Reactions of Coordinated Dinitrogen. 4.[1] Reactions of Bromoalkanes with Bis(dinitrogen)bis[ethylenebis(diphenylphosphine)]molybdenum. Formation of Ammonia and Amines[2]

Gerald E. Bossard, David C. Busby, Molly Chang, T. Adrian George,* and S. D. Allen Iske, Jr.

Contribution from the Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588. *Received February 12, 1979*

Abstract: Bis(dinitrogen)bis[ethylenebis(diphenylphosphine)]molybdenum, $Mo(N_2)_2(dppe)_2$ (**1**), reacts with CH_3Br, n-C_4H_9Br, and $(CH_3)_3CCH_2CH_2Br$, respectively, to form the corresponding 2-alkyldiazenido-*N* derivative, $MoBr(N_2R)(dppe)_2$, with loss of 1 equiv of dinitrogen. Reaction of **1** with 6-bromo-1-hexene yields the cyclopentylmethyldiazenido complex, providing support for a radical pathway involving an alkyl radical. Protonation of the alkyldiazenido complexes with aqueous fluoroboric acid produces a 2-alkylhydrazido(2−)-*N* complex $[MoBr(N_2HR)(dppe)_2]BF_4$ in which the proton is attached to the carbon-bound nitrogen atom. $MoBr(N_2C_4H_9)(dppe)_2$ (**5**) forms an adduct with methanol that exhibits physical properties (IR and UV-visible spectra) very similar to those of the corresponding butylhydrazido complex suggesting strong hydrogen bonding with methanol. The bromide ion of **5** can be replaced by azide and thiocyanate ion in a metathesis reaction. Reaction of **5** with sodium borohydride or sodium methoxide in benzene-methanol solution at elevated temperature produces almost equal quantities of ammonia and butylamine. Yields approached 60%. Butylmethylamine was also formed in the reactions. Use of ethanol in place of methanol dramatically reduced the yields of ammonia and amine, and $MoH_4(dppe)_2$ (ca. 24% yield) was identified among the products.

Introduction

In 1967 Parshall reported the stepwise reduction of 2-aryldiazenido-*N* (ArNN-) and 1-aryldiazene-N^2 (ArNNH-) complexes of platinum(II) to aniline and ammonia using dihydrogen over a Pt/C catalysis.[3] Ammonia and substituted anilines have also been produced by treating salts of the type $[RuCl(N_2Ar)_2(P(C_6H_5)_3)_2]^+$ (where Ar = p-$CH_3C_6H_4$ and p-$CH_3OC_6H_4$) with excess sodium amalgam in ethanol.[4] No yields were given. Reactions of sodium borohydride with cationic aryldiazenido complexes, e.g., $[Os(CO)_2(N_2C_6H_5)(P(C_6H_5)_3)_2]^+$, result in the displacement of the aryldiazenido ligand with hydride ion (to form $OsH_2(CO)_2(P(C_6H_5)_3)_2$).[5] No mention was made of the fate of the organonitrogen moiety.

The interest in reducing the well-characterized alkyldiazenido complexes of molybdenum and tungsten to amines and ammonia lies in their origin, namely, that the initial dinitrogen complexes are prepared using molecular nitrogen rather than an organonitrogen precursor and that a carbon-nitrogen bond is formed to coordinated dinitrogen (e.g., eq 1). We have been able to accomplish this reduction (e.g., eq 2) under different

$$Mo(N_2)_2(dppe)_2 + CH_3I \rightarrow MoI(N_2CH_3)(dppe)_2 + N_2 \quad (1)$$

$$MoBr(N_2C_4H_9)(dppe)_2 \rightarrow NH_3 + C_4H_9NH_2 + 2dppe + Br^- + (Mo) \quad (2)$$

conditions in yields close to 60%. In this paper we present the preparation and characterization of alkyldiazenido and alkylhydrazido complexes derived from reactions of alkyl bromides with **1** and report data on the reduction of $MoBr(N_2C_4H_9)(dppe)_2$ to ammonia and amines. Some of this work has already been communicated.[6-8]

Recently, the reduction of 2,2-dialkylhydrazido(2−)-*N* complexes $[-N_2(CH_3)_2$ and $-\overline{NCH_2CH_2CH_2CH_2}]$ of molybdenum and tungsten has been reported.[9] Yields of dimethylamine and pyrrolidine, respectively, were almost quantitative using lithium aluminum hydride in diethyl ether at 80 °C for 65 h followed by methanol and hydrogen bromide treatment. However, no ammonia was detected so that only one-half of the theoretical amount of nitrogen present per molecule was reduced.

Experimental Section

All preparations and crystallizations were carried out under a dinitrogen atmosphere using standard vacuum line or glovebag techniques unless otherwise specified. Irradiation of solutions in Pyrex vessels was accomplished using either a 100-W B-100A Blak-Ray lamp, Ultra-Violet Products, Inc., or three Sylvania 100- or 150-W, 125-V lamps each placed ca. 25 cm from the flask, or Westinghouse 40-W cool white fluorescent lamps used for normal lighting in the fume hoods and laboratory.

Organic solvents were reagent grade unless noted otherwise and were dried by distillation from the drying agent indicated: benzene, heptane, and dichloromethane (calcium hydride), tetrahydrofuran (sodium benzophenone ketyl or calcium hydride), and methanol (magnesium methoxide). All solvents were deoxygenated before use by bubbling dinitrogen through them for at least 0.5 h, and then the reaction solutions were further deoxygenated by a series of freeze-pump-thaw cycles.

trans-$Mo(N_2)_2(dppe)_2$ was prepared by one of two different methods.[10,11] Modifications were made to the latter method.[1] Hexafluorophosphoric acid-diethyl ether complex and methanol-d_1 were purchased from Aldrich Chemical Co. The bromoalkanes were purchased from commercial sources.

Infrared spectra were obtained on a Perkin-Elmer 621 grating spectrophotometer from samples prepared as indicated in Table I. ^1H NMR spectra were recorded in the deuterated solvents indicated on either a Varian A-60D or a Varian XL-100 NMR spectrometer. Electronic absorption data were recorded on a Cary 14 spectrophotometer in 1.0-cm Lightpath Cells, Inc., solution cells. Melting points or decomposition points were measured in sealed, evacuated capillaries in a Mel-Temp apparatus, and are uncorrected.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N.Y.

Syntheses. Bromo(2-methyldiazenido-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum, $MoBr(N_2CH_3)(dppe)_2$ (2). Methyl bromide (2.06 mmol) was condensed into 1.70 g (1.79 mmol) of **1** in benzene (220 mL) on the vacuum line. Upon reaching room temperature, the stirred solution was irradiated (3 × 100-W lamps) at 27 °C for 44 h. Excess anhydrous hydrogen bromide was added to the solution. A color change from yellow-orange to cherry red occurred followed by precipitation of a pink solid, which was removed by filtration. The solution was reduced in volume (ca. 150 mL) in vacuo. Addition of

