Reactions of Coordinated Diazene in Rhenium and Tungsten Complexes. Deprotonation of Ligated NH=NH and Subsequent H-Migration to Carbonyl Ligands To Give Metal Formyls

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Received August 5, 1993[⊗]

Abstract: The tungsten diazene complex [*trans,trans*-$\mathrm{W(NH{=}NH)(CO)_2(NO)(PPh_3)_2^+}$][$\mathrm{SO_3CF_3^-}$] (**1**) reacts with $\mathrm{NH_2R}$ (R = H, $\mathrm{CH_3}$, $\mathrm{NH_2}$) to give *trans,trans*-$\mathrm{W(\eta^1\text{-}OSO_2CF_3)(CO)_2(NO)(PPh_3)_2}$ (**2**), *trans,trans*-$\mathrm{W(H)(CO)_2(NO)(PPh_3)_2}$ (**3**), and [*trans,trans*-$\mathrm{W(NH_2NH_2)(CO)_2(NO)(PPh_3)_2^+}$][$\mathrm{SO_3CF_3^-}$] (**4**). If the reaction of $\mathrm{NH_2R}$ with **1** is monitored at –78 °C, intermediates in the formation of **3** can be observed, which have been characterized as the neutral 6-coordinate formyl complexes *trans*-$\mathrm{W(CH{=}O)(CO)(NO)(NH_2R)(PPh_3)_2}$ (**5a**, R = H; **5b**, R = $\mathrm{CH_3}$; **5c**, R = $\mathrm{NH_2}$) on the basis of multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy and ^{2}H and ^{13}C labeling experiments. The noncoordinating Brønsted base $\mathrm{NaN(SiMe_3)_2}$ reacts with **1** to give **3** in 47% isolated yield, but because of the absence of a coordinating Lewis base, no formyl intermediate was observed. A reaction mechanism for the formation of hydride **3** is proposed involving (i) deprotonation of the diazene ligand in **1** by $\mathrm{NH_2R}$, (ii) H-migration from nitrogen to a carbonyl ligand to give the formyl complexes **5**, and (iii) H-migration from the formyl ligand to the metal to give the neutral hydride product **3**. The isoelectronic rhenium diazene complex [*trans,mer*-$\mathrm{Re(NH{=}NH)(CO)_3(PPh_3)_2^+}$][$\mathrm{SO_3CF_3^-}$] (**9**) has been prepared and shown to undergo a similar reaction with $\mathrm{NH_2CH_3}$ to give *trans,mer*-$\mathrm{Re(H)(CO)_3(PPh_3)_2}$ (**6**) in 80% yield.

Introduction

Several examples of diazene (NH=NH) coordination complexes have been reported and a few have been crystallographically characterized,[1–3] but we currently have a poor understanding of the reaction chemistry of the NH=NH ligand. This deficiency is significant in view of the importance of free diazene in organic chemistry (i.e., its use in stereoselective reductions),[4] as well as diazene's relevance as a ligand in inorganic and bioinorganic $\mathrm{N_2}$-reducing systems.[5,6]

We recently reported the preparation of a tungsten diazene complex cation in which the *trans*-NH=NH ligand is susceptible to nucleophilic displacement by bromide ion at 0 °C, as shown in Scheme 1).[3] At this temperature, NH=NH is unstable and undergoes rapid disporportionation to dinitrogen and hydrazine, thus attempts to detect free diazene (by ^{1}H NMR spectroscopy) in this displacement reaction were unsuccessful, although its decomposition products ($\mathrm{N_2}$, $\mathrm{N_2H_4}$) were observed in high yields.[7] Since it has been reported that diazene exhibits enhanced thermal stability in ammonia solution,[8] we attempted to carry out the diazene displacement from **1** in the presence of $\mathrm{NH_3}$. Interestingly, **1** was found to react rapidly with $\mathrm{NH_3}$ at low temperature (–78 °C) independent of added $\mathrm{Br^-}$. Herein we elaborate on this observation and describe the reactions of cationic diazene complexes of rhenium and tungsten with simple amines to yield, ultimately, the corresponding neutral metal hydrides, $\mathrm{H^+}$, and $\mathrm{N_2}$. The mechanism for this transformation is an interesting one!

