S, 20.27. Found: C, 45.85; H, 3.72; S, 20.23.

$[C_5H_5Mo(S)SC_2H_5]_2$. A procedure analogous to that described above was followed. The solution was stirred at 60 °C for 48 h. The product was recrystallized from chloroform/hexane. Yield: 14%. Anal. Calcd: C, 33.08; H, 3.94; S, 25.23. Found: C, 32.81; H, 3.86; S, 25.02.

Reactions with Unsaturated Molecules. $[CH_3C_5H_4Mo(S)SH]_2$ (0.20 g, 0.4 mmol) was dissolved in 25 mL of $CHCl_3$ in a 60-mL reaction vessel, the solution was degassed in two freeze–pump–thaw cycles, and the unsaturated species was added (2 atm of $C{=}C$, 1 atm of $C{\equiv}C$, or 2 mL of $C_6H_5CH_2NC$). The solution was stirred at room temperature for 1–2 days. In the reaction with ethylene, vapors from the reaction vessel were sampled and analyzed by GC to identify hydrogen. The product molybdenum complexes were crystallized by partial evaporation of the solvent and characterized by NMR and elemental analyses. For $[CH_3C_5H_4MoSC_2H_4S]_2$ NMR ($CDCl_3$): δ 1.69 (s, 8, C_2H_4), 2.04 (s, 6, CH_3), 4.98 (s, 8, C_5H_4). Anal. Calcd: C, 35.96; H, 4.12; S, 23.97. Found: C, 36.02; H, 4.08; S, 23.78. For $[CH_3C_5H_4MoSC_2H_2S]_2$ NMR ($CDCl_3$): δ 2.06 (s, 6, CH_3), 5.82 (br s, 8, C_5H_4), 6.49 (s, 4, C_2H_2). Anal. Calcd: C, 36.23; H, 3.42; S, 24.18. Found: C, 36.43; H, 3.37; S, 24.30. For $[CH_3C_5H_4MoS_2CNCH_2C_6H_5]_2$ NMR ($CDCl_3$): δ 1.88 (s, 6, CH_3), 4.41 (s, 4, $-CH_2-$), 5.21 (br s, 8, C_5H_4), 7.28 (s, 10, C_6H_5). Anal. Calcd: C, 47.18; H, 3.97; S, 17.99. Found: C, 46.93; H, 3.90; S, 17.89. The reaction of $[(CH_3)_5C_5Mo(S)SH]_2$ with ethylene was carried out in dry THF in an analogous manner. NMR of $[(CH_3)_5C_5MoSC_2H_4S]_2$ ($CDCl_3$): δ 1.68 (s, 8, C_2H_4), 1.80 (s, 30, CH_3). Anal. Calcd: C, 44.57; H, 5.92; S, 19.83. Found: C, 44.53; H, 5.89; S, 19.76. Reactions of the unsubstituted cyclopentadienyl derivative were analogous. Products were identified by comparison of NMR spectra with those of known samples.[38,40]

H_2/D_2 Exchange. $[CH_3C_5H_4Mo(S)SH]_2$ (0.2 g) was dissolved in dry benzene (10 mL) in a 50-mL flask, and the solution was degassed in two freeze–pump–thaw cycles. Approximately 0.75 atm of H_2 and 0.25 atm of D_2 were added, and the solution was stirred at 25 °C for 3 days. Mass spectrum analysis showed that approximately 12% of the gas was HD. A blank with no complex present was run simultaneously. No HD was detected.

H_2/D_2O Exchange. $[CH_3C_5H_4Mo(S)SH]_2$ (0.17 g) was dissolved in 10 mL of THF and 2 mL of D_2O. The solution was degassed in two freeze–pump–thaw cycles, and 1 atm of H_2 was added at −196 °C. The solution was stirred at room temperature for 5 days. Mass spectrum analysis showed 37% H_2, 16% HD, and 47% D_2. The mass spectrum of the blank, run simultaneously, showed only H_2. The molybdenum complex was recovered by evaporation of the solvent and identified by NMR. The SH ligands were partially substituted by deuterium.

Catalytic Hydrogenation of Sulfur. Sublimed sulfur (1.2 g) and $[Me_nCpMo(S)SH]_2$ (0.03–0.05 g) were accurately weighed and were slurried in 50 mL of $CHCl_3$ in a 500-mL flask. The solution was degassed in freeze–pump–thaw cycles and 1 atm H_2 was added at −196 °C. The solution was stirred for 24 h at room temperature or in an oil bath. The solvent was evaporated, and the remaining solid was weighed to determine the amount of sulfur consumed. In some cases the product H_2S was distilled on a vacuum line and weighed.

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Supplementary Material Available: Table of observed and calculated structure amplitudes (4 pages). Ordering information is given on any current masthead page.

Protonation Reactions of Molybdenum and Tungsten Dinitrogen Complexes with Halogen Acids. Hydride Hydrazido(2−) and Diazenido Complexes as Intermediate Stages of Reduction[1]

Tamotsu Takahashi, Yasushi Mizobe, Maki Sato, Yasuzo Uchida, and Masanobu Hidai*

Contribution from the Department of Industrial Chemistry, University of Tokyo, Hongo, Tokyo 113, Japan. *Received February 12, 1980*

Abstract: Reactions of dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) with an excess of HCl in 1,2-dimethoxyethane give hydrazine in moderate yields. This stands in sharp contrast to the formation of ammonia on treatment with H_2SO_4 in methanol. The hydrazido(2−) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$, which is obtained from *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and HBr, reacts with 1 molar equiv of HCl to afford a hydride hydrazido(2−) complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$. The structure has been definitely determined by infrared and NMR spectra and X-ray analysis. Anion exchange with $NaBPh_4$ gives a novel diazenido complex $[WHClBr(\Leftarrow N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$ in a low yield, in addition to $[WHClBr(NNH_2)(PMe_2Ph)_3][BPh_4]$, whose molecular structure has been determined by X-ray analysis. A mechanism for reduction of coordinated dinitrogen is proposed on the basis of these results.

Several systems are now known with which the ligating dinitrogen in well-defined complexes is converted into ammonia and hydrazine under mild conditions.[2] However, the detailed mechanism for the reduction of dinitrogen in the above systems is not well understood. Its clarification may shed some light on the mechanism of nitrogen fixation in biological systems.

Recently we have briefly reported that hydrazine is formed in moderate yield on treatment of dinitrogen complexes $[M(N_2)_2(PMe_2Ph)_4]$ or hydrazido(2−) complexes $[MBr_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W) with HCl in 1,2-dimethoxyethane (DME).[3] This is in sharp contrast to the protonation reactions with H_2SO_4 in methanol, where ammonia is mainly produced.[4]

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[1] Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 13. For the previous paper (part 12) in this series, see: Mizobe, Y.; Uchida, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1781.

[2] Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589 and references therein.

[3] Hidai, M.; Mizobe, Y.; Takahashi, T.; Uchida, Y. *Chem. Lett.* **1978**, 1187.