0002-7863/80/1502-1001\$01.00/0

Table I. Spectral Data

	infrared, $\mathrm{cm^{-1}}$[a]				^{1}H NMR, τ (rel area)[b]						electronic absorption	
compd	ν(NN)-(br)	ν(NH)-(br)	other(s)	phase	solvent	alkyl	NH[c]	$\mathrm{CH_2(P)}$	phenyl	other	solvent[d]	λ, nm ($\epsilon_{\max}$, $\mathrm{M^{-1}\,cm^{-1}}$)
$\mathrm{MoBr(N_2CH_3)(dppe)_2}$ (**2**)	1535 vs		1353 vs	KBr	$\mathrm{CD_2Cl_2}$	8.44 (4) s		6.9-7.6 (8) s,	2.4-3.1 (40) m	2.65	$\mathrm{C_6H_6}$	364 (6240), 500 (160)[e]
$\mathrm{MoBr(N_2C_4H_9)(dppe)_2}$ (**5**)	1530, 1516 s (1472 s)[f]		1395 sh, 1360 w-m 1334 m, 1308 m (1386 w-m, 1335 m, sh, 1328 m, 1308 m)[f]	CsI	$\mathrm{C_6D_6}$	7.9-9.3 m		6.9-7.6 s	2.2-3.3 m		$\mathrm{C_6H_6}$ $\mathrm{C_6H_6/DMF}$[g]	362 (7160), 510 (170)[e] 363 (7330), 510 (170)[e]
$\mathrm{MoBr(N_2C_4H_9)(dppe)_2\cdot CH_3OH}$ (**6**)	n.a.		2786 m (2788 m, 2290 w, 2190 w)[h]	CsI							$\mathrm{C_6H_6/CH_3OH}$[g]	310 (7010)[e]
$\mathrm{MoBr(N_2CH_2CH_2C(CH_3)_3)(dppe)_2}$ (**8**)	1525 s (1505 s)[i]			KBr	$\mathrm{CDCl_3}$	9.52 s, 8.0 m		6.9-7.6 s	2.4-3.1 m	8.77 t 6.30 q	$\mathrm{C_6H_6}$	364 (7830), 500 (100)[e]
$\mathrm{MoBr(N_2CH_2\overline{CHCH_2CH_2CH_2C}H_2)\text{-}(dppe)_2}$ (**10**)	1536 s			KBr	$\mathrm{CDCl_3}$	8.5-9.0 m, 8.23 d		7.0-7.7 s	2.4-3.1 m			
$\mathrm{Mo(NCS)(N_2C_4H_9)(dppe)_2}$ (**11**)	1529 s		2080 vs, 2000 s	KBr							$\mathrm{C_6H_6}$	355 (7910), 410 (6790)[e] 430 (4030),[e] 510 (160)
$\mathrm{Mo(N_3)(N_2C_4H_9)(dppe)_2}$ (**13**)	1523 s		2085 vs	KBr							$\mathrm{C_6H_6}$	358 (7060), 515 (160)[e]
$\mathrm{[MoBr(N_2HCH_3)(dppe)_2]Br}$(**3**)	n.a.	2780 w	1352 m	KBr	$\mathrm{CDCl_3}$	8.65 d	n.a.	6.7-7.5 s	2.3-3.1 m			
$\mathrm{[MoBr(N_2HCH_3)(dppe)_2]BF_4}$ (**4**)	n.a.	3260 w	1351 m, 1020-1100 br, vs	KBr	$\mathrm{C_6D_6}$	8.64 d	7.04 br,s	7.1-7.8 s	2.0-3.3 m			
$\mathrm{[MoBr(N_2HC_4H_9)(dppe)_2]BF_4}$ (**7**)	n.a.	3282 w (3273 w)[f]	1020-1100 br, vs	CsI	$\mathrm{CDCl_3}$	8.1-9.3 m	6.05 br,s	6.8-7.5 s	2.4-3.1 m		$\mathrm{C_6H_6}$	460 (1000),[e] 560 (60)[e]
$\mathrm{[MoBr(N_2HCH_2CH_2C(CH_3)_3)\text{-}(dppe)_2]BF_4}$ (**9**)	n.a.	3137 w-m	1020-1100 br, vs	KBr	$\mathrm{CDCl_3}$[j]	9.6-9.8 m, 9.49 s	5.78 br, s	6.7-7.5 s	2.4-3.1 m	8.79 t 6.30 q	$\mathrm{CH_2Cl_2}$	285 (12 300,[e] 400 (370),[e] 550 (40)
$\mathrm{[Mo(NCS)(N_2HC_4H_9)(dppe)_2]BF_4}$ (**12**)	n.a.	3270 w	2038 vs, 1020-1100 br, vs	KBr							$\mathrm{C_6H_6/CH_2Cl_2}$[k]	300 (18 500), 435 (260)[e]
$\mathrm{[Mo(N_3)(N_2HC_4H_9)(dppe)_2]BF_4}$ (**14**)	n.a.	3295 w	2085 vs, 1020-1100 br, vs	KBr							$\mathrm{CH_2Cl_2}$	300 (19 300), 440 (220),[e] 560 (60)

[a] n.a. = not assignable; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [b] Relative to $\mathrm{Si(CH_3)_4}$; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. [c] Resonance disappears upon addition of $\mathrm{D_2O}$. [d] THF = tetrahydrofuran. [e] Shoulder. [f] ^{15}N analogue. [g] 1:1 (by vol) solution; DMF = *N,N*-dimethylformamide. [h] $\mathrm{CH_3OD}$ analogue. [i] $\mathrm{N_2CHDCHDC(CH_3)_3}$ analogue. [j] $\mathrm{PF_6}$ salt. [k] 3:2 (by vol) solution.

heptane (150 mL) produced a tan precipitate that was filtered off, dried, and shown to be $[MoBr(N_2HCH_3)(dppe)_2]Br$ (**3**, 0.75 g, 38%), mp 155 °C dec. Anal. Calcd for $[MoBr(N_2HCH_3)_2(dppe)_2]Br\cdot{}^1\!/\!_2C_6H_6$ ($C_{56}H_{55}Br_2MoN_2P_4$): C, 59.22; H, 4.89; N, 2.47; Br, 14.07. Found: C, 58.88; H, 4.81; N, 2.06; Br, 14.76.

A dilute water–ethanol solution of potassium carbonate was added to an ethanol solution of **3** (0.50 g, 0.46 mmol). Immediately, the solution turned from a yellow-brown to an orange-yellow color and yellow crystals precipitated, which were collected by filtration, washed with ethanol and heptane, and dried in vacuo to yield **2** (95%, 0.44 g), mp 215 °C dec. Anal. Calcd for $MoBr(N_2CH_3)(dppe)_2\cdot{}^1\!/\!_2C_6H_6$($C_{56}H_{54}BrMoN_2P_4$): C, 63.76; H, 5.17; N, 2.66; Br, 7.58. Found: C, 63.40; H, 4.95; N, 2.89; Br, 7.14.

Bromo(2-methylhydrazido(2−)-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum Tetrafluoroborate, $[MoBr(N_2HCH_3)(dppe)_2]BF_4$ (4). As described above, **1** (1.34 g, 1.41 mmol) and methyl bromide (1.56 mmol) in benzene (100 mL) were reacted for 63 h at 38 °C. To the resulting suspension was added 48% aqueous fluoroboric acid (1.5 mL) dissolved in ethanol (450 mL). After stirring (0.2 h) a yellow solid (0.68 g) was separated by filtration. The filtrate was reduced in volume to ca. 100 mL and heptane (100 mL) added to yield a pink solid. After filtration, the pink solid was stirred (0.5 h) with benzene (200 mL) and filtered. The filtrate was reduced in volume to ca. 100 mL and heptane (100 mL) slowly added to precipitate the tan product that was dried in vacuo and shown to be $[MoBr(N_2HCH_3)(dppe)_2]BF_4$ (**4**, 0.15 g, 10%), mp 146 °C dec. Anal. Calcd for $[MoBr(N_2HCH_3(dppe)_2]BF_4\cdot{}^1\!/\!_2C_6H_6$ ($C_{56}H_{55}BBrF_4MoN_2P_4$): C, 58.86; H, 4.86; N, 2.45; total halogen, 13.56. Found: C, 58.53; H, 5.00; N, 2.29; total halogen, 14.24.

A small amount of **4** was dissolved in ethanol (100 mL) followed by addition of a saturated solution of ethanolic sodium hydroxide (50 mL). The solution immediately became yellow in color and a yellow solid precipitated. The yellow product was washed with ethanol and heptane, dried in vacuo, and shown to be **2** by spectroscopic methods.

Bromo(2-*n*-butyldiazenido-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum, $MoBr(N_2C_4H_9)(dppe)_2$ (5). *n*-Butyl bromide (0.7789 g, 5.684 mmol) and benzene (150 mL) were added to **1** (3.3250 g, 3.495 mmol) in a round-bottom flask (500 mL). Following the freeze-pump-thaw cycles, the reaction was maintained under its own vapor pressure (i.e., N_2 was not readmitted) and was irradiated (3 × 150-W lamps) for 9.5 h at ambient temperature. The volume of the dark red-orange solution was reduced to ca. 25 mL and methanol (150 mL) added. After stirring (1.5 h), the solution was filtered to remove a yellow solid and the filtrate evaporated to dryness to yield a yellow-orange solid. This solid was washed (swirling) briefly with ethanol (50 mL) and the resulting suspension was rapidly filtered to remove an orange solid. The product, **5** (2.787 g, 75.4%), that precipitated as orange crystals from the filtrate over a 24-h period, was filtered off, washed with ethanol, and dried under dinitrogen. A further 0.325 g of crystalline **5** was obtained from the filtrate (after evaporation) by redissolving in benzene and repeating the methanol–ethanol treatment. Total yield of **5**, mp 175 °C dec, was 84.2%. Anal. Calcd for $MoBr(N_2C_4H_9)(dppe)_2$($C_{56}H_{57}BrMoN_2P_4$): C, 63.58; H, 5.43; N, 2.65; Br, 7.55. Found: C, 63.37; H, 5.39; N, 2.63; Br, 7.38.

