$]**5a**) have also been prepared. Although stable in the solid state, **5a** is thermally unstable in solution (CH_2Cl_2), and on standing at ~0 °C, it decomposes over a period of days to give **3a** as the major metal-containing product, suggesting that even the relatively weakly nucleophilic triflate anion effects a displacement of NH═NH at a modest rate. Similar nucleophilic displacement reactions of NH═NR (R = Me, Ph) from related W and Mo complexes have been observed.[13,15,16] A more robust derivative, [*trans,trans*-W(NH═NH)$(CO)_2(NO)(PPh_3)_2{}^+$]-[$BPh_4{}^-$] (**5c**), can be prepared in good yield by exchange of the triflate anion with a more innocent counterion, tetraphenylborate (Scheme I).

NH═NH Ligand. It is noteworthy that the monohapto coordination geometries for NH_2—NH_2 and NH═NH attached to the formally d^6 tungsten centers in **4** and **5** differ from the usual η^2-binding of a variety of related hydrazine, hydrazido, and diazene ligands found in mononuclear tungsten complexes in which the metal is in a high-oxidation state (d^0).[14,17] The signature downfield resonances for the diazenyl protons (δ 14.15, 14.48) observed in the ^{1}H NMR spectrum of [$^{15}N_2$]**5a** (20 °C, 500 MHz, CD_2Cl_2) along with a computer simulation of this ABM_2XY spin system are shown in Figure 1. The magnitudes of the two $^1J_{NH}$ (−46.0, −65.0 Hz) exhibited by the NH═NH ligand indicate that the diazene is coordinated to tungsten via a single nitrogen atom (a unique coordination mode for diazene),[18] and the $^3J_{HH}$ (27.0 Hz) suggests a probable *trans*-NH═NH geometry.[19] Consistent with this structure is the observation of two resonances at δ 450.1 (dd, N_A) and δ 563.9 (dd, N_B) ($^1J_{NN}$ = 14.7 Hz) in the ^{15}N NMR spectrum of [$^{15}N_2$]**5a**. Models (based on the solid-state structure of **6**, in which the Me group was replaced with a hydrogen atom in the diazene ligand) show that a trans geometry for the coordinated NH═NH ligand in **5a** thrusts H_B of the diazene close to the PPh_3 phenyl rings. An interesting consequence of this is that the chemical shifts of H_A and H_B in [W($N_AH{=}N_BH$)$(CO)_2(NO)(PPh_3)_2{}^+$] are strongly temperature dependent, with the resonances shifting to higher field with decreasing temperature. Variable-temperature ^{1}H NMR spectra of the NH protons of **5a** are shown in Figure 2, and a plot of the chemical shifts as a function of reciprocal temperature shows a linear relationship of the form $\delta(NH) \propto 1/T$ (Figure 3). The magnitude of the effect on H_A is less than that on H_B (since H_B is closer to the phenyl rings, it experiences a more pronounced ring-current effect), and this results in an accidental degeneracy for the two chemically distinct protons at −70 °C (500 MHz, CD_2Cl_2), where they appear as a singlet at δ 13.58. Upon further cooling, the expected AB multiplet pattern reemerges.

To verify that the aryl rings of the phosphine ligands are responsible for the dramatic temperature dependence of the

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(18) The −46.0-Hz $^1J_{NH}$ is a diagnostic coupling constant for an sp^2 hybridized nitrogen having an uncomplexed lone pair of electrons.[15,18a,b] The −65.0-Hz $^1J_{NH}$ is a typical value for an sp^2 hybridized nitrogen coordinated to a metal.[10,15,16,18c–f] (a) Binsch, G.; Lambert, J. B.; Roberts, B. W.; Roberts, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 5564. (b) Lambert, J. B.; Roberts, B. W.; Binsch, G.; Roberts, J. D. In *Nuclear Magnetic Resonance in Chemistry*; Pesce, B., Ed.; Academic: New York, 1965; p 269 ff. (c) Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 2713. (d) Haymore, B. L.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 5369. (e) Barrientos-Penna, C. F.; Einstein, F. W. B.; Jones, T.; Sutton, D. *Inorg. Chem.* **1983**, *22*, 2614. (f) Albertin, G.; Antoniutti, S.; Lanfranchi, M.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1986**, *25*, 950.

(19) For example, $^3J_{HH}$ = 28.0 Hz in {[$(CO)_5Cr]_2$(*trans*-$^{15}NH{=}^{15}NH$)}[19a] and 23.5 Hz in {[Cp$(CO)_2$Mn](*trans*-NH═NH)[Cr$(CO)_5$]}.[19b] (a) Rajpal, A.; Hillhouse, G. L. Unpublished results. (b) See ref 8f.

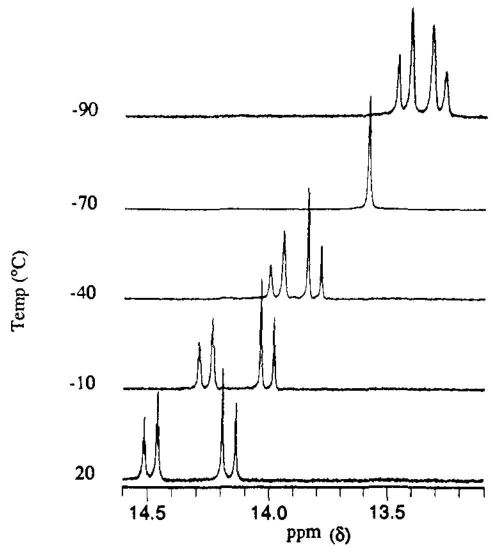


Figure 2. Variable-temperature ^1H NMR spectra (500 MHz, CD_2Cl_2 solution) of the NH protons of [*trans,trans*-W(NH=NH)$(CO)_2(NO)(PPh_3)_2^+$][$SO_3CF_3^-$] (**5a**).