Experimental Section

General Considerations. Reactions were carried out using standard high-vacuum and Schlenk techniques with dry, air-free solvents. ^{1}H NMR spectra were recorded at 500 MHz using the Chicago built 500-MHz spectrometer or a General Electric Ω-500 or Ω-300 spectrometer. The ^{1}H data listed do not include the resonances for the aryl protons of the $\mathrm{PPh_3}$ groups, which are observed as multiplets at δ 7.6–7.3. ^{31}P{^{1}H} NMR spectra were recorded using a General Electric Ω-500 (^{31}P = 202.4 MHz) or Ω-300 (^{31}P = 121.5 MHz) spectrometer and referenced to external 85% phosphoric acid (δ 0). ^{13}C{^{1}H} NMR spectra were recorded in $\mathrm{CDCl_3}$ or $\mathrm{CD_2Cl_2}$ using a GE Ω-300 spectrometer (^{13}C = 75.5 MHz) with chemical shifts referenced to the solvent carbons (δ 77.0 and δ 53.8,

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[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1993.

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(7) Monosubstituted diazenes are more thermally robust than NH=NH, and thus NH=NPh and NH=NMe can be observed in analogous displacement reactions with [$\mathrm{W(NH{=}NPh)(CO)_2(NO)(PPh_3)_2^+}$] and [$\mathrm{W(NH{=}NMe)(CO)_2(NO)(PPh_3)_2^+}$], respectively.[7a–c] (a) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1988**, *110*, 4066. (b) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1989**, *111*, 3764. (c) Smith, M. R., III; Keys, R. L.; Hillhouse, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8312.

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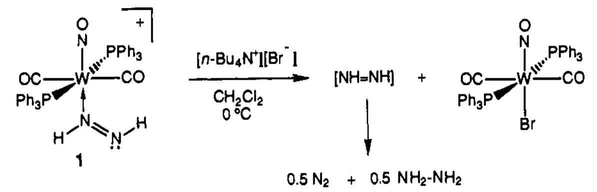
Scheme 1



respectively). Infrared spectra were recorded on a Nicolet 20SXB spectrometer in a Fluorolube-S30 mull with CaF_2 plates. Hydrazine (98%), trifluoromethanesulfonic acid, and lead tetraacetate were purchased from Aldrich Chemical Co. ^{13}CO (99.2% ^{13}C) was purchased from Matheson, and ND_3 (99% ^{2}H) was purchased from Cambridge Isotopes. [*trans,trans*-W(NH=NH)(CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (**1**),[3] *trans,trans*-W(η^1-OSO$_2$CF$_2$)(CO)$_2$(NO)(PPh$_3$)$_2$ (**2**),[3] and *trans,trans*-W(H)(CO)$_2$(NO)(PPh$_3$)$_2$ (**3**)[9] were prepared according to the literature procedures.

Preparation of [*trans,trans*-W(NH=NH)(^{13}CO)$_2$(NO)(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (1-[^{13}C]). A 0.50-g (0.53 mmol) sample of *trans,trans*-W(η^1-OSO$_2$CF$_3$)(CO)$_2$(NO)(PPh$_3$)$_2$ (**2**) was placed in a Fischer-Porter pressure bottle along with 20 mL of dry benzene and 38 psig of ^{13}CO. The vessel was heated to 60 °C and the contents were stirred for 1 h after which time the gas was vented and the solution was filtered in the air. The volume of the filtrate was reduced to about 5 mL, and then 10 mL of Et$_2$O and 5 mL of petroleum ether were added sequentially to complete the precipitation of the product. The mixture was filtered and the solids were washed with petroleum ether to give 0.40 g of **2**-[^{13}C]. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 24.5 (m, J_{PW} = 292 Hz, $^2J_{PC}$ = 5.8 Hz). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 209.48 (t, *C*O, J_{CW} = 137 Hz, $^2J_{CP}$ = 6.1 Hz). The ratio of W(^{13}CO)$_2$:W(^{13}CO)(^{12}CO):W(^{12}CO)$_2$ is 1:2:1 as determined from the ^{31}P{^{1}H} NMR spectrum (i.e., 50% ^{13}C incorporation, statistically distributed). Conversion of this material to the labeled diazene complex **1**-[^{13}C] (having the same ^{13}C isotopic ratios as given above for **2**-[^{13}C]) followed the literature procedure reported for the unlabeled derivative.[3] ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 209.67 (t, *C*O, J_{CW} = 139 Hz, $^2J_{CP}$ = 6.1 Hz).