The $^{15}N_2$-labeled compound was prepared from *trans*-$Mo(^{15}N_2)_2(dppe)_2$ by a similar procedure except that argon was used as the inert atmosphere for all manipulations other than workup of product.

Bromo(2-*n*-butylhydrazido(2−)-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum Methanolate, $MoBr(N_2C_4H_9)(dppe)_2\cdot CH_3OH$ (6). According to the above procedure, **1** (2.81 g, 2.96 mmol), *n*-butyl bromide (5% excess), and benzene (150 mL) were irradiated together. Methanol (200 mL) was added and the solution allowed to stand (0.5 h). The volume was reduced to ca. 50 mL and the resulting yellow precipitate filtered off. The light-orange filtrate was evaporated to dryness and the solid washed with benzene until the filtrate was colorless (ca. 150 mL). The light-orange product, **6**, was dried under dinitrogen. A further batch of **6** was obtained by adding methanol to the benzene washing and repeating the isolation procedure. Total yield of **6**, mp 182 °C dec, was 1.65 g (51%). Anal. Calcd for $MoBr(N_2C_4H_9)(dppe)_2\cdot CH_3OH$ ($C_{57}H_{61}BrMoN_2OP_4$): C, 62.82; H, 5.64; N, 2.57; Br, 7.33. Found: C, 62.42; H, 5.51; N, 2.30; Br, 7.02.

The methanol-d_1 analogue was prepared by the same procedure.

Bromo(2-*n*-butylhydrazido(2−)-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum Tetrafluoroborate, $MoBr(N_2HC_4H_9)(dppe)_2BF_4$ (7). Compound **5** (0.16 g, 0.15 mmol) was dissolved in benzene (15 mL) in an Erlenmeyer flask (125 mL). Ethanol (10 mL) containing 2 drops of 48% aqueous fluoroboric acid was added to the orange solution. The color immediately changed to a brown-yellow. Heptane (25 mL) was added in three portions over a 2-h period, and the resulting feathery, tan precipitate was filtered off and washed with 25 mL of a 1:1 ethanol–heptane solution. The product, **7** (0.13 g, 77%), mp 252 °C, was dried in vacuo.

$^{15}N_2$-labeled compound was prepared similarly from $^{15}N_2$-labeled **5**.

The hexafluorophosphate analogue of **7** was prepared in a similar manner by protonating with hexafluorophosphoric acid–diethyl ether complex, mp 236 °C.

Bromo[2-(3,3-dimethylbutyl)diazenido-*N*]bis[ethylenebis(diphenylphosphine)]molybdenum, $MoBr(N_2CH_2CH_2C(CH_3)_3)(dppe)_2$ (8). Benzene (75 mL) was added to **1** (0.5075 g, 0.535 mmol) and 3,3-dimethylbutyl bromide (0.0942 g, 0.571 mmol) in a flask with vacuum stopcock. The reaction was allowed to proceed (48 h) at ambient temperature in the dark. The volume was reduced to ca. 25 mL and methanol (50 mL) added. The solution was stirred (1 h) and evaporated to dryness. Ethanol (50 mL) was added, and after swirling (0.1 h) the suspension was filtered. Orange crystals precipitated (48 h) from the filtrate and were filtered off and dried in vacuo. Yield of **8**, mp 173 °C dec, was 0.415 g (69%). Anal. Calcd for $MoBr(N_2CH_2CH_2C(CH_3)_3)(dppe)_2\cdot C_2H_5OH$ ($C_{60}H_{67}BrMoN_2OP_4$): C, 63.67; H, 5.97; N, 2.48. Found: C, 63.70; H, 5.79; N, 2.43.

Bromo[2-(3,3-dimethylbutyl)hydrazido(2−)-*N*]bis[ethylenebis(diphenylphosphine)]molybdenum Tetrafluoroborate, $[MoBr(N_2HCH_2CH_2C(CH_3)_3)(dppe)_2]BF_4$ (9). To a benzene (20 mL) solution of **8** (0.4150 g, 0.3666 mmol) was added 48% aqueous HBF_4 (0.3405 g, 1.86 mmol) in ethanol (15 mL). The solution immediately changed from red-orange to red-green in color. Heptane (50 mL) was added over a 1-h period to the stirred solution, producing a green powder. The mixture was stirred overnight. The green product was collected by filtration, washed with 50 mL of 1:1 ethanol–heptane solution, and dried in vacuo to yield $[MoBr(N_2HC_6H_{13})(dppe)_2]BF_4\cdot{}^1\!/\!_3EtOH$ (0.4058 g, 93.1%), mp 240 °C dec.

Bromo(2-cyclopentylmethyldiazenido-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum, $MoBr(N_2CH_2\overline{CHCH_2CH_2CH_2CH_2})(dppe)_2$ (10). 6-Bromo-1-hexene (0.0951 g, 0.5832 mmol) and **1** (0.5436 g, 0.5729 mmol) were dissolved in benzene (75 mL). After two freeze-pump-thaw cycles, the mixture was warmed to 22 °C and stirred under solvent vapor for 48 h in the dark. The volume was reduced to 25 mL using a Buchi rotary evaporator, methanol (50 mL) was added, and the solution was stirred (1 h). A small amount of a yellow solid was removed by filtration and the filtrate taken to dryness. Ethanol (30 mL) was added to the residue and the mixture swirled (0.05 h) and then filtered through a fine frit. After 12 h, large red crystals of product were collected by filtration, washed with a small volume of ethanol, and dried in vacuo to give $MoBr(NNC_6H_{11})(dppe)_2$ (0.4548 g, 73.2%), mp 183 °C dec. Anal. Calcd for $C_{58}H_{59}BrMoN_2P_4$: C, 64.27; H, 5.49; N, 2.58. Found: C, 63.90; H, 5.47; N, 2.39.

Thiocyanato(2-*n*-butyldiazenido-*N*)bis[(ethylenebis(diphenylphosphine)]molybdenum, $Mo(NCS)(N_2C_4H_9)(dppe)_2$ (11). To a solution of **5** (0.574 g, 0.542 mmol) in benzene (50 mL) were added potassium thiocyanate (0.484 g, 4.98 mmol) and acetone (30 mL). The mixture was heated at reflux (21 h) with magnetic stirring. Upon cooling, the suspension was filtered. The filtrate was evaporated to dryness, and the resulting solid redissolved in benzene (30 mL). After filtration, solvent was removed and the orange product washed with heptane and ethanol and dried in vacuo. The yield of **11**, mp 174 °C dec, was 0.412 g (73%). Anal. Calcd for $Mo(NCS)(N_2C_4H_9)(dppe)_2$ ($C_{57}H_{57}MoN_3P_4S$): C, 66.08; H, 5.55; N, 4.06. Found: C, 65.02; H, 5.76; N, 3.04.

Thiocyanato(2-*n*-butylhydrazido(2−)-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum Tetrafluoroborate, $[Mo(NCS)(N_2HC_4H_9)(dppe)_2]BF_4$ (12). To **11** (0.047 g, 0.039 mmol) dissolved in benzene (10 mL) was added ethanol (7 mL) containing 2 drops of 48% aqueous fluoroboric acid. The solution rapidly turned from an orange to greenish-brown color. Heptane (20 mL) was added over a 2-h period. Long, greenish-brown needles crystallized (24 h) from the solution, and were filtered off, washed with heptane and ethanol, and dried in vacuo, mp 225 °C dec. Anal. Calcd for $[Mo(NCS)(N_2HC_4H_9)(dppe)_2]BF_4\cdot{}^1\!/\!_2C_6H_6$ ($C_{60}H_{61}BF_4MoN_3P_4S$): C, 61.97; H, 5.25; N, 3.61. Found: C, 61.64; H, 5.12; N, 2.94.