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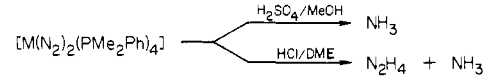
Table I. Yields of N_2H_4 and NH_3

complex	mmol	solvent	mL	acid	t/h	N_2H_4[a]	NH_3[a]
$[W(N_2)_2(PMe_2Ph)_4]$	0.318	DME	5	HCl	192	0.49	0.26
	0.261	MeOH	4	HCl	192	0.33	0.64
	0.191	DG	4	HCl	116	0.34	0.42
	0.194	THF	4	HCl	116	0.16	0.15
	0.196	DME	4	HBr	114	0.16	0.34
	0.197	DME	4	HI	116	0.26	0.92
	0.189[b]	MeOH	30	H_2SO_4	20	0.03	1.98
$[WCl_2(NNH_2)(PMe_2Ph)_3]$	0.188	DME	4	HCl	116	0.50	0.47
	0.192	DG	4	HCl	116	0.30	0.31
	0.207	THF	4	HCl	116	0.32	0.16
		MeOH[c]		H_2SO_4		0.12	1.26
$[WBr_2(NNH_2)(PMe_2Ph)_3]$	0.232	DME	4	HCl	214	0.50	0.65
	0.192	DG	4	HCl	116	0.45	0.26
	0.189	THF	4	HCl	116	0.34	0.29
		MeOH[c]		H_2SO_4		0.05	1.58
$[WHClBr(NNH_2)(PMe_2Ph)_3]Br$	0.186	DME	4	HCl	24	0.55	0.50
	0.169	DME	4	HBr	110	0.29	0.34
	0.155	MeOH	4	H_2SO_4[d]	24	0.34	0.63
	0.156	DME	4	H_2SO_4[d]	24	0.30	0.45
$[WHClBr(NNH_2)(PMe_2Ph)_3][BPh_4]$	0.113	DME	4	HCl	22	0.53	0.32
$[Mo(N_2)_2(PMe_2Ph)_4]$	0.172	DME	3	HCl	23	0.32	0.31
	0.258	DG	5	HCl	20	0.06	0.35
	0.265	THF	5	HCl	20	0.04	0.33
	0.213	DME	4	HBr	116	0.15	0.25
	0.214	DME	4	HI	116	0.01	0.53
	0.213[b]	MeOH	40	H_2SO_4	0.25	*e*	0.64
$[MoCl_2(NNH_2)(PMe_2Ph)_3]$	0.267	DME	5	HCl	24	0.52	0.24
$[MoBr_2(NNH_2)(PMe_2Ph)_3]$	0.256	DME	5	HCl	21	0.48	0.31
$[W(N_2)_2(dpe)_2]$	0.236	DME	5	HCl	20.5	tr	0.00
$[Mo(N_2)_2(dpe)_2]$	0.211	DME	5	HCl	21	0.00	tr

[a] Mole per M atom (M = W or Mo). [b] Reference 4. [c] Chatt, J.; Fakley, M. E.; Richards, R. L. *J. Organomet. Chem.* 1979, *170*, C6. [d] 12 mol/W atom. [e] Less than 0.005 mol/Mo atom.

In the course of our studies on these protonation reactions, a new complex was isolated as an intermediate stage of reduction from the reaction of $[WBr_2(NNH_2)(PMe_2Ph)_3]$ with 1 molar equiv of HCl in DME. In a previous communication,[5] the complex was tentatively formulated as a hydrazido(1−) complex $[WClBr(NHNH_2)(PMe_2Ph)_3]Br$. Very recently Chatt and his co-workers[6] also prepared similar tungsten complexes and concluded from the ^{15}N NMR spectra that the hydrogen atom is not bonded to the nitrogen atom adjacent to the metal. We have now obtained direct evidence from ^1H NMR spectra that the above complex is correctly formulated as a hydride hydrazido(2−) complex containing the $MH(NNH_2)$ group. Furthermore, a novel diazenido complex was derived from the hydride hydrazido(2−) complex, and its molecular structure has been determined by X-ray structural analysis. This paper is concerned with the protonation reactions of molybdenum and tungsten dinitrogen complexes with halogen acids, where the mechanism for reduction of dinitrogen will be discussed on the basis of structures and chemical properties of several intermediate complexes mentioned above.

Reactions of Dinitrogen Complexes with Halogen Acids. Reactions of dinitrogen complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) with halogen acids HX (X = Cl, Br, or I) were carried out in various kinds of solvents, and the yields of ammonia and hydrazine were determined by color tests as shown in Table I. The tungsten dinitrogen complex reacts more slowly with halogen acids compared with the molybdenum dinitrogen complex. It is of great interest to note that treatment of the molybdenum and tungsten dinitrogen complexes with an excess of HCl gas in DME yields hydrazine in moderate yields. In contrast, when the above dinitrogen complexes or *trans*-$[M(N_2)_2(PMePh_2)_4]$ (M = Mo or W) is treated with H_2SO_4 in methanol, ammonia is obtained in good yields, together with a little hydrazine for M = W and a trace for M = Mo, as already reported by Chatt and his co-workers.[4] They proposed a disproportionation step as in the equation $M{=}N\text{-}NH_2 \rightarrow M + {}^2/_3N_2 + {}^2/_3NH_3$ for M = Mo since the yield of ammonia is essentially 2 mol of ammonia/metal atom for M = W but only ca. 0.66 mol of ammonia/metal atom for M = Mo. Among halogen acids tested here, HCl is the best for converting the ligating dinitrogen into hydrazine. Use of HBr or HI decreases the yield of hydrazine, while the yield of ammonia is highest in the case of HI. When tetrahydrofuran, diglyme (DG), or methanol is used as solvent instead of DME, the yield of hydrazine is lower than that in DME.



The hydrazido(2−) complexes $[MCl_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W),[7] which are isolated from *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ and 3 molar equiv of HCl in DME, are treated with an excess of HCl to produce hydrazine and ammonia in similar yields to those obtained from the parent dinitrogen complexes. Moderate yields of hydrazine (0.52 mol of hydrazine/Mo atom) and ammonia (0.24 mol of ammonia/Mo atom) are given by reaction of $[MoCl_2(NNH_2)(PMe_2Ph)_3]$ with an excess of HCl in DME, although treatment of the above hydrazido(2−) complex with sulfuric acid in methanol yields only 0.67 mol of ammonia/Mo atom.[2] This finding is incompatible with the view of the disproportionation of the N_2H_2 ligand at the hydrazido(2−) stage of the reduction proposed by Chatt et al.[4] in the case of molybdenum (vide supra). The results presented here strongly suggest that the NNH_2 ligands in both molybdenum and tungsten complexes are, on treatment with halogen acids, further protonated essentially in a similar way to give hydrazine and ammonia.

Hydride Hydrazido(2−) Complexes. An orange-yellow crystalline complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$ is isolated in a good yield when the hydrazido(2−) complex $[WBr_2(NNH_2)$-

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(4) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852.

(5) Takahashi, T.; Mizobe, Y.; Sato, M.; Uchida, Y.; Hidai, M. *J. Am. Chem. Soc.* **1979**, *101*, 3405.

(6) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luong-Thi, N. T. *J. Organomet. Chem.* **1979**, *172*, C55.

(7) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1766.