Generation of *trans*-W(CH=O)(CO)(NO)(NH$_3$)(PPh$_3$)$_2$ (5a). A 0.025-g (0.026 mmol) sample of **1** and 0.4 mL of CD$_2$Cl$_2$ were placed in a 5-mm sealable NMR tube attached to a calibrated volume. The apparatus was placed on a vacuum line, the contents were cooled to −198 °C, and then 1.2 equiv of anhydrous NH$_3$ were condensed from the calibrated volume onto the frozen solution. The tube was sealed under vacuum, the contents were thawed and warmed to −78 °C, and then the tube was inserted into a precooled (−78 °C) spectrometer probe. The formyl species **5a** was generated (ca. 20% based on **1**) and observed to be stable at this temperature for at least 10 h; warming the solution to 0 °C resulted in conversion of **5a** to the hydride complex **3**, identified by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR (CD$_2$Cl$_2$, −78 °C): δ 15.05 (s, W-C*H*O, $^2J_{WH}$ = 14.5 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −78 °C): δ 33.7 (s, *P*Ph$_3$, $^1J_{PW}$ = 293 Hz). ***trans*-W(CH=O)(CO)(NO)(ND$_3$)(PPh$_3$)$_2$ (5a-[*d*$_3$])** was prepared in an analogous fashion except that an excess of ND$_3$ was used instead of NH$_3$. ^{1}H NMR (CD$_2$Cl$_2$, −78 °C): δ 15.06 (br, W-C*H*O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −30 °C): δ 33.7 (septet, $^1J_{PW}$ = 293 Hz, $^3J_{PD}$ = 3.7 Hz). ^{2}H NMR spectroscopy indicated no resonance in the formyl region. Warming the solution to 0 °C resulted in conversion of **5a**-[*d*$_3$] to the hydride complex **3**, with no ^{2}H incorporation in the hydride position. ***trans*-W(CH=O)(CO)(NO)(NH$_2$CH$_3$)(PPh$_3$)$_2$ (5b)** was prepared analogously to **5a** except that methylamine was used instead of ammonia. ^{1}H NMR (CD$_2$Cl$_2$, −78 °C): δ 15.15 (s, W-C*H*O, $^2J_{WH}$ = 14.5 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −78 °C): δ 33.1 (s, *P*Ph$_3$, $^1J_{PW}$ = 293 Hz). Warming the solution to 0 °C resulted in conversion of **5b** to the hydride complex **3**. ***trans*-W(^{13}CH=O)(^{13}CO)(NO)(NH$_2$CH$_3$)(PPh$_3$)$_2$ (5b-[^{13}C])** was prepared analogously to **5a** except that **1**-[^{13}C] was used instead of **1** (with methylamine). ^{1}H NMR (CD$_2$Cl$_2$, −78 °C): δ 15.15 (d, W-^{13}C*H*O, $^1J_{CH}$ = 118.4 Hz, $^2J_{WH}$ = 14.5 Hz). ^{13}C NMR (CD$_2$Cl$_2$, −30 °C): δ 308.6 (dm, W-*C*HO, $^1J_{CH}$ = 118.5 Hz, $^2J_{CC}$ = 10.6 Hz, $^2J_{CP}$ = 5.3 Hz), δ 238.1 (m, W-*C*O, $^2J_{CC}$ = 10.6 Hz, $^2J_{CP}$ = 5.3 Hz).

Generation of *trans*-W(CH=O)(CO)(NO)(NH$_2$NH$_2$)(PPh$_3$)$_2$ (5c). A 5-mm NMR tube with an open-faced screw cap equipped with a Teflon-backed septum was charged with 0.025 g (0.026 mmol) of **1** and 0.4 mL of CD$_2$Cl$_2$ under an inert atmosphere. The tube was immersed in a dry ice–ethanol bath (−78 °C) and then 1 μL (1.2 equiv) of N$_2$H$_4$ was added via a syringe. The sample was inserted into a precooled spectrometer probe (−78 °C). The formyl species **5c** was characterized by ^{1}H and ^{31}P NMR spectroscopy. ^{1}H NMR (CD$_2$Cl$_2$, −78 °C): δ 15.19 (br s, W-C*H*O). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, −78 °C): δ 33.3 (s, *P*Ph$_3$, J_{PW} = 293 Hz). Warming the solution to 0 °C resulted in conversion of **5c** to the hydride complex **3**.