Azido(2-*n*-butyldiazenido-*N*)bis[ethylenebis[diphenylphosphine)]-molybdenum, $Mo(N_3)(N_2C_4H_9)(dppe)_2$ (13). Sodium azide (0.156 g, 2.40 mmol) was added to a benzene (25 mL) solution of **5** (0.254 g, 0.240 mmol) followed by ethanol (25 mL). The mixture was heated at reflux (21 h) with magnetic stirring. After filtration, the bright orange solution was evaporated to dryness, washed with heptane, and redissolved in ethanol. Orange crystals precipitated overnight and were filtered off, washed with heptane, and dried in vacuo. Yield of **13**, mp 155 °C dec, was 0.13 g (50%). Anal. Calcd for $Mo(N_3)(N_2C_4H_9)(dppe)_2{\cdot}C_2H_5OH$ ($C_{58}H_{63}MoN_5P_4O$): C, 65.35; H, 5.91; N, 6.57. Found: C, 64.41; H, 5.63; N, 6.27.

Azido(2-*n*-butylhydrazido(2−)-*N*)bis[ethylenebis(diphenylphosphine)]molybdenum Tetrafluoroborate, $[Mo(N_3)(N_2HC_4H_9)(dppe)_2]BF_4$ (14). To **13** (0.045 g, 0.039 mmol) dissolved in benzene (10 mL) was added ethanol (7 mL) containing 2 drops of 48% aqueous fluoroboric acid. The color rapidly changed from bright orange to yellow-brown. Heptane (20 mL) was added over a period of 3 h. Brown crystals of **14** were filtered off, washed with heptane and ethanol, and dried in vacuo, mp 200-201 °C dec. Anal. Calcd for $[Mo(N_3)(N_2HC_4H_9)(dppe)_2]BF_4{\cdot}{}^1\!/_2C_6H_6$ ($C_{59}H_{61}BF_4MoN_5P_4$): C, 61.79; H, 5.32; N, 6.10. Found: C, 61.91; H, 5.40; N, 5.42.

Reduction Reactions. A large number of reduction reactions of **5** were conducted. Two different types of apparatus were used for the reaction. One of these was a 500-mL Parr bottle with a ball joint added in place of the normal neck. A vacuum stopcock could be connected to the Parr bottle via the ball joint connection. Typically, 0.4-0.6 g of **5** was added to the Parr bottle containing a magnetic stir bar. Benzene (30 mL) and the reagent ($NaBH_4$ or sodium methoxide, both in ca. 10 mol excess) were added, followed by methanol (50 mL). The bottle was sealed and either charged with dinitrogen or dihydrogen or evacuated (−196 °C) and run under the vapor pressure of the solvents. The bottle was then immersed in an oil bath at the desired temperature, and the mixture magnetically stirred for the desired time interval. Following completion of the reaction, the bottle was allowed to cool, and then the volatiles were removed in vacuo and collected in a cooled (−196 °C) flask. Hydrobromic acid (48% aqueous) was added to the still-frozen distillate, and the flask was allowed to warm to room temperature. All volatiles were removed in vacuo. This solid residue was treated with a small amount of deionized water (5 mL) and solid sodium hydroxide and the volatiles were distilled into a receiver cooled to −196 °C. The distillate was analyzed for total base, or ammonia and amines.

The second apparatus used was a 1-L MagneDrive packless autoclave which was charged with reagents and solvents (same ratios as mentioned above) and a magnetic stir bar was added. The autoclave was sealed, flushed twice with dinitrogen or dihydrogen, and then heated to the desired temperature for the requisite period of time. The solution was magnetically stirred during the reaction. Following the reaction, the autoclave was allowed to cool and the pressure released, carefully. The cover was then removed and the solution rapidly pipetted into a 250-mL round-bottomed flask. This material was then worked up in an identical manner with the product from the Parr bottle reactions described above.

Total base was determined in the following way. The final distillate collected as described above was diluted to ca. 15 mL with distilled water which had been boiled to expel carbon dioxide. The solution was transferred to a beaker (30 mL) and titrated with 0.104 M hydrochloric acid while being stirred magnetically. The titration was monitored by use of a Corning Semimicro Combination pH electrode (catalog no. 476050) and a Fischer Accumet pH meter, Model 210. The titrations were carried out under dinitrogen. The standard acid was dispensed via a Gilmont 2-mL micrometer buret whose tip was immersed continuously in the solution. End points were sharp and assigned to the point of greatest slope. Yields reported by this method are the average of at least two determination, and were for total base, that is, for butylamine, butylmethylamine, and ammonia, since they could not be determined separately by this analytical method.

Determination of yields of ammonia and amines was carried out as follows. To the solution obtained from the base distillation of the ammonium and amine hydrobromide salts was added 1.0 mL of a 0.299 M aqueous di-*n*-propylamine solution (as an internal reference). The combined solution was made up to a volume of 10 mL. Ammonia was determined by the indophenol method[12] with incubation carried out at 37 °C. At this temperature neither butylamine nor di-*n*-propylamine inhibited the color formation. Butylamine yields were determined using a portion of the same solution, by gas chromatography using a Varian Aerograph Model 1520B gas chromatograph equipped with a Varian Aerograph alkali flame ionization detector and a Leeds and Northrup Speedomax W recorder. An 8 ft by 1/8 in. stainless steel column packed with 60/80 mesh Chromosorb 103 was used in the separation and identification of the amines. Oven temperature was generally 140-160 °C. At least three injections of 0.0347, 0.0231, and 0.0116 M standard butylamine-di-*n*-propylamine solutions were made for each group of unknowns, and at least three injections of each unknown were made. Injection size was ca. 2 μL. Integration of the butylamine, di-*n*-propylamine, and butylmethylamine peaks was made by cutting the peaks out of the chart paper and weighing them. Average deviations for the several injections of each standard and each unknown were usually less than 5%. Yields given in Table III are the average of at least two separate experiments carried out at the same temperature. Mass spectral data in both the direct inlet and gas chromatographic inlet modes were obtained on a computer-assisted AEI MS-50 mass spectrometer.

Investigation of the residue left behind in the pressure vessel after removal of all volatiles is summarized below. In $NaBH_4$-benzene-methanol reactions with **5**, (1) extraction with ethanol left a white solid that was shown to be dppe in yields up to 89%; (2) unreacted **5** was often recovered; (3) treatment of the residue with concentrated H_2SO_4, and then 10 M NaOH solution, followed by distillation gave 2% ammonia (of that not previously accounted for in that particular experiment) by the indophenol method. In two reactions of **5** with $NaBH_4$-benzene-ethanol, extraction of the residue with benzene gave yellow solutions from which $MoH_4(dppe)_2$ in yields of 25.5 and 21.8%, respectively, was obtained after addition of ethanol.

Three other alkyldiazenido complexes (besides **5**) were subjected to reduction in the presence of $NaBH_4$-benzene-methanol: $MoI(N_2C_6H_{11})(dppe)_2$, $WBr(N_2C_4H_9)(dppe)_2$, and $MoBr(N_2CH_2COOC_2H_5)(dppe)_2$ (see Table III). In all three cases only ammonia yields were determined quantitatively.