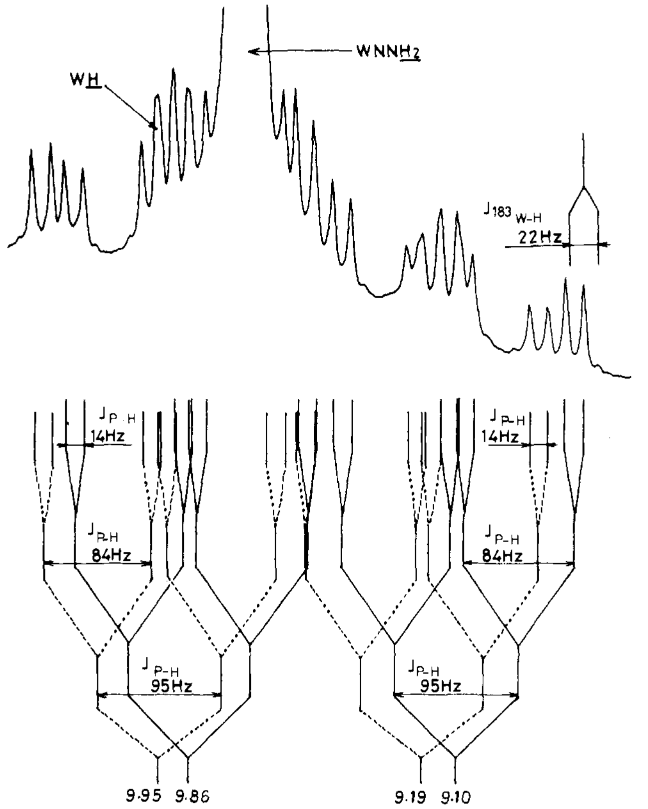


Figure 1. The 270-MHz ^1H NMR spectrum of $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$.

$(PMe_2Ph)_3]$ is treated with 1 molar equiv of HCl gas in DME at room temperature (see eq 1). The complex is characterized

$$[WBr_2(NNH_2)(PMe_2Ph)_3] + HCl \xrightarrow{DME} [WHClBr(NNH_2)(PMe_2Ph)_3]Br \quad (1)$$

by a strong band at 2820 cm^{-1} in the infrared spectrum assignable to ν(N–H), which shifts to 2100 cm^{-1} on treatment with D_2O, and a weak band at 1980 cm^{-1} assignable to ν(W–H). The X-ray analysis of the complex[5] revealed that the W–N–N linkage is essentially linear, indicating hydrogen atoms bonded to the terminal nitrogen, and there is a strong hydrogen-bonding interaction between the NNH_2 group and two bromide anions, one of which is in another complex. The shift of ν(N–H) to low frequency around 2820 cm^{-1} with a strong intensity is ascribed to this hydrogen bonding. The 270-MHz ^1H NMR spectrum exhibits a broad band at 9.70 ppm assigned to the $WNNH_2$ protons and a multiplet band assigned to the W–H proton, as given in Figure 1. Around the multiplet band, ^{183}W (14% relative abundance) spin-coupling satellites are clearly observed. The coupling constant of 22 Hz is in the lower range of those in the tungsten hydride complexes reported previously[8] but rather greater than those in the novel complexes $[(CO)_5WHX]$ (X = Cl, Br, or I) (6–9 Hz), where the proton is presumed to be bonded to the halogen.[9] This provides good evidence for the existence of a W–**H** bond in the complex. Furthermore, the complex slowly reacts with carbon tetrachloride at room temperature to give chloroform. Therefore, the complex is reasonably formulated as a hydride hydrazido(2–) complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$ rather than a hydrazido(1–) complex $[WClBr(NHNH_2)(PMe_2Ph)_3]Br$ proposed previously.[5] The complex multiplet band assigned to the W–H proton may be interpreted by assuming that the complex is a mixture of four kinds of hydride hydrazido(2–) complexes, whose

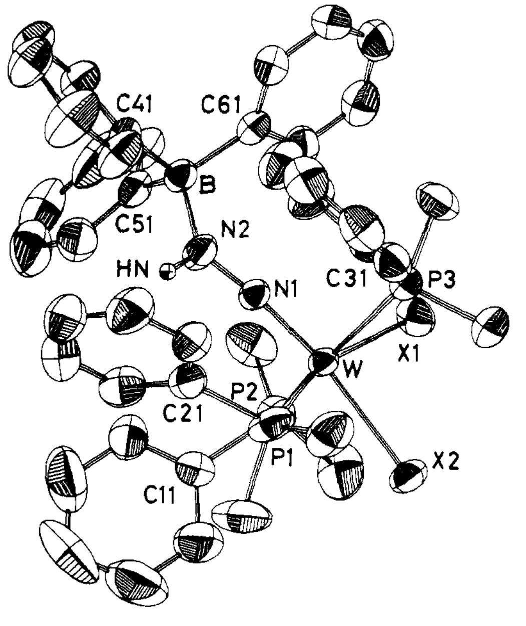
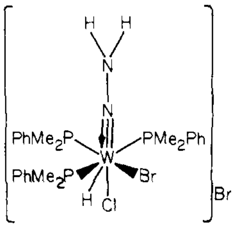


Figure 2. Perspective view of $[WHClBr(\overset{\leftarrow}{=}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

chemical shifts are given in Figure 1. The resonance of the W–H proton in the 100-MHz ^1H NMR spectrum is also consistent with this interpretation. Their structures are shown in I and II, where



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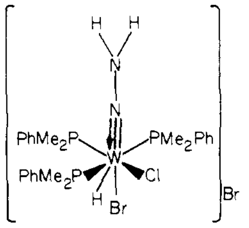
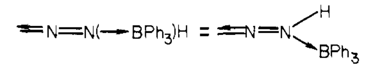


II

the hydridic proton may occupy two independent coordination sites, but the positions have not been definitely determined. The occupation of chloride and bromide anions at the two octahedral sites with the almost same probability is also supported by the X-ray structural analysis.[5]

Metathetical replacement of the bromide anion in the above complex with $NaBPh_4$ produces another hydride hydrazido(2–) complex, $[WHClBr(NNH_2)(PMe_2Ph)_3][BPh_4]$. The complex gives rise to three bands in the infrared spectrum at 3320, 3200, and 3105 cm^{-1} assigned to ν(N–H). The ^1H NMR spectrum shows resonances at 3.6 ppm assigned to the $WNNH_2$ protons and a multiplet band at 9.3 ppm assigned to the W–H proton similar to that in the original hydride hydrazido(2–) complex. The $WNNH_2$ resonance appears at relatively high field, and ν(N–H) frequencies are observed at relatively high wavenumbers with a weak intensity since an anion $[BPh_4]$ is not capable of strong hydrogen bonding in contrast to bromide anion.

Adduct of a Diazenido Complex with BPh_3. In the above anion-exchange reaction with $NaBPh_4$, a novel complex is isolated in a low yield in addition to a hydride hydrazido(2–) complex. Analytical data of a diazenido complex are consistent with the formula $[WHClBr(\overset{\leftarrow}{=}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]$ where



$$\overset{\leftarrow}{=}N{=}N(\rightarrow BPh_3)H \;=\; \overset{\leftarrow}{=}N{=}N\genfrac{}{}{0pt}{}{\diagup H}{\searrow BPh_3}$$

Its infrared spectrum shows a band at 3230 cm^{-1} assigned to ν(N–H), a weak band at 1950 cm^{-1} assigned to ν(W–H), and a strong band at 1385 cm^{-1} assigned to ν(B–N). The molecular structure of the complex determined from three-dimensional X-ray counter data is shown in Figures 2 and 3, which provides the first

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[8] Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231 and references therein.