Reaction of 1 with NaN(SiMe$_3$)$_2$. A 25-mL round-bottomed flask attached to a swivel frit assembly was charged with 0.100 g (0.103 mmol) of **1** and 0.021 g (0.114 mmol) of NaN(SiMe$_3$)$_2$. Upon addition of 5 mL of CH$_2$Cl$_2$ via vacuum transfer at −78 °C, gas evolution was observed. The solution was stirred for 5 min and then filtered. The volume of the filtrate was reduced to 2 mL and petroleum ether was added to precipitate the product. The solids were collected on the frit, washed with petroleum ether, and dried under vacuum to give 0.038 g (47% yield) of **3**.

Preparation of *trans,mer*-Re(H)(CO)$_3$(PPh$_3$)$_2$ (6). Compound **6** was prepared as a fine white powder in 91% yield by carbonylation of Re(H)(CO)$_2$(PPh$_3$)$_3$.[10] IR: ν(CO) 2017 (vw), 1925 (vs), 1913 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$, 20 °C): δ −5.08 (t, $^2J_{PH}$ = 18.3 Hz, Re*H*). ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ 22.82 (s).

Preparation of *trans,mer*-Re(η^1-OSO$_2$CF$_3$)(CO)$_3$(PPh$_3$)$_2$ (7). A 1.59-g (2.00 mmol) sample of **6** was placed in a round-bottomed flask and dissolved in 35 mL of CH$_2$Cl$_2$. Triflic acid (0.3 mL, 2.8 mmol) was added slowly via syringe, causing vigorous evolution of gas. The volume of the solution was reduced to 5 mL on a rotary evaporator, and then 70 mL of diethyl ether were added to precipitate the product. The solids were isolated by filtration and then washed sequentially with diethyl ether and petroleum ether to afford 1.77 g (94% yield) of white, microcrystalline **7**. Anal. Calcd for C$_{40}$H$_{30}$O$_6$SF$_3$P$_2$Re: C, 50.84; H, 3.20; N, 0.0. Found: C, 50.90; H, 3.02; N, 0.04. IR: ν(CO) 2071 (vw), 1952 (s), 1915 (s) cm^{-1}; ν(OSO$_2$CF$_3$) 1331 cm^{-1}. ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ 17.1 (s).

Preparation of [*trans,mer*-Re(NH$_2$NH$_2$)(CO)$_3$(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (8). A 0.50-g (0.62 mmol) sample of **2** was placed in a round-bottomed flask and dissolved in 10 mL of CH$_2$Cl$_2$. The vessel was flushed with nitrogen and then 51 μL (1.59 mmol) of 98% hydrazine were added slowly via syringe under N$_2$. The solution was allowed to stir for 30 min at room temperature and then concentrated to 3 mL on a rotary evaporator. Addition of 30 mL of diethyl ether caused a precipitate to form. The solid was collected on a frit and washed sequentially with diethyl ether and petroleum ether to afford 0.51 g (98% yield) of white, microcrystalline **8**. The complex decomposes slowly in air and can be conveniently recrystallized from CH$_2$Cl$_2$. Anal. Calcd for C$_{40}$H$_{34}$O$_6$N$_2$SF$_3$P$_2$Re: C, 49.18; H, 3.51; N, 2.87. Found: C, 48.73; H, 3.46; N, 2.91. IR: ν(CO) 2066 (w), 1968 (s), 1925 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$, 20 °C): δ 4.52 (br s, ReN*H*$_2$NH$_2$), 2.61 (br s, ReNH$_2$N*H*$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ 16.35 (s).

Preparation of [*trans,mer*-Re(NH=NH)(CO)$_3$(PPh$_3$)$_2$$^+$][SO$_3CF_3$$^-$] (9). A two-necked, round-bottomed flask attached to a swivel-frit assembly was charged with 0.100 g (0.10 mmol) of **8** and connected to a sidearm containing 0.050 g (0.11 mmol) of Pb(OAc)$_4$. The apparatus was placed on a vacuum line and 5 mL of CH$_2$Cl$_2$ were vacuum transferred into the flask at −78 °C. The lead tetraacetate was added to the solution in portions over a period of 10 min and the flask was warmed gradually, causing the reaction mixture to turn pink in color. When addition was complete and the evolution of gas had ceased, the heterogeneous mixture was rapidly filtered, the filtrate was concentrated to a volume of 1 mL, and the product was precipitated by addition of 15 mL of pentane via vacuum transfer at −78 °C. The mixture was allowed to stand at −78 °C for 30 min to complete precipitation of the product which was collected by filtration, washed with pentane (2 × 5 mL), and dried under vacuum to afford 0.058 g (58% yield) of **9** as a pale pink powder. IR: ν(CO) 2068 (w), 1952 (s), 1915 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 15.15 (d, ReN*H*=NH, $^3J_{HH}$ = 25.4 Hz), 14.65 (dt, ReNH=N*H*, $^3J_{HH}$ = 25.4 Hz, $^4J_{PH}$ = 2.4 Hz). ^{31}P{^{1}H} NMR (CDCl$_3$, 20 °C): δ 14.9 (s).

