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Reactions of Coordinated Dinitrogen.[1] 3. Reactions of Iodoalkanes with Bis(dinitrogen)bis[ethylenebis(diphenylphosphine)]molybdenum[2]

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Bis(dinitrogen)bis[ethylenebis(diphenylphosphine)]molybdenum, $Mo(N_2)_2(dppe)_2$ (**1**), reacts with CH_3I, n-C_4H_9I, $C_6H_{11}I$, and n-$C_8H_{17}I$, respectively, to form the corresponding 2-alkyldiazenido-*N* derivative, $MoI(N_2R)(dppe)_2$, with loss of 1 equiv of dinitrogen. In benzene solution, these reactions occur slowly in the dark but much faster in light. The carbon-bound nitrogen atom is protonated by strong acid to form 2-alkylhydrazido(2−)-*N* complexes of the type $[MoI(N_2HR)(dppe)_2]^+$. $MoI(N_2C_6H_{11})(dppe)_2$ is converted into $Mo(OH)(N_2C_6H_{11})(dppe)_2$ when it is eluted on an alumina column with tetrahydrofuran. The ν(NN) stretching frequency has moved 75 cm^{-1} to lower energy. The preparation and characterization of all new compounds are presented together with a discussion of their spectral properties.

Introduction