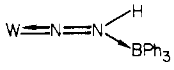
[9] Fischer, E. O.; Walz, S.; Kreis, G.; Kreissl, F. R. *Chem. Ber.* **1977**, *110*, 1651.

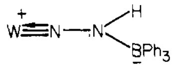
Table II. Positional and Thermal Parameters of Nonhydrogen Atoms of $[\mathrm{WHClBr}(\overset{\leftarrow}{=}\mathrm{N}{=}(\rightarrow \mathrm{BPh}_3)\mathrm{H})(\mathrm{PMe}_2\mathrm{Ph})_3]\cdot\mathrm{CH}_2\mathrm{Cl}_2$

atom	x^a	y	z	$B_{11}{}^b$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	3755 (0)	1423 (0)	2969 (0)	45 (0)	22 (0)	69 (0)	10 (0)	8 (0)	15 (0)
P(1)	4858 (2)	1962 (1)	1297 (2)	77 (2)	49 (1)	139 (3)	34 (1)	51 (2)	51 (1)
P(2)	4723 (2)	1903 (1)	5110 (2)	71 (2)	35 (1)	83 (2)	8 (1)	−6 (1)	20 (1)
P(3)	2302 (2)	567 (1)	1301 (2)	57 (1)	26 (1)	85 (2)	11 (1)	4 (1)	4 (1)
X(1)	2798 (1)	464 (1)	4190 (1)	75 (1)	35 (0)	97 (1)	4 (1)	8 (1)	30 (1)
X(2)	5223 (1)	509 (1)	2442 (1)	66 (1)	33 (0)	126 (1)	24 (0)	15 (1)	22 (0)
N(1)	2954 (4)	2159 (3)	3169 (5)	52 (4)	23 (2)	72 (5)	11 (2)	15 (3)	15 (2)
N(2)	2477 (5)	2742 (3)	3172 (6)	72 (5)	28 (2)	108 (7)	19 (3)	32 (5)	24 (3)
C(11)	4451 (6)	2846 (4)	1038 (7)	66 (6)	35 (3)	106 (8)	12 (3)	21 (5)	33 (4)
C(12)	3831 (7)	2816 (5)	−45 (9)	85 (7)	36 (3)	122 (9)	16 (4)	−1 (6)	20 (4)
C(13)	3561 (9)	3469 (6)	−317 (10)	121 (10)	57 (5)	143 (12)	35 (5)	−18 (8)	28 (6)
C(14)	3880 (9)	4150 (6)	445 (11)	124 (10)	42 (4)	176 (13)	24 (5)	0 (9)	42 (6)
C(15)	4477 (10)	4186 (6)	1559 (11)	121 (10)	36 (3)	167 (13)	7 (5)	0 (9)	7 (5)
C(16)	4754 (8)	3533 (6)	1837 (8)	89 (7)	52 (4)	99 (8)	18 (4)	−6 (6)	22 (5)
C(17)	6350 (8)	2257 (8)	1622 (13)	55 (7)	88 (7)	253 (18)	18 (5)	21 (9)	91 (9)
C(18)	4801 (9)	1341 (6)	−265 (10)	125 (10)	54 (4)	140 (11)	36 (5)	57 (9)	25 (6)
C(21)	5805 (6)	2754 (4)	5301 (7)	59 (5)	37 (3)	73 (6)	6 (3)	3 (5)	8 (3)
C(22)	6904 (9)	2704 (7)	5163 (13)	85 (8)	59 (5)	243 (18)	18 (5)	34 (10)	52 (8)
C(23)	7720 (11)	3348 (10)	5266 (19)	92 (11)	94 (9)	389 (32)	−4 (8)	27 (15)	98 (14)
C(24)	7454 (12)	4058 (9)	5514 (15)	150 (14)	83 (7)	224 (20)	−63 (9)	−16 (13)	39 (10)
C(25)	6368 (13)	4105 (7)	5638 (15)	208 (18)	40 (4)	246 (21)	−8 (7)	63 (16)	22 (8)
C(26)	5543 (6)	3462 (6)	5530 (13)	106 (9)	35 (3)	241 (18)	12 (5)	54 (10)	14 (6)
C(27)	3754 (8)	2183 (7)	6292 (9)	93 (8)	63 (5)	94 (9)	2 (5)	15 (7)	14 (5)
C(28)	5388 (11)	1222 (6)	5702 (11)	162 (12)	50 (4)	156 (13)	18 (6)	−71 (10)	37 (6)
C(31)	1844 (6)	983 (4)	32 (7)	45 (5)	30 (3)	96 (7)	3 (3)	6 (5)	−3 (3)
C(32)	2000 (7)	713 (5)	−1214 (8)	75 (6)	35 (3)	105 (8)	3 (3)	14 (6)	9 (4)
C(33)	1573 (8)	1045 (6)	−2125 (8)	105 (8)	50 (4)	89 (8)	−6 (4)	13 (6)	17 (5)
C(34)	1014 (9)	1639 (6)	−1802 (9)	117 (9)	48 (4)	114 (10)	5 (5)	−17 (7)	25 (5)
C(35)	865 (9)	1902 (6)	−597 (10)	130 (10)	49 (4)	129 (11)	33 (5)	−25 (8)	14 (5)
C(36)	1278 (8)	1581 (6)	336 (8)	109 (8)	50 (4)	87 (8)	34 (5)	−13 (6)	4 (4)
C(37)	954 (7)	252 (5)	1937 (9)	63 (6)	44 (3)	123 (9)	−5 (4)	7 (6)	6 (5)
C(38)	2685 (8)	−320 (5)	565 (9)	92 (7)	33 (3)	135 (10)	22 (4)	11 (7)	0 (4)
C(41)	946 (6)	3548 (4)	3064 (7)	63 (5)	25 (2)	88 (7)	10 (3)	3 (5)	10 (3)
C(42)	1235 (9)	3604 (5)	1857 (8)	135 (10)	48 (4)	95 (9)	44 (5)	35 (7)	23 (5)
C(43)	833 (11)	4109 (7)	1233 (9)	196 (14)	68 (5)	83 (8)	69 (7)	31 (9)	35 (5)
C(44)	123 (9)	4563 (6)	1786 (9)	138 (10)	47 (4)	115 (9)	40 (5)	3 (8)	34 (5)
C(45)	−172 (8)	4525 (5)	2980 (9)	99 (8)	41 (3)	135 (10)	31 (4)	8 (7)	19 (5)
C(46)	252 (7)	4039 (5)	3623 (8)	80 (6)	37 (3)	99 (8)	24 (3)	22 (6)	19 (4)
C(51)	1749 (6)	3439 (4)	5239 (7)	78 (6)	27 (2)	89 (7)	21 (3)	−5 (5)	6 (3)
C(52)	1133 (8)	3360 (5)	6314 (8)	117 (8)	42 (3)	85 (8)	40 (4)	6 (6)	14 (4)
C(53)	1430 (11)	3833 (7)	7450 (9)	201 (14)	62 (5)	82 (8)	76 (7)	−12 (9)	−1 (5)
C(54)	2351 (12)	4408 (6)	7576 (10)	208 (15)	48 (4)	134 (11)	56 (7)	−98 (11)	−21 (6)
C(55)	2974 (11)	4519 (6)	6555 (13)	163 (13)	41 (4)	210 (17)	15 (6)	−100 (13)	−16 (7)
C(56)	2693 (8)	4037 (5)	5427 (10)	99 (8)	38 (3)	156 (12)	12 (4)	−29 (8)	10 (5)
C(61)	429 (6)	2195 (4)	3853 (6)	63 (5)	27 (2)	73 (6)	17 (3)	11 (4)	8 (3)
C(62)	−567 (7)	2027 (4)	3132 (8)	80 (6)	28 (3)	113 (9)	12 (3)	5 (6)	10 (4)
C(63)	−1401 (7)	1397 (5)	3210 (9)	58 (6)	38 (3)	161 (12)	8 (3)	−4 (6)	5 (5)
C(64)	−1256 (7)	933 (5)	4029 (9)	83 (7)	32 (3)	134 (10)	4 (3)	29 (7)	13 (4)
C(65)	−267 (8)	1077 (5)	4721 (8)	108 (8)	35 (3)	89 (8)	16 (4)	21 (6)	18 (4)
C(66)	557 (7)	1686 (4)	4624 (4)	81 (6)	27 (2)	93 (7)	8 (3)	17 (5)	11 (3)
B	1375 (7)	2961 (4)	3849 (7)	58 (6)	26 (3)	80 (7)	13 (3)	22 (5)	15 (3)
Cl(1)	−1831 (6)	2574 (5)	−1582 (7)	281 (9)	157 (5)	405 (12)	109 (5)	53 (8)	92 (6)
Cl(2)	−3256 (6)	3650 (4)	−795 (7)	289 (8)	125 (4)	418 (12)	76 (4)	179 (8)	113 (5)
CCl	−1979 (20)	3509 (13)	−1186 (27)	246 (29)	109 (13)	514 (56)	−11 (15)	125 (33)	86 (22)