Reaction of 9 with NH$_2$CH$_3$. A 0.013-g (13.3 mmol) sample of **9** was placed in a sealable NMR tube attached to a calibrated volume. The system was evacuated, and then 0.5 mL of CD$_2$Cl$_2$ was condensed into the NMR tube at −198 °C, followed by 20.5 mmol of methylamine. The tube was thawed at −78 °C (the color of the solution changed immediately from pink to colorless at this temperature) and then placed into an NMR spectrometer prove precooled to −78 °C. No diazenyl or formyl protons were observed in the ^{1}H NMR spectrum. The temperature of the probe was gradually raised to 20 °C. Both ^{1}H and ^{31}P{^{1}H} NMR spectroscopy

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indicated that the major product (80%) which formed was the hydrido complex **6**. The product was crystallized from solution and its identity was confirmed to be **6** by its IR, ^{1}H NMR, and ^{31}P{^{1}H} NMR spectra.

Results and Discussion

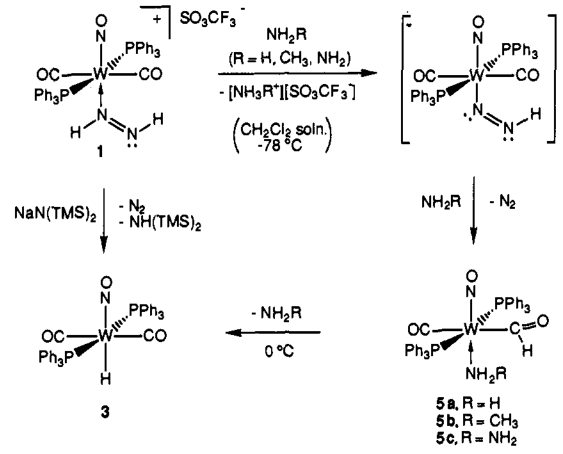
As we have noted, the unidentate diazene ligand in [*trans,trans*-$W(NH{=}NH)(CO)_2(NO)(PPh_3)_2{}^+$][$SO_3CF_3{}^-$] (**1**) is relatively labile and subject to a rapid and clean displacement by bromide at 0 °C (Scheme 1).[3] Even in the absence of bromide, **1** is thermally unstable in solution because the triflate counterion effects slow diazene displacement with formation of *trans,trans*-$W(\eta^1\text{-}OSO_2CF_3)(CO)_2(NO)(PPh_3)_2$ (**2**)[3] as the major metal-containing product, along with significant amounts of *trans,trans*-$W(H)(CO)_2(NO)(PPh_3)_2$ (**3**)[9] and [*trans,trans*-$W(NH_2NH_2)(CO)_2(NO)(PPh_3)_2{}^+$][$SO_3CF_3{}^-$] (**4**).[3] Control experiments demonstrate that hydrazine, formed by the disproportionation of free NH=NH displaced from **1** (by triflate), gives rise to **3** (**1** + N_2H_4 → **3**; *vide infra*) and **4** (**2** + N_2H_4 → **4**).

When the reactions of NH_2R (R = H, CH_3, NH_2) with **1** are monitored at −78 °C, intermediates in the formation of hydride **3** are observed. These intermediates have been characterized as the neutral 6-coordinate formyl complexes *trans*-$W(CH{=}O)(CO)(NO)(NH_2R)(PPh_3)_2$ (**5a**, R = H; **5b**, R = CH_3; **5c**, R = NH_2) on the basis of multinuclear (^{1}H, ^{13}C, ^{31}P) NMR spectroscopy and ^{2}H and ^{13}C labeling experiments. The amine (or hydrazine) acts first as a Brønsted base, and its initial role is to deprotonate the cationic diazene complexes to yield an (unobserved) coordinated N_2H intermediate that rapidly transfers its remaining hydrogen to a *cis*-carbonyl ligand (see Scheme 2). In the presence of excess NH_2R, the moderately stable formyl complexes **5** are formed by loss of N_2 and coordination of NH_2R (now acting as a Lewis base).