Results and Discussion

Synthesis and Characterization. Simply alkyl bromides such as CH_3Br, n-C_4H_9Br, and $(CH_3)_3CCH_2CH_2Br$ react with $Mo(N_2)_2(dppe)_2$ (**1**) in benzene solution to give alkyldiazenido complexes of the type $MoBr(N_2R)(dppe)_2$. These complexes are analogous to the alkyldiazenido complexes derived from the reaction of simple alkyl iodides with **1** for which two X-ray crystal structure determinations have been made.[1,8,13] The coordinated bromine atom trans to the alkyldiazenido ligand is labile to exchange by azide and thiocyanate ion. Protonation of the complexes with either anhydrous hydrogen bromide, hexafluorophosphoric acid-diethyl ether complex, or aqueous-ethanolic fluoroboric acid produces the corresponding alkylhydrazido complex. Spectroscopic studies indicate that the site of protonation is the carbon-bound nitrogen atom by analogy with the corresponding alkylhydrazido complexes derived from alkyl iodides and subsequent protonation. An X-ray diffraction study of $[MoI(N_2HC_8H_{17})(dppe)_2]I$ has shown the site of protonation to be indeed the carbon-bound nitrogen atom.[1,13]

All new compounds have been characterized by elemental analysis and infrared spectroscopy, and in most cases ^1H NMR spectroscopy (see Table I). The electronic absorption spectra of many of the new compounds have also been recorded (see Table I). The alkyldiazenido complexes are yellow, yellow-orange, or orange while the alkylhydrazido complexes are tan, brownish-green, or brown. Both types of compounds are air stable in the solid state and are stable in solution in the absence of oxygen.

Alkyldiazenido Complexes. Methyl bromide reacts with **1** in benzene solution to form $MoBr(N_2CH_3)(dppe)_2$ (**2**):

$$Mo(N_2)_2(dppe)_2 + CH_3Br \rightarrow MoBr(N_2CH_3)(dppe)_2 + N_2 \quad (3)$$

The reaction occurs more rapidly in the light than in total darkness at room temperature.[14] A frequent coproduct in this reaction is $MoBr_2(dppe)_2$, which could not be removed totally by fractional recrystallization. However, addition of anhydrous hydrogen bromide to the crude reaction suspension produces the methylhydrazido complex as the bromide salt (eq 4). Subsequent deprotonation (eq 5) using an aqueous-ethanolic solution of potassium carbonate produced analytically pure **2**, containing one-half a molecule of benzene of solvation. The benzene of solvation was detected in the ^1H NMR spectrum of **2** as a distinct, sharp singlet in the multiplet due to the phenyl protons of the dppe ligands. Compound **2** is considerably less soluble in organic solvents than its longer chain homologues. Similar purification can be achieved using tetrafluoroboric acid, followed by deprotonation.

$$\mathrm{MoBr(N_2CH_3)(dppe)_2 + HBr \rightarrow [MoBr(N_2HCH_3)(dppe)_2]Br} \quad (4)$$

$$\mathrm{[MoBr(N_2HCH_3)(dppe)_2]^+ + CO_3{}^{2-} \rightarrow MoBr(N_2CH_3)(dppe)_2 + HCO_3{}^-} \quad (5)$$

A considerable amount of our chemical studies are being carried out using $MoBr(N_2C_4H_9)(dppe)_2$ (**5**) because of its ease of preparation and high yield of isolated, pure product. The reactions of *n*-butyl bromide and **1** in benzene may be carried out in the dark or under normal laboratory lighting. The resulting clear solution is reduced in volume using a rotary evaporator to a small solution volume, at which point a large quantity of methanol is added. Either immediately, or after stirring for a short time, a yellow solid precipitates; this is $MoBr_2(dppe)_2$ with occasionally a trace of $MoH_4(dppe)_2$, which is a holdover from the preparation of **1** and results if the latter compound is not recrystallized carefully.[14] After filtration, solvent is removed in vacuo leaving a yellow-orange solid, **6**. This solid is primarily a methanol adduct of **5** and in many ways behaves like a hydrazido complex (vide infra). It is not a simple methanol solvated complex. Washing this yellow-orange solid, **6**, with benzene removes remaining traces of $MoBr_2(dppe)_2$ to produce pure **6** (see Experimental Section). Removal of a molecule of methanol from **6** (analogous to deprotonating an alkylhydrazido complex) produces pure **5**. This requires dissolving **6** in ethanol, filtering rapidly to remove any $MoBr_2(dppe)_2$ that may have not been removed previously, and allowing **5** to crystallize from the filtrate. While **6** is insoluble in benzene and soluble in ethanol, **5** is insoluble in ethanol. By this method we were able to avoid the protonation-deprotonation route to purifying the complexes $MoBr(N_2CH_2CH_2C(CH_3)_3)(dppe)_2$ (**8**) and $MoBr(N_2CH_2\overline{CHCH_2CH_2CH_2CH_2})(dppe)_2$ (**10**). However, no attempt was made to purify **2** by this method because of its low solubility in benzene solution.

The infrared spectra (see Table I) of **2, 5, 8, 10,** and **11** all show the characteristic strong to very strong, broad absorption band at between 1535 and 1516 cm^{-1} due to the N-N stretching vibration. In the case of **5** this absorption band is a broad doublet. The broadness persists in solution. Complete isotopic labeling with nitrogen-15 atoms shifts $\nu(NN)$ to 1472 cm^{-1} in **5**. However, while small changes are observed in a few infrared bands, it is not possible to assign $\nu(CN)$, for example, with any certainty. Haymore and Ibers have noted that $\nu(NN)$ is often vibrationally coupled with phenyl vibrational modes in compounds that contain the aryldiazenido (arylazo) ligand.[9,15] We have been able to demonstrate that $\nu(NN)$ also vibrationally couples with the attached methylene group in $MoBr(N_2CH_2CH_2C(CH_3)_3)(dppe)_2$ (**8**). The $\nu(NN)$ band in **8** appears at 1525 cm^{-1}, whereas a mixture of the erythro and threo isomers of the 1,2-dideuterio derivative of **8**, $MoBr(NNCHDCHDC(CH_3)_3)(dppe)_2$,[16] exhibits a $\nu(NN)$ at 1505 cm^{-1}. The low symmetry associated with the alkyldiazendio ligand (approximately C_s) allows the symmetric CH_2 bending mode to couple with $\nu(NN)$. Coupling had been anticipated because the observed isotopic shift was less than the calculated shift. The partial deuteration experiment confirmed that expectation.

The ^1H NMR spectra (see Table I) of the alkyldiazenido complexes are not particularly informative. The singlet due to the $-C(CH_3)_3$ group of **8** is shifted upfield by 0.47 ppm compared with the same group in 3,3-dimethylbutyl bromide (τ 9.05) and 3,3-dimethylbutanol (τ 9.05). This same shift to higher field has been observed in other alkyldiazenido complexes, except the methyldiazenido complexes. The likely cause of this upfield shift is the diamagnetic anisotropy created by phenyl groups of the phosphine ligands.[18] In the solid state, two phenyl groups are reasonably close to the alkyl group chain, although no atom-atom interligand distances are less than the sum of the corresponding van der Waals radii.[1]

All the alkyldiazenido complexes have similar room-temperature electronic absorption spectra in benzene solution (see Table I), namely, a low-intensity shoulder at ca. 500 nm (ϵ ca. 150 M^{-1} cm^{-1}) and a broad band at ca. 360 nm (ϵ ca. 7000 M^{-1} cm^{-1}) beyond which it climbs toward the ultraviolet region. The former absorption is undoubtedly due to a d-d transition.[14] The broad absorption band at ca. 360 nm probably contains one or more charge transfer (CT) transitions, as well as possibly a second d-d transition. MLCT transitions could be $Mo \rightarrow P$ or $Mo \rightarrow N_2R$, whereas LMCT transitions could be $Br \rightarrow Mo$ or $RN_2 \rightarrow Mo$. Halogen LMCT is unlikely to cause the 360-nm absorption since the region of the spectra observed (300-650 nm) is invariant to changes in halogen or other trans ligand,[1] e.g., $MoX(N_2R)(dppe)_2$ where X = Cl, Br, I, OH, NCS, and N_3. For a series of (diazene)pentacarbonyl metal complexes of the type $M(RN{=}NR)(CO)_5$, where M = Cr, Mo, and W,[19] the effect of changing solvent polarity upon the position and intensity of MLCT transitions has been noted, and gives rise to a characteristic blue shift (1900-3200 cm^{-1}) as the polarity of the solvent increases (*n*-hexane to acetonitrile). Similar large blue shifts have been observed for the MLCT state of d^6 group 6B $M(CO)_4$(1,10-phen)(phen = phenanthroline) complexes on substituting cyclohexane for acetonitrile as solvent.[20,21] However, $MoBr(N_2C_4H_9)(dppe)_2$ displays an identical spectrum in benzene solution and in 1:1 (by volume) benzene-*N,N*-dimethylformamide (DMF) solution (see Table I). A small hyperchromic shift in the 360-nm band is the only change observed. These data would suggest that both $Mo \rightarrow N_2R$ and $Mo \leftarrow N_2R$ CT transitions do not arise in the region of the spectrum studied.