[a] The quantities given in the table are the positional coefficients × 10^4. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^4.

structural data of a diazenido complex. The atomic positions are shown in Tables II and III and selected bond distances and angles in Table IV. A difference-Fourier synthesis showed a clear peak of a hydrogen atom on the terminal nitrogen. The W–N–N linkage is essentially linear, while the angles N–N–H and N–N–B are 114 (7)° and 130.3 (6)°, respectively. The atoms W, N, N, B, and H lie nearly on the same plane. The N–N distance 1.30 (1) Å is shorter than those in hydrazido(2−) complexes, $[\mathrm{WCl(NNH_2)(dpe)_2}][\mathrm{BPh_4}]$ (1.37 Å)[10] and $[\mathrm{MoF(NNH_2)(dpe)_2}][\mathrm{BF_4}]$ (1.33 Å),[11] where dpe is $\mathrm{Ph_2PCH_2CH_2PPh_2}$, but longer than those in *trans*-diazene (1.23 Å)[12] and $\mathrm{N_2H_2[Cr(CO)_5]_2{\cdot}2THF}$ (1.25 Å).[13] The N–N distance in this complex indicates a bond order of approximately 1.6. This is interpreted in terms of a combination of two resonance structures described below, where the contribution of i is greater. Thus, the complex may be regarded as an adduct of a diazenido complex with a Lewis acid $\mathrm{BPh_3}$.


i


ii

Mechanism for Reduction of Dinitrogen. Treatment of the hydride hydrazido(2−) complex $[\mathrm{WHClBr(NNH_2)(PMe_2Ph)_3}]\mathrm{Br}$ with an excess of HCl in DME gives hydrazine and ammonia in

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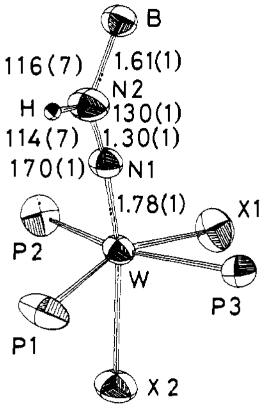


Figure 3. Perspective view of $[\mathrm{WHClBr}(\underline{\leftarrow}\mathrm{N{=}N}(\rightarrow\mathrm{BPh_3})\mathrm{H})(\mathrm{PMe_2Ph})_3]\cdot\mathrm{CH_2Cl_2}$. The shapes of the atoms in this drawing represent 50% probability contours of thermal motions.

Table III. Positional Parameters for the Hydrogen Atoms of $[\mathrm{WHClBr}(\underline{\leftarrow}\mathrm{N{=}N}(\rightarrow\mathrm{BPh_3})\mathrm{H})(\mathrm{PMe_2Ph})_3]\cdot\mathrm{CH_2Cl_2}$

atom	x^a	y	z
HN	286 (9)	308 (6)	276 (9)
H(12)	353 (8)	226 (5)	−62 (8)
H(13)	318 (8)	341 (5)	−125 (8)
H(14)	391 (10)	477 (7)	25 (11)
H(15)	472 (9)	465 (6)	204 (9)
H(16)	516 (9)	355 (6)	263 (10)
H(22)	710 (10)	221 (7)	482 (11)
H(23)	872 (10)	352 (7)	538 (11)
H(24)	811 (10)	452 (7)	573 (11)
H(25)	618 (10)	458 (7)	574 (11)
H(26)	504 (10)	352 (7)	597 (11)
H(32)	247 (8)	33 (6)	−157 (9)
H(33)	185 (9)	76 (6)	−298 (10)
H(34)	69 (8)	183 (6)	−257 (9)
H(35)	52 (10)	246 (7)	−18 (11)
H(36)	113 (7)	175 (5)	117 (8)
H(42)	165 (8)	326 (6)	135 (9)
H(43)	101 (9)	404 (6)	32 (10)
H(44)	−20 (10)	494 (7)	119 (11)
H(45)	−54 (9)	495 (6)	356 (10)
H(46)	6 (7)	401 (5)	451 (8)
H(52)	40 (7)	297 (5)	631 (8)
H(53)	112 (10)	408 (7)	829 (11)
H(54)	281 (9)	481 (6)	798 (9)
H(55)	356 (8)	500 (5)	658 (9)
H(56)	299 (8)	416 (6)	466 (9)
H(62)	−69 (8)	240 (5)	259 (8)
H(63)	−218 (8)	124 (5)	264 (8)
H(64)	−183 (10)	53 (6)	403 (10)
H(65)	−8 (9)	69 (6)	524 (9)
H(66)	118 (8)	176 (6)	510 (9)
HC(11)	−174 (10)	375 (7)	−199 (11)
HC(12)	−159 (10)	370 (7)	−28 (11)
H(171)	655 (7)	277 (5)	240 (8)
H(172)	671 (10)	250 (7)	84 (11)
H(173)	668 (10)	180 (7)	189 (11)
H(181)	379 (9)	120 (6)	−78 (10)
H(182)	508 (10)	72 (6)	−5 (10)
H(183)	538 (9)	169 (6)	−76 (9)
H(271)	413 (10)	227 (7)	700 (11)
H(272)	323 (9)	175 (6)	636 (9)
H(273)	337 (10)	253 (7)	596 (11)
H(281)	611 (9)	112 (6)	544 (10)
H(282)	573 (10)	146 (7)	662 (11)
H(283)	517 (10)	109 (7)	647 (11)
H(371)	59 (8)	2 (6)	111 (9)
H(372)	52 (10)	58 (6)	206 (10)
H(373)	63 (10)	−28 (7)	182 (11)
H(381)	337 (10)	−18 (7)	15 (11)
H(382)	196 (9)	−66 (6)	5 (9)
H(383)	288 (8)	−57 (5)	136 (9)

[a] The quantities given in the table are the positional coefficients $\times 10^3$.