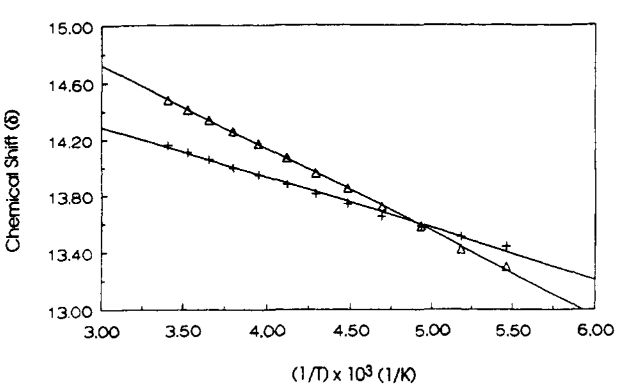


Figure 3. Plot of the chemical shifts of the NH protons of [*trans,trans*-W(NH_A=NH_B)$(CO)_2(NO)(PPh_3)_2^+$][$SO_3CF_3^-$] (**5a**) as a function of reciprocal absolute temperature. Cross marks (+) denote H_A data, and triangles (Δ) denote H_B data.

chemical shifts of the diazenyl protons of **5a**, the tricyclohexylphosphine analogue was prepared. A plot of the chemical shifts of the NH protons of the diazene ligand in **5b** as a function of reciprocal temperature is shown in Figure 4. In contrast to the case of **5a**, the protons of the diazene ligand in **5b** show no unusual temperature dependence, since the phenyl rings of the phosphine ligands of **5a** have been replaced with magnetically innocent cyclohexyl groups in **5b**.

The diazene ligand can be effectively displaced from **4a** by reaction of CH_2Cl_2 solutions of the complex with tetrabutylammonium bromide at 0 °C, as shown in Scheme II. While free NH=NH could not be spectroscopically detected (^1H NMR) at this temperature, we have characterized and quantified the products of its bimolecular disproportionation (N_2 and N_2H_4).[7] The expected amount of dinitrogen (0.50 equiv of N_2/**5a**) is quantitatively obtained as determined by a Toepler experiment. However, only 62% of the anticipated amount of hydrazine (0.31 equiv of N_2H_4/**5a**) was obtained, as determined by spectrophotometry.[12a,b] The lower yield of hydrazine can be explained by the fact that, in a control experiment, hydrazine and W(Br)$(CO)_2(NO)(PPh_3)_2$ were shown to slowly react to give an uncharacterized mixture. If the diazene displacement is carried out in the presence of excess diphenylacetylene (16 equiv), stilbene (*cis*/*trans* > 8:1) can be isolated in 12% yield (based on **5a**), analogous to the known reaction of alkynes with diazene generated by other methods.[1,4]

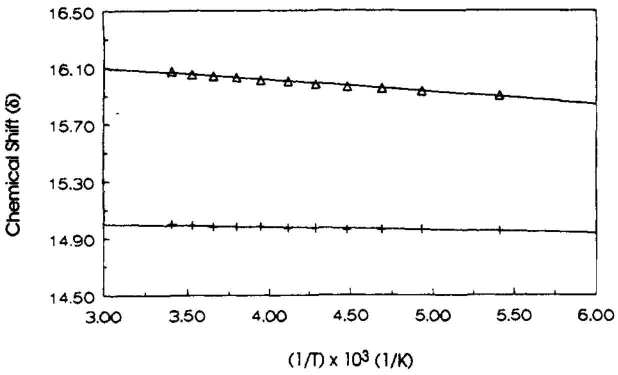
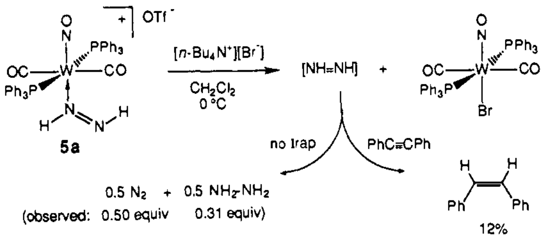


Figure 4. Plot of the chemical shifts of the NH protons of [*trans,trans*-W(NH_A=NH_B)$(CO)_2(NO)(PCy_3)_2^+$][$SO_3CF_3^-$] (**5b**) as a function of reciprocal absolute temperature. Cross marks (+) denote H_A data, and triangles (Δ) denote H_B data.

Scheme II



Conclusions

Diazene (NH=NH) can be stabilized by coordination via a single nitrogen lone pair to a sterically demanding d^6, pseudooctahedral tungsten fragment. Spectroscopic data strongly suggest that the diazene molecule is coordinated to W as *trans*-NH=NH. This is in contrast to previously known complexes of substituted diazenes (like NH=NMe and NH=NPh) in which the diazenes are bound with *cis*-NH=NR geometries. The NH=NH ligand can be cleanly displaced under mild conditions to give free NH=NH, which undergoes disproportionation to N_2 and N_2H_4. In the presence of excess diphenylacetylene, the free NH=NH can be trapped to give N_2 and *cis*-stilbene. We are presently exploring the reactivity of the NH=NH molecule while it is still bound to the metal center, since such reactions could have relevance to N_2-reduction processes.

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