These alkyldiazenido complexes of molybdenum have a closed-shell electronic configuration with the N_2R ligand behaving as a three-electron donor. The three pieces of evidence that support this contention are (1) the very short Mo-N bond length,[1] (2) the similarity of the molybdenum $3d_{5/2}$ binding energies determined by X-ray photoelectron spectroscopy of **1** (227.2 eV), $MoI(N_2CH_3)(dppe)_2$ (227.5 eV), and $MoI(N_2C_6H_{11})(dppe)_2$ (227.4 eV),[22] and (3) the diamagnetism displayed by the alkyldiazenido complexes.[1] If this is the case, it might be expected that there would be some similarity between the spectrum of **1** and the spectra of the alkyldiazenido complexes. In fact, the broad absorption band at ca. 370 nm appears in the spectrum of **1** and the alkyldiazenido complexes. This band has been assigned by three different groups as being due to $Mo \rightarrow P$ CT.[13,23,24] Of the three phosphorus orbitals[25] (considering MoP_4 in C_{2v} symmetry) to which $Mo \rightarrow P_4$ CT transitions are allowed, only one, the a_1, is delocalized over all four phosphorus atoms and hence $Mo \rightarrow P_4(a_1)$ CT transition would be less likely to be affected by changes in solvent polarity. Therefore, we assign the absorption band at ca. 360 nm in the spectra of the alkyldiazenido complexes primarily to a $Mo \rightarrow P_4$ CT. Further experimental support for this assignment comes from the electronic absorption spectrum of $MoBr(N_2C_4H_9)(depe)_2$ (depe = $Et_2PCH_2CH_2PEt_2$) in heptane solution.[26] The 360-nm band has been blue shifted by ca. 2200 cm^{-1} to 335 nm upon replacing dppe by depe. Since depe is a poorer π acceptor than dppe the Mo$\rightarrow$P$_4$ CT transition should occur at higher energy,[14] which is precisely what appears to have happened upon replacing dppe by depe in **5**.

A dramatic change is noted in the spectrum of **5** when run in a 1:1 (by volume) benzene–methanol solution, a solution having a dielectric constant very similar to that of the benzene–DMF solution. The spectrum is very similar to that of the butylhydrazido complex [MoBr($N_2HC_4H_9$)(dppe)$_2$]BF$_4$ in benzene solution. The difference between methanol and DMF in this case is the hydrogen-bonding ability of the former solvent. We are seeing the effect of strong hydrogen bonding between methanol and the alkyldiazenido ligand. The degree of hydrogen bonding, determined by measuring the change in the electronic absorption spectrum of **5** upon addition of equal quantities of different alcohols, varied predictably in the order $CH_3OH > C_2H_5OH > (CH_3)_2CHOH$. The infrared spectrum of the methanol adduct of **5** in the solid state was very similar to that of the butylhydrazido complex **7**, including the disappearance of the ν(NN) stretch (vide infra). Bands in the infrared spectrum of the methanol adduct at 2960 (w), 2905 (w), 2875 (w, sh), 2842 (w), and 2783 (m) cm^{-1} can be assigned to ν(CH) for the butyl group and for methanol. The 2783-cm^{-1} band is shifted significantly from free methanol where it occurs at 2840 cm^{-1}. There is also a band at 3025 cm^{-1} partially obscured by the aromatic ν(CH) vibrations of dppe, and a strong band assigned to ν(CO) at 1092 cm^{-1}, compared to 1025 cm^{-1} in free methanol.[27] When CH_3OD is used to form the methanol adduct, all of the above bands remain unchanged except the 3025-cm^{-1} band, which disappears. A new weak band appeared at 2292 cm^{-1} that is assigned to ν(OD). In free CH_3OD, ν(OD) appears at 2430–2500 cm^{-1}.[27]

Exchange Reactions. Complex **5** undergoes bromide ion exchange very slowly with azide and thiocyanate ion in solution at room temperature. Heating a mixture of **5** and either sodium azide in a benzene–ethanol solvent mixture or potassium thiocyanate in an acetone–benzene solvent mixture at reflux produced the corresponding azido- and thiocyanato-alkyldiazenido complexes. In the infrared spectra of **9** and **11** new sharp bands appear at 2080 and 2000 [ν(NCS)] and 2085 cm^{-1} [ν(N$_3$)], respectively. The two ν(NCS) bands are present in a solution (CH_2Cl_2) spectrum of **9**. There is no firm evidence that there is a mixture of S- and N-bonded isomers. No further supporting information could be obtained from the spectrum because of absorptions due to the phenyl groups obscurring regions of interest.[28a,b]

Reaction with 6-Bromo-1-hexene. One of the most valuable chemical methods of determining if reactions of primary alkyl bromides proceed by a free-radical process is to carry out the reaction using 6-bromo-1-hexene.[29] The 6-hexenyl radical is known to cyclize rapidly to form the cyclopentylmethyl radical.[30] This same reaction (together with other evidence) has been used to show that **1** reacts with alkyl bromides by a free-radical pathway.[31] We have also carried out the same reaction and find that indeed **1** reacts with 6-bromo-1-hexene in benzene (48 h) at 22 °C to produce the cyclopentylmethyl diazenido complex. The product is isolated and purified by the methanol-adduct method in high yield. ^{1}H and ^{13}C NMR spectroscopy showed no evidence of the noncyclized product.[32]

Alkylhydrazido Complexes. Protonation of the alkyldiazenido complexes with anhydrous hydrogen bromide (**2**), aqueous-ethanolic fluoroboric acid (**2**, **5**, **8**, **11**, and **13**), and hexafluorophosphoric acid–diethyl ether complex (**5**) produced the corresponding alkylhydrazido complex in high yield. Previous work has established the site of protonation as the carbon-bound nitrogen atom.[1] The infrared spectra all exhibit ν(NH) at ca. 3275 cm^{-1} except for complex **3**, where ν(NH) appears at 2780 cm^{-1}. We believe that this rather dramatic difference between the bromide and the tetrafluoroborate salts is due to hydrogen bonding between the nitrogen-bound hydrogen atom and the counterion.[1] The nitrogen-nitrogen stretching vibration has been shifted to lower energy upon protonation but it has not been possible to assign a band to the new nitrogen-nitrogen stretch despite $^{15}N_2$ labeling.

Protonation of the azide complex **13** causes no change in the ν(N$_3$) frequency upon forming the hydrazido complex. However, protonation of the thiocyanate complex **11** produces a hydrazido complex with only one broad ν(NCS) band at 2038 cm^{-1}. The CS stretching and NCS bending regions are obscured by ligand phenyl bands. However, **12** is probably the N-bonded isomer since (a) the ν(CN) frequency occurs below 2100 cm^{1} and (b) the presence of the π-accepting ligands and the unit of positive charge on the complex will tend to make molybdenum less electron rich with the result that molybdenum will be a hard acid toward a sixth ligand (i.e., thiocyanate ion).[28a]

In the ^{1}H NMR spectra (Table I) a broad N–H resonance is observed in **4**, **7**, and **9** but not in **3**. However, in both **3** and **4** the methyl protons appear as a doublet due to coupling with the nitrogen-bound proton.

Formation of Amines and Ammonia. The results of the hydrogenolysis of **5** are summarized in Tables II and III. Yields of ammonia and amine determined as total base are given in Table II while yields of ammonia and amine determined separately are given in Table III. Ammonia and amines were removed from the product mixture by distillation in vacuo and then converted to the hydrobromide salts in order to isolate them from the organic solvents. For reactions run under similar conditions the data in the two tables correlate well. Yields of ammonia and amine are roughly equal in most reactions, although the amine yields are often slightly higher, which is probably due to loss of ammonia during workup. In addition to establishing the yields of butylamine, the gas chromatogram also indicated the presence of another nitrogen-containing compound. This compound was shown to be butylmethylamine by GC–MS and by comparison with an authentic sample. In similar reactions with MoI($N_2C_6H_{11}$)(dppe)$_2$, both cyclohexylamine and *N*-cyclohexyl-*N*-methylamine were identified as products.