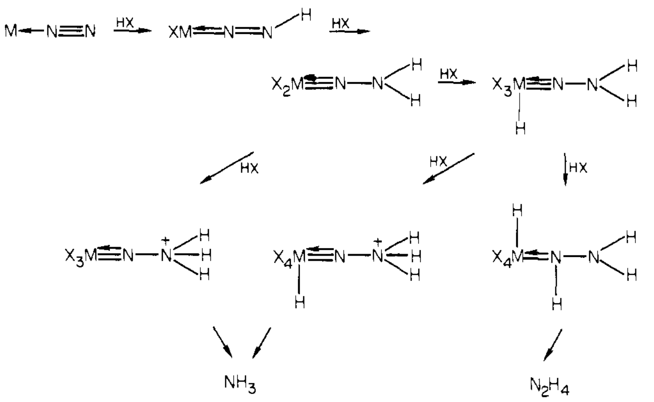
Table IV. Selected Bond Distances (Å) and Angles (Deg) of $[\mathrm{WHClBr}(\underline{\leftarrow}\mathrm{N{=}N}(\rightarrow\mathrm{BPh_3})\mathrm{H})(\mathrm{PMe_2Ph})_3]\cdot\mathrm{CH_2Cl_2}$

atoms	distances	atoms	angles
W-N(1)	1.781 (5)	W-N(1)-N(2)	170.01 (50)
W-P(1)	2.536 (3)	P(1)-W-P(2)	112.65 (8)
W-P(2)	2.551 (2)	P(1)-W-P(3)	90.19 (7)
W-P(3)	2.603 (2)	P(1)-W-X(2)	77.32 (6)
W-X(1)	2.533 (1)	P(1)-W-N(1)	91.79 (18)
W-X(2)	2.655 (1)	P(2)-W-X(1)	77.29 (6)
N(1)-N(2)	1.302 (9)	P(2)-W-X(2)	88.66 (5)
P(1)-C(11)	1.841 (8)	P(2)-W-N(1)	92.60 (18)
P(1)-C(17)	1.807 (15)	P(3)-W-X(1)	79.50 (5)
P(1)-C(18)	1.881 (11)	P(3)-W-X(2)	92.04 (5)
P(2)-C(21)	1.820 (8)	P(3)-W-N(1)	91.26 (18)
P(2)-C(27)	1.832 (12)	X(1)-W-X(2)	85.94 (4)
P(2)-C(28)	1.808 (13)	X(1)-W-N(1)	105.38 (18)
P(3)-C(31)	1.842 (8)	N(1)-N(2)-B	130.25 (61)
P(3)-C(37)	1.825 (10)	N(1)-N(2)-HN	114.0 (71)
P(3)-C(38)	1.811 (10)	B-N(2)-HN	115.6 (71)
N(2)-B	1.614 (10)		
C(41)-B	1.650 (11)		
C(51)-B	1.626 (11)		
C(61)-B	1.640 (11)		
C-C- (phenyl)	av 1.385 (19)		

similar yields to those obtained from the hydrazido(2−) complex $[\mathrm{WBr_2(NNH_2)(PMe_2Ph)_3}]$ as shown in Table I. It is of great interest to recognize that hydrazine is produced in moderate yield on treatment of the above hydride hydrazido(2−) complex with $\mathrm{H_2SO_4}$ in methanol, although ammonia is almost exclusively formed in a similar reaction with the hydrazido(2−) complex $[\mathrm{WBr_2(NNH_2)(PMe_2Ph)_3}]$. This indicates that the $\mathrm{MH(NNH_2)}$ stage of reduction is on the route to hydrazine.

On the basis of these results, routes to ammonia and hydrazine starting from ligating dinitrogen are proposed as given in the scheme, which are remarkably affected by the sort of acids, metals, ligands, and solvents. Chatt et al. previously proposed a mechanism for the formation of ammonia via an intermediate containing the $\mathrm{M{=}N{-}N^+H_3}$ group.[2] The proton attack to dinitrogen complexes $[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$ (M = Mo or W) first occurs on the terminal nitrogen to give diazenido complexes. Preparation and structure of a diazenido complex stabilized by formation of an adduct with $\mathrm{BPh_3}$ have been described above. The second proton attack takes place on the terminal nitrogen to afford hydrazido(2−) complexes. Many complexes of this type have been prepared from dinitrogen complexes $[\mathrm{M(N_2)_2(PMe_2Ph)_4}]$ and *trans*-$[\mathrm{M(N_2)_2(dpe)_2}]$ (M = Mo or W).[2,7,11] The next proton attack is, on treatment with the HCl/DME system, mainly directed not to the nitrogen adjacent to the metal but to the metal, giving hydride hydrazido(2−) complexes (vide supra). The hydrazido(2−) complexes containing $\mathrm{HSO_4}$ anion derived from dinitrogen complexes and $\mathrm{H_2SO_4}$ in methanol may be further protonated by $\mathrm{H_2SO_4}$ to give the $\mathrm{MNN^+H_3}$ complexes, which leads finally to formation of ammonia. Alternatively, the hydrazido(2−) complexes may decompose in methanol to produce ammonia (see Scheme I). Recently, Chatt et al. have found that the hydrazido(2−) complex $[\mathrm{W(NNH_2)(PMe_2Ph)_3(HSO_4)_2}]$ degrades in methanol to give ammonia (95%) and hydrazine (5%) quantitatively.[16] Anions of acids coordinated to the metal would determine the most electron-rich position in the $\mathrm{M{=}N{-}NH_2}$ or $\mathrm{HM{=}N{-}NH_2}$ moiety, and ammonia and hydrazine may be formed according to the routes shown in the scheme. Good yields of ammonia with X = $\mathrm{HSO_4}$ and I (vide supra) probably lie in their effectiveness as a π-electron donor to the metal which makes the terminal nitrogen attacked by proton. On the other hand, chloride is more effective as an electron acceptor which results in an electron flow of the lone pair on the terminal nitrogen to the metal. This may cause the proton attack on the metal, yielding hydrazine as a main product. This electronic nature of halide ions is reflected in the variation in the N-H resonances of hydrazido(2−) complexes $[\mathrm{MoX[N_2H(CH_2COOCH_2CH_3)](dpe)_2][BF_4]}$ (X = Cl, 6.10 ppm; X = Br, 5.98 ppm; X = I, 5.35 ppm).[14] Furthermore, it

Scheme I



may be reasonable to consider that hydrogen-bonding interactions between $MNNH_2$ and anions of acids (vide supra)[7,11] or solvents also play an important role in determining the reaction courses in the scheme.