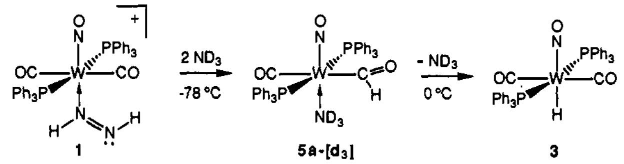
Since the diazenido intermediate in the transformation of **1** → **5** was not spectroscopically detected, the site of deprotonation (i.e., at the α- or β-position) cannot be unambiguously determined. However, since the α-proton is expected to be by far the more acidic of the two,[11] and since there is ample literature precedence for α-deprotonation of substituted diazene complexes (to give diazenido derivatives $L_nM{-}N{=}NR$),[1,12] we favor this alternative. As shown in Scheme 2, this would give rise to a "doubly-bent" diazenido ligand (M—N=NH) whose hydrogen is spatially positioned for intramolecular transfer to a *cis*-disposed carbonyl ligand. Stable complexes containing the N_2H ligand have been prepared in only one system. $WX(N_2H)(diphos)_2$ (X = F, Cl, Br; diphos = 1,2-bis(diphenylphosphino)ethane), possessing "singly-bent" diazenido ligands (M=N=NH), are formed by deprotonation of [$WX(NNH_2)(diphos)_2{}^+$][X^-] with NEt_3.[13]

In a typical reaction, treatment of **1** with excess NH_2CH_3 (−78 °C, CD_2Cl_2 solution) affords **5b** (~20%) which exhibits a characteristic resonance in its ^{1}H NMR spectrum at δ 15.15 (s, $^2J_{WH}$ = 14.5 Hz) for the formyl proton and a singlet resonance in its ^{31}P{^{1}H} NMR spectrum with W–P coupling typical of *trans*-disposed phosphines (δ 33.1, $^1J_{WP}$ = 293 Hz). The ^{13}C NMR spectrum of *trans*-$W(^{13}CH{=}O)(^{13}CO)(NO)(NH_2CH_3)(PPh_3)_2$ (**5b**-[^{13}C]) shows typical resonances for the formyl and carbonyl ligands at δ 308.6 ($^1J_{CH}$ = 118.5 Hz, $^2J_{CC}$ = 10.6 Hz, $^2J_{CP}$ = 5.3 Hz) and δ 238.1 ($^2J_{CC}$ = 10.6 Hz, $^2J_{CP}$ = 5.3 Hz), respectively. Treatment of **1** with ammonia-d_3 at −78 °C gives **5a**-[d_3] with no incorporation of deuterium in the formyl ligand (see Scheme 3), indicating that the source of the formyl proton is the diazene ligand.[14] Moreover, the ^{31}P{^{1}H} NMR spectrum of **5**-[d_3] is a septet with $^3J_{PD}$ = 3.7 Hz, demonstrating that the amine is coordinated to W. Further evidence that the position trans to the nitrosyl ligand in **5** is occupied by NH_2R is obtained by treatment of **1** with a 1:1 mixture of CH_3NH_2 and NH_3. ^{1}H and ^{31}P{^{1}H} NMR spectra clearly indicate that two different formyl complexes, **5a** and **5b**, are formed in this mixed-base experiment.

Scheme 2



Scheme 3



In CD_2Cl_2 solution at −78 °C, the complexes **5a–c** are stable and show no indication of decomposition when monitored over a 10-h period. However, on warming to 0 °C, **5a–c** cleanly convert to the hydrido complex **3**. Significantly, **5a**-[d_3] is exclusively converted to protio **3**, indicating the hydrido ligand is derived from the formyl ligand, probably via an intramolecular 1,2-H shift for which there is ample organometallic precedence (Scheme 3).[15]

Other proton-specific bases will effect the deprotonation of **1**, but unless a sterically unencumbered amine (like NH_3, NH_2CH_3, or N_2H_4) is present to coordinate to the metal to stabilize the formyl complexes, then only hydride **3** is observed (even at −78 °C). This is reasonable since such 16-electron formyl intermediates would be expected to have low activation barriers to α-H elimination. Thus, reaction of **1** with $NaN(SiMe_3)_2$ gives **3** in 47% isolated yield (Scheme 2).