No hydrogenolysis was observed with palladium on charcoal and dihydrogen. At temperatures below 200 °C, unreacted complex could be recovered. However, sodium borohydride and sodium methoxide in a benzene–methanol solution were effective in hydrogenolysis reactions of **5**. Sodium borohydride reacts rapidly with methanol in a 1:1 benzene–methanol solution at 60 °C to produce sodium tetramethylborate and liberate 99% of the theoretical amount of dihydrogen in 0.5 h.[33] Yields of ammonia and amine were lower when sodium methoxide was used compared with sodium tetramethylborate. Methanol was chosen as a cosolvent for two reasons. Firstly, it had been noted that methanol interacts strongly with **5** and it was felt that this might provide sufficient perturbation for subsequent attack by other reagents. Secondly, methanol had previously been shown to be far superior to other solvents for the production of ammonia in the reaction of compounds of the type M(N_2)$_2$(PR$_3$)$_4$ (M = Mo, W) with sulfuric acid, and it was later shown that methanol alone at reflux or under irradiation was able to effect the reduction of dinitrogen to ammonia in the complex *cis*-W(N_2)$_2$(PMe$_2$Ph)$_4$.[34] Methanol alone did not hydrogenolyze **5**. When ethanol was used as a cosolvent, yields of nitrogen-containing base were lower than with methanol and MoH$_4$(dppe)$_2$ was isolated among the products.

The temperature at which reactions were run has been found to be an important factor in controlling the extent to which reduction occurs. This, coupled with the necessity for a definite

Table II. Reduction of $MoBr(N_2C_4H_9)(dppe)_2$. Determination of Total Base[a]

reductant[b]	system[c]	solvent[d]	atm[e]	temp, °C	time, h	yield, %[f]
$NaBH_4$	A	b/m	H_2	50	64	*g, h*
Pd/C	A	b/m	H_2	70	100	*i*
None	A	b/m	H_2	75	64	*i*
$NaBH_4$	A	b/m	H_2	75	96	33.4
$NaBH_4$	A	b/m	H_2	75	69	37.5
$NaBH_4$	A	b/m	H_2	75	64	50.3[h]
$NaBH_4$	A	b/m	H_2	85	86	50.4
None	A	b/m	H_2	85	83	<1
None	A	b/m	H_2	85	86	<1
Pd/C	A	b/m	H_2	85	87	<1
$NaBH_4$	A	b/m	H_2	150	36	55.4
$NaBH_4$	A	b/m	H_2	85	36	49.9
$NaBH_4$	A	b/m	N_2	85	36	50.6
$NaBH_4$	A	b/e	H_2	85	37	8.5
$NaBH_4$	A	b/e	H_2	85	18	14.5
$NaBH_4$	A	b/m	H_2	50	18	8
$NaBH_4$	A	b/m	H_2	70	16	31.0
$NaBH_4$[j]	A	b/m	H_2	70	18	<0.5
$NaBH_4$	A	b/m	H_2	100	16	57.6
$NaBH_4$	B	b/m	N_2	104	16	23.6
$NaBH_4$	B	b/m	N_2	104	22	30.7
$NaBH_4$	B	b/m	V	100	37.5	32.9
$NaBH_4$	B	b/m	V	90	1.25	<1
$NaOCH_3$	B	b/m	V	78	16	12.1
$NaOCH_3$	B	b/m	V	91	23	8.5
$NaOCH_3$	B	m	V	90	60	4.3
$NaOCH_3$	A	b/m	H_2	100	16	29.9
$NaOCH_3$	B	b/m	V	90	22	10.8

[a] Determined by titration. [b] Initial reductant or catalyst added. [c] A = 1 L MagneDrive packless autoclave; B = modified Parr bottle. [d] b/m = 3:5 (by vol) benzene–methanol solvent; b/e = 1:1 (by vol) benzene–ethanol solvent; m = methanol solvent. [e] Gas added to the reaction vessel; V = no gas added. [f] Yield is percent total base as determined by titration with 0.104 M HCl solution. [g] Not determined. [h] $C_4H_9NH_2$ identified by mass spectroscopy. [i] No $C_4H_9NH_2$ produced. [j] Blank reaction; no diazenide used.

Table III. Reduction of $MoBr(N_2C_4H_9)(dppe)_2$. Determination of Ammonia and Amines[a]

temp, °C	time, h	% yield (amine)[b]	% yield (NH_3)[c]
100	10	53.8	34.2
75	10	32.8	25.8
50	10	*d*	0.5
125	10	58.3	50.2
140	10	55.1	56.2
140	10	38.0 (56.1)	55.0
125	10	52.6 (71.1)	47.0
100	10	53.8 (63.4)	50.7
75	10	31.5 (45.1)	39.4
65	10	26.3 (35.8)	26.5
60	10	9.6 (14.8)	4.2
100[e]	9	*f*	46.2
100[g]	10	*h*	18.7
85[i]	10	*j*	10.8

[a] Reaction carried out in a 1-L MagneDrive packless autoclave in a 3:5 (by vol) benzene–methanol solvent with ca. 10 mol of $NaBH_4$/mol of diazenide complex. [b] Determined by quantitative gas chromatography; number in parentheses is the yield of butylamine and *N*-methylbutylamine. [c] Determined by the indophenol method.[16] [d] Trace. [e] Reduction of $MoI(N_2C_6H_{11})(dppe)_2$. [f] Not determined; cyclohexylamine and *N*-methylcyclohexylamine identified by GC–MS. [g] Reduction of $WBr(N_2C_4H_9)(dppe)_2$. [h] Not determined; butylamine identified by GC–MS. [i] Reduction of $MoBr(N_2CH_2COOC_2H_5)(dppe)_2$. [j] Not determined.

initiation period during which time no nitrogen base formation occurred (1.25 h at 90 °C), may point to the existence of a slow, rate-controlling step in the reduction sequence. In light of the observation that substitution reactions of $MoBr(N_2C_4H_9)(dppe)_2$, in which the bromide ion is replaced with a pseudohalide ion, are facilitated by raising the temperature, it is probable that the first step in the reduction of the butyldiazenido complex is the replacement of bromide ion by methoxide ion:

$$MoBr(N_2C_4H_9)(dppe)_2 + B(OCH_3)_4^- \rightarrow Br^- + B(OCH_3)_3 + Mo(OCH_3)(N_2C_4H_9)(dppe)_2 \quad (6)$$

Replacement of the relatively soft bromide ion by the much harder oxygen atom of a methoxide ion will raise the energy level of the molybdenum d orbitals and cause the metal to feed more electron density into the diazenido ligand.[34] Undoubtedly, molybdenum provides the six electrons required for reduction of the butyldiazenido ligand to ammonia and butylamine.

The source of hydrogen atoms during hydrogenolysis remains uncertain. Our data show that all borohydride ion has been converted to tetramethylborate ion long before any formation of nitrogen base occurs, which proves that a boron hydride species is not the hydrogen source. In reactions in which borohydride ion is not completely consumed (namely, in ethanol solution) $MoH_4(dppe)_2$ is isolated. No reduction occurred when **5** was heated alone in a 1:1 benzene–methanol solution. This means that methanol alone cannot be the initial source of hydrogen during the reduction. However, it says nothing about methanol as a hydrogen source at a later stage in the reduction pathway. It is known that alcohols can function as sources of hydrogen in reactions with transition-metal complexes,[35] and base often promotes these reactions. The hydride ion transfer from the alcohol or alkoxide ion produces an aldehyde or ketone.

Reactions in which sodium methoxide was reacted with **5** gave two interesting results. First of all yields of nitrogen base were significantly lower than when "sodium borohydride–methanol" was used. Secondly, varying quantities of *cis*-$Mo(CO)_2(dppe)_2$ were isolated. The reduced yield of nitrogen base may be the result of methoxide ion degradation of **5** to liberate dinitrogen in competition with hydrogenolysis of the alkyldiazenido ligand. A second reason for the better yields of nitrogen base when "sodium borohydride–methanol" was used could arise if tetramethylborate ion or methoxyborane species are more effective hydrogen transfer agents than methoxide ion or methanol. The formation of the carbonyl complex suggests that methoxide ion is behaving as a hydride ion source producing formaldehyde which is able to transfer two hydrogen atoms and form carbon monoxide.