The nitrogen atom which is not involved in the formation of nitrogen hydrides either escapes as N_2 gas or remains in the residue after extraction with water. The quantitative determination of the N_2 gas was impossible when an excess of HCl gas was bubbled in, because it was allowed to escape from the system with unreacted HCl. The amount of the N_2 gas was, therefore, measured in the model reactions, in which the dinitrogen complex $[W(N_2)_2(PMe_2Ph)_4]$ or its derivatives were treated with 100 mol of HCl/metal atom in a closed Schlenk tube. The model reactions proceed much more slowly compared with the reactions with a large amount of HCl gas bubbled. The dinitrogen complex in DME liberates 1.03 mol of N_2/metal atom, with the formation of ammonia (0.18 mol) and hydrazine (0.08 mol) after 10 days at room temperature. The hydrazido(2−) complex $[WBr_2(NNH_2)(PMe_2Ph)_3]$ in DME gives hydrazine (0.13 mol of hydrazine/metal atom) and ammonia (0.28 mol) accompanied by evolution of N_2 gas (0.02 mol) after 9 days. A small amount of N_2 gas (0.01 mol) is also evolved in the case of the hydride hydrazido(2−) complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$, together with the formation of hydrazine (0.07 mol) and ammonia (0.14 mol) after 24 h. On the other hand, the elemental analyses of the residues after extraction with water show the presence of nitrogen in them, when an excess of HCl is bubbled in.

The initial step of the reactions of $[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) with acids is the proton attack on the terminal nitrogen which causes electron withdrawal from the metal and results in the liberation of the second dinitrogen ligand. A disproportionation reaction of hydrazido(2−) complexes[4] as in the equation $M{=}N{-}NH_2 \rightarrow M + {}^2/_3N_2 + {}^2/_3NH_3$ might explain the evolution of N_2 gas from hydrazido(2−) complexes. On the other hand, the hydride hydrazido(2−) complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$ decomposes in Me_2SO, evolving 1 mol of N_2/metal atom without any formation of H_2 or nitrogen hydrides. In the NMR spectrum of the solution, the band assigned to the $WNNH_2$ protons and the multiplet band assigned to the W–H proton disappear and a new singlet band at 11.0 ppm appear with intensity 3 H, which disappears immediately on addition of D_2O. This indicates the presence of a different pathway of decomposition of hydrazido(2−) complexes to evolve N_2 gas. Unfortunately any pure compound could not be isolated from the above solution. Future work will shed more light on this decomposition.

Experimental Section

All manipulations were carried out under dry dinitrogen by using standard Schlenk tube techniques. Infrared spectra were determined with a Hitachi 215 double-beam spectrometer and ^1H NMR spectra with JEOL PS-100 and Bruker WH-270 spectrometers. The complexes *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) were prepared by published methods.[15]

Reaction of *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ or $[MX_2(NNH_2)(PMe_2Ph)_3]$ (M = Mo or W, X = Cl or Br) with an Excess of HX (X = Cl, Br, or I). Dry HX gas (ca. 700 mL) was bubbled through a suspension of a complex (ca. 150 mg) in a solvent (3–5 mL) such as DME, THF, DG, or MeOH for 5 min at ambient temperature. After the mixture was stirred for the times given in Table I, the color turned into green (X = Cl), brown (X = Br), or red (X = I) for W and pink (X = Cl), dark brown (X = Br), or brown (X = I) for Mo. In the case of W, the formation of white solid was observed. The reaction mixture was then concentrated to a minimum volume by evaporation in vacuo, and the residue was extracted with water. Potassium hydroxide solution (40 wt %) was added to the extractive, and the mixture distilled into dilute H_2SO_4 (1 N) which was diluted to a known volume with distilled water. Ammonia and hydrazine were quantitatively analyzed by using indophenol[17] and *p*-(dimethylamino)benzaldehyde[18] reagents, respectively. The residue after extraction with water was found to contain nitrogen by its elemental analysis. For example, the residue (38 mg) obtained from $[WBr_2(NNH_2)(PMe_2Ph)_3]$ and HCl gas contained 1.3% of nitrogen.

When the reaction was carried out in a closed Schlenk tube, the gas evolved was measured by means of a Toepler pump and analyzed by gas chromatography (SHIMADZU GC4A, column, Molucular Sieve 13X).

Preparation of $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$. One molar equivalent of HCl gas (3.4 mmol) was condensed on to a suspension of $[WBr_2(NNH_2)(PMe_2Ph)_3]$ (2.69 g, 3.4 mmol) in DME (10 mL) at liquid-nitrogen temperature. The orange-yellow solid obtained was filtered off, washed with ether, and dried in vacuo. Then it was crystallized as orange-yellow needles from CH_2Cl_2–hexane; yield 2.26 g (80.3%). Anal. Calcd for $C_{24}H_{36}N_2Br_2ClP_3W$: C, 34.96; H, 4.40; N, 3.40; Br, 19.38; Cl, 4.30. Found: C, 35.16; H, 4.88; N, 3.48; Br, 18.81; Cl, 4.10.

Preparation of $[WHClBr(NNH_2)(PMe_2Ph)_3][BPh_4]$. To the complex $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$ (0.804 g, 0.97 mmol) dissolved in CH_2Cl_2–THF (5 mL–5 mL) was added $NaBPh_4$ (1.33 g, 3.9 mmol) in CH_2Cl_2–THF (5 mL–5 mL). The greenish yellow mixture was stirred for 2 h at room temperature and taken to dryness, and the residue was extracted with CH_2Cl_2 (5 mL). The extractive was dried in vacuo again, and the residue was dissolved in THF (3 mL). Ether was then added to the solution drop by drop with stirring till turbidity was observed. On standing at 5 °C for 10 h, a mixture of a white solid and orange crystals (vide post) was deposited. The white solid was then extracted with a small amount of THF (2 mL) from the mixture because it dissolved much easier than the orange crystals. Addition of ether to the extractive gives a pure white solid; yield 0.602 g (58.1%). Anal. Calcd for $C_{48}H_{56}N_2BrClBP_3W$: C, 54.19; H, 5.31; N, 2.63; Br, 7.51; Cl, 3.33. Found: C, 54.36; H, 5.80; N, 2.86; Br, 7.53; Cl, 3.34.

Preparation of $[WHClBr(\underline{\leftarrow}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]$. The complex $[WHClBr(\underline{\leftarrow}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]$ was obtained as orange crystals together with the white solid $[WHClBr(NNH_2)(PMe_2Ph)_3][BPh_4]$ in the reaction of $[WHClBr(NNH_2)(PMe_2Ph)_3]Br$ with $NaBPh_4$ which was already described above. The orange crystals which remained after the extraction of the mixture with THF were collected and washed with ether and then dried in vacuo; yield 0.110 g (11.4%). Anal. Calcd for $C_{42}H_{50}N_2BrClBP_3W$: C, 51.17; H, 5.11; N, 2.84. Found: C, 51.49; H, 5.50; N, 2.87. Recrystallization from CH_2Cl–hexane afforded the complex as CH_2Cl_2 solvate $[WHClBr(\leftarrow N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]CH_2Cl_2$. Anal. Calcd for $C_{42}H_{52}N_2BrCl_3BP_3W$: C, 48.24; H, 4.89; N, 2.62. Found: C, 48.54; H, 5.00; N, 3.41.