The reaction of cationic diazene complexes with Brønsted bases to yield neutral hydrides, as described in Scheme 2, is not unique to the tungsten complex **1**. A rhenium diazene derivative has been prepared as summarized in Scheme 4. Reaction of *trans,mer*-$Re(H)(CO)_3(PPh_3)_2$ (**6**) with triflic acid gives *trans,mer*-$Re(\eta^1\text{-}OSO_2CF_3)(CO)_3(PPh_3)_2$ (**7**). Reaction of **7** with hydrazine yields [*trans,mer*-$Re(NH_2NH_2)(CO)_3(PPh_3)_2{}^+$][$SO_3CF_3{}^-$] (**8**), which in turn can be oxidized with $Pb(OAc)_4$ at −78 °C to give [*trans,mer*-$Re(NH{=}NH)(CO)_3(PPh_3)_2{}^-$][$SO_3CF_3{}^-$] (**9**). This protocol is analogous to that previously reported for the preparation of **1**.[3] Complex **9** is moderately thermally stable, but it undergoes rapid reaction with NH_2CH_3 (CD_2Cl_2 solution, −78 °C) to give the neutral hydride **6** in 80% yield (see Scheme 4). Unlike the isoelectronic tungsten system, no intermediates were

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(11) For comparisons of pK_a values of coordinated versus free amines, see: Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*, 2nd ed.; Wiley & Sons: New York, 1967.

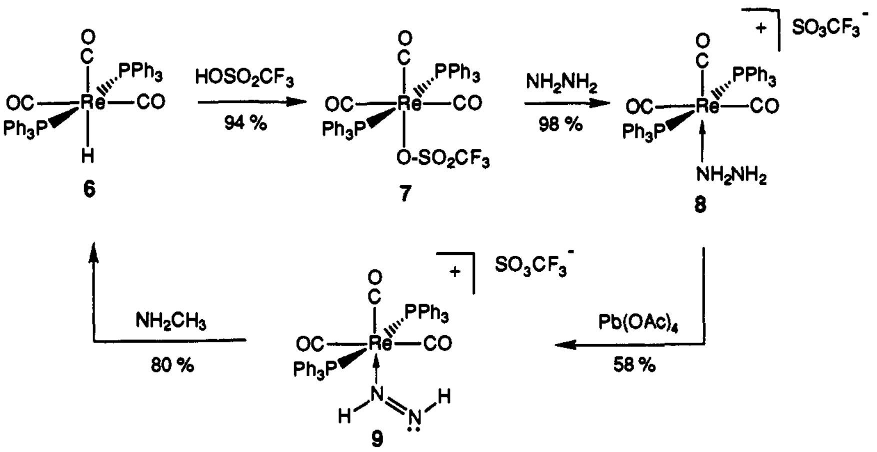
(12) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, pp 130–141.

(13) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1520.

(14) Intramolecular H-migrations between (i) formyl and carbonyl ligands and (ii) formyl and imido ligands in Tp′W(CO)(NPh)(CH=O) have been reported. Brookhart, M.; Luan, L.; Templeton, J. L. *Organometallics* **1992**, *11*, 1433.

(15) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1 (and references therein).

Scheme 4



detected in the 9 → 6 conversion. It seems reasonable to speculate, however, that a similar mechanistic pathway is operative in these two closely related systems.

In summary, diazene ligands in the isoelectronic cations [*trans,mer*-Re(NH=NH)(CO)$_3$(PPh$_3$)$_2^+$] and [*trans,trans*-W(NH=NH)(CO)$_2$(NO)(PPh$_3$)$_2^+$] react with amines to undergo deprotonation to give the corresponding neutral hydrido complexes and dinitrogen. The reaction mechanism for hydride formation in the tungsten system has been shown to involve (i) deprotonation of the diazene ligand (probably at the α-NH position) by NH$_2$R, (ii) H-migration from nitrogen to a carbonyl ligand to give N$_2$ and neutral formyl complexes that can be stabilized by NH$_2$R coordination, and (iii) H-migration from the formyl ligands to the metal to give the hydride *trans,trans*-W(H)(CO)$_2$(NO)(PPh$_3$)$_2$.

Acknowledgment. We are grateful to the National Institutes of Health (PHS GM-41650-01A1) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 21031-AC3), for financial support of this research. J.C.P. acknowledges receipt of a Richter Grant for Undergraduate Research.