Perhaps the easiest way of accounting for the formation of butylmethylamine is to allow for the production of formaldehyde (vide supra) which is known to react at elevated temperatures with primary and secondary amines to give *N*-methyl substituted amines.[36] An alternative route to butylmethylamine would involve a methyl group transfer from a methoxyborate species to the coordinated butyldiazenido ligand or a reduced form of the ligand. Alkoxyboranes are known to behave as alkylating agents in the presence of Lewis acids or strong anhydrous proton acids.[37] However, if this were the mechanism, higher yields of the secondary amine might be anticipated.

Similar reduction reactions using sodium borohydride in a benzene–methanol solvent system have been carried out with

$MoI(N_2C_6H_{11})(dppe)_2$, $WBr(N_2C_4H_9)(dppe)_2$, and $MoBr(N_2CH_2COOC_2H_5)(dppe)_2$. Only ammonia was analyzed for quantitatively in all three cases (see Table III). The yield of ammonia was considerably lower in the tungsten compound compared with its analogue **5**.

Studies are underway that will hopefully provide a more complete picture of the mechanism of this reaction.[38] One final point: ammonia and amines are formed during the reaction and are not the result of the acid hydrolysis of the final reaction mixture.

Acknowledgments. We are grateful to the National Science Foundation for partial support of this work through Grant CHE76-80878. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Gratitude is expressed for miscellaneous support from the Nebraska Council and NIH Biochemical Science Support Grants, the 3M Co. (summer fellowship), Conoco (summer fellowship), and Molybdenum Climax (chemicals). Thanks are also expressed to Carol M. Fendrick and Andrew Tang of our department for experimental assistance, and Dr. P. Lyon for the mass spectral data. One of us (S.D.A.I.) thanks Sigma Xi (Scientific Research Society of North America) for a Grant-in-Aid of Research.

References and Notes

(1) Part 3: Busby, D. C.; Day, V. W.; George, T. A.; Iske, Jr., S. D. A.; Wagner, S. D. *J. Am. Chem. Soc.*, *submitted for publication.*

(2) Based in part on (a) Busby, D. C. Ph.D. Thesis, University of Nebraska—Lincoln, 1978. (b) Iske, Jr., S. D. A. Ph.D. Thesis, University of Nebraska—Lincoln, 1977.

(3) Parshall, G. W. *J. Am. Chem. Soc.* **1967,** *89*, 1822–1826.

(4) McCleverty, J. A.; Seddon, D.; Whiteley, B. N. *J. Chem. Soc., Dalton Trans.* **1975,** 839–844.

(5) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975,** *14*, 2784–2795.

(6) Busby, D. C.; George, T. A. "Abstracts of Papers", 13th Midwest Regional Meeting of the American Chemical Society, Rolla, Mo., 1977; American Chemical Society: Washington, D.C., **1977**.

(7) Busby, D. C.; George, T. A. *Inorg. Chim. Acta Lett.* **1978,** *29*, L273–L274.

(8) Day, V. W.; George, T. A.; Iske, Jr., S. D. A. *J. Am. Chem. Soc.* **1975,** *97*, 4127–4128.

(9) Bevan, P. C.; Chatt, J.; Leigh, G. J.; Leelamani, E. G. *J. Organomet. Chem.* **1977,** *139*, C59–C62.

(10) George, T. A.; Noble, M. E. *Inorg. Chem.* **1978,** *17*, 1678–1679.

(11) Chatt, J.; Heath, G. A.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974,** 2074–2082.

(12) Weatherburn, M. W. *Anal. Chem.* **1967**, *39*, 971–974.

(13) Day, V. W.; George, T. A.; Iske, Jr., S. D. A.; Wagner, S. D. *J. Organomet. Chem.* **1976,** *112*, C55–C58.

(14) George, T. A.; Busby, D. C.; Iske, Jr., S. D. A. *Adv. Chem. Ser.* **1978,** *168*, 147–157.

(15) Haymore, B. L.; Ibers, J. A.; Meek, D. W. *Inorg. Chem.* **1975,** *14*, 541–546.

(16) Complex **8** was prepared by the reaction of **1** with $(CH_3)_3C$-CHDCHDBr.[17]

(17) Bossard, G. E.; George, T. A., unpublished results.

(18) Lewis, R. A.; Korpiun, O.; Mislow, K. *J. Am. Chem. Soc.* **1967,** *89*, 4786–4787.

(19) Frazier III, C. C.; Kisch, H. *Inorg. Chem.* **1978,** *17*, 2736–2744.

(20) Wrighton, M.; Morse, D. *J. Organomet. Chem.* **1975,** *97*, 405–420.

(21) Saito, H.; Fujeta, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1968,** *41*, 359–364, 863–874.

(22) Bant, P.; Feltham, R. D. *J. Organomet. Chem.* **1976,** *120*, C53–C57.

(23) Caruana, A.; Kisch, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 328.

(24) Carter, J. B., personal communication. We wish to thank Dr. Carter for providing us with a copy of his thesis prior to publication.

(25) In C_{2v} symmetry, phosphorus d orbitals combine to give a_1, b_1, and b_2 molecular orbitals to which $Mo \rightarrow P_4$ CT transitions are allowed; these are $^1A_1 \rightarrow {}^1B_1,B_2$.[24]

(26) Fendrick, C. M.; George, T. A., unpublished results.

(27) Pouchert, C. J., Ed. "The Aldrich Library of Infrared Spectra," 2nd ed.; Aldrich Chemical Co.: Milwaukee, 1975.

(28) (a) The stretch at 2000 cm^{-1} is probably due to $Mo(NCS)_2(dppe)_2$ as an impurity: Pickett, C. L., personal communication. (b) Turco, A.; Pecile, C. *Nature (London)* **1961,** *191*, 66–67. Burmeister, J. L. *Coord. Chem. Rev.* **1966,** *1*, 205–221.

(29) Walling, C.; Colffari, A. *J. Am. Chem. Soc.* **1970,** *92*, 6609–6611, and references cited therein.

(30) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968,** *90*, 7047–7055. Walling, C.; Cooley, J. H.; Ponaras, A.; Racah, E. J. *Ibid.* **1966,** *88*, 5361–5362.

(31) Chatt, J.; Head, R. A.; Leigh, G. J.; Pickett, C. L. *J. Chem. Soc., Dalton Trans.* **1978**, 1638–1647.

(32) $NNC_dH_2\overline{C_cHC_bH_2C_aH_2C_aH_2C_b}H_2$. ^{13}C NMR (C_6D_6, δ): C(a), 25.8; C(b), 30.4; C(c), 39.3; C(d), 54.5 ppm. ^1H NMR ($CDCl_3$, τ): 8.22 (d, 2, J = 5.5 Hz), *8.54–8.94 (m, 9). The* ^{13}C *NMR data are similar to those reported for* the cyclopentylmethylhydrazido complex $[WBr(NNHCH_2\overline{CHCH_2CH_2CH_2CH_2})(dppe)_2]Br$,[31] and the ^1H NMR data agree well with organic cyclopentylmethyl derivatives.[33]

(33) "Sadler Standard Carbon-13 NMR Spectra"; Sadler Research Laboratories Inc.: Philadelphia, 1978.

(34) (a) This work. (b) Steinberg, H.; Brotherton, R. J. "Organoboron Chemistry", Vol. **1**; Wiley: New York, 1966; p 614.

(35) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977,** 1852–1860.

(36) Sasson, Y.; Blum, J. *J. Chem. Soc., Chem. Commun.* **1974,** 309–310. Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977,** *16*, 137–142. Shunn, R. A. In "Transition Metal Hydrides", Muetterties, E. L., Ed.; Marcel Dekker: New York, 1971; pp 222–223. Cross, R. J. *Inorg. Chim. Acta Rev.* **1969,** *3*, 75–79, and references cited therein.

(37) Walker, J. F. "Formaldehyde", 2nd ed.; Reinhold: New York, 1953; p 285.

(38) See ref 34b, p 152.