Reaction of $[WHClBr(NNH_2)(PMe_2Ph)_3]X$ (X = Br or BPh_4) with an Excess of HCl or HBr Gas. Dry HCl or HBr gas (ca. 700 mL) was bubbled into a suspension of the complex (ca. 160 mg) in the solvent (4 mL). The reaction mixture obtained was similar to the case of bis(dinitrogen) or hydrazido(2−) complexes mentioned above. Quantitative analysis of ammonia and hydrazine was performed according to the same procedure.

Crystal Data of the Diazenido Complex $[WHClBr(\underline{\leftarrow}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]CH_2Cl_2$. A crystal was sealed in a Pyrex capillary under nitrogen. The crystal was a thick plate with the approximate dimensions 0.23 × 0.31 × 0.33 mm. Weissenberg photographs indicated that the crystal belongs to the triclinic system characteristic of the centrosymmetric space group $P\bar{1}$ or noncentric space group $P1$. The centrosymmetric space group was shown to be the correct one on the basis of the following results: (a) acceptable positional parameters, thermal

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Table V. Crystallographic Data and Intensity Collections of $[WHClBr(\overset{\leftarrow}{-}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$

a, Å	12.095 (5)
b, Å	18.148 (8)
c, Å	10.975 (5)
α, deg	101.03 (1)
β, deg	90.59 (1)
γ, deg	100.52 (1)
V, $Å^3$	2322.2 (18)
Z	2
d(calcd), g cm^{-3}	1.507
d(found), g cm^{-3}	1.497
systematic absences	none
space group	$P\bar{1}$
F(000)	1068
cryst dimens, mm	0.23 × 0.31 × 0.33
μ, cm^{-1}	37.9
scan	2θ-ω
2θ limits, deg	$0° < 2\theta < 50°$

parameters, and agreement indexes in successful refinements; (b) the clear and distinct location of 51 unique hydrogen atoms in a difference Fourier synthesis. The unit cell dimensions were obtained by least-squares refinement of 12 high-angle reflections in diverse regions of reciprocal space. The pertinent crystal information and details of data are shown in Table V. With $Z = 2$ and the molecular weight of this complex, the calculated density is 1.507 g cm^{-3} compared with a measured density of 1.497 g cm^{-3} obtained by flotation in a $ZnCl_2$ aqueous solution.

Data collection was carried out by using a Rigaku four-circle diffractometer. Background counts were measured in both ends of the scan range with both the counter and crystal stationary. The intensities of four standard reflections were measured every 50 reflections and were found to decrease uniformly and linearly about 4% during the course of data collection. The observed intensities were modified to correct for this apparent isotropic crystal decomposition.

All possible reflections with $2\theta \geq 50°$ were collected by using Mo Kα radiation (0.7107 Å) monochromatized by graphite. Of the 8667 reflections collected, 6895 reflections had $F_o > 3\sigma(F_o)$, were considered observed, and were used in subsequent calculations. Lorentz and polarization corrections were applied.

Solution and Refinement of the Structure.[19] The structure was solved using a Patterson synthesis to locate the tungsten atom. Subsequent refinements and difference Fourier syntheses were used to locate the remaining atoms, including 51 hydrogen atoms. The structure was refined by using block-diagonal least-squares techniques. The isotropic model converged to *R* indexes of $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.094$ and $R_w = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2} = 0.111$. During the refinements, the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and the weights, *w*, are taken as $w = 1$ for $|F_o| > 30$. Atomic scattering factors were taken from Cromer and Waber's tabulation.[20a] The anomalous dispersion terms for W, P, Br, and Cl were included in Fc.[20b]

The position indicated by X1 was shown to be occupied by Cl (70%) and Br (30%), and the position X(2) by Cl (30%) and Br (70%), respectively, on the basis of the following results: (a) the distinction of X(1) and X(2) from Br or Cl in a difference Fourier synthesis; (b) the minimized *R* index in this ratio of Cl and Br in refinements. At this stage, the structure was refined by block-diagonal least-squares by using anisotropic thermal factors for nonhydrogen atoms. A difference Fourier synthesis was computed to reveal clear peaks of hydrogen atoms. The final cycle was then carried out including the positional parameters of the above hydrogen atoms, the isotropic temperature parameters of which were fixed at 6.0 $Å^2$. The final refinement resulted in final values of 0.044 and 0.059 for *R* and R_w, respectively.

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Supplementary Material Available: A listing of structure factor amplitudes of $[WHClBr(\overset{\leftarrow}{-}N{=}N(\rightarrow BPh_3)H)(PMe_2Ph)_3]\cdot CH_2Cl_2$ (31 pages). Ordering information is given on any current masthead page.

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(19) The UNICS program for the HITAC 8700/8800 computers was employed at Tokyo University Computer Center: Sakurai's RSLC-3 lattice constants program, Ueda's PAMI Patterson and minimum function program, Iwasaki's ANSFR-2 Fourier synthesis program, Ashida's HBLS-4 block-diagonal least-squares and Fourier program, Ashida's DAPH distance, angle, etc. program, and modified Johnson's ORTEP thermal ellipsoid plot program.

(20) (a) Cromer, D. T.; Waber, J. T. "International Tables for x-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2a. (b) Cromer, D. T.; Liberman, D. *Ibid.*, Table 2.3.1.

Tricyclo[4.2.0.0^{1,4}]octane

Kenneth B. Wiberg,* Larry K. Olli, Nancy Golembeski, and Richard D. Adams*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received June 12, 1980*

Abstract: The synthesis of tricyclo[4.2.0.0^{1,4}]octane-3-carboxylic acid (**15**) was effected via a diazoketone ring contraction of tricyclo[5.2.0.0^{1,5}]nonan-4-one. The structure was determined by X-ray crystallographic analysis of the *p*-bromoanilide derived from **15**. The parent hydrocarbon (**2**) may be formed via conversion of **15** to the 3-acetoxy compound and photolysis of the acetate in HMPA-water. Thermolysis of **2** occurs at 140–180 °C with an $E_a = 36.5$ kcal/mol and forms a mixture of products which could be derived from initial cleavage of one of the internal C–C bonds. The solvolyses of the 3-*endo*- and -*exo*-3,5-dinitrobenzoates derived from **2** strongly resemble those of the corresponding bicyclo[2.2.0]hexyl-2 dinitrobenzoates with regard both to rates and products. The energies of **2** and of some related hydrocarbons have been estimated by using molecular mechanics.

Planar tetravalent carbon has been the subject of several recent investigations.[1] In the absence of stabilizing substituents, planar methane has been calculated to be 150 kcal/mol less stable than tetrahedral methane.[2] Although this large destabilization makes it clear that such a simple planar carbon species will not be achieved, it is still of interest to have information concerning the potential function for flattening the bonds about a carbon.[2a] One experimental approach would be to synthesize and examine the tetracyclic hydrocarbon, **1**, which has been called "windowpane" or "fenestrane"[3] and which is properly named tetracyclo[5.1.1.0^{3,8}.0^{5,8}]nonane. On the basis of models and the calculations on methane,[2a] we estimate that the angle C_1–C_8–C_5 should be

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(3) Georgian, V.; Saltzman, M. *Tetrahedron Lett.* **1972**, 4315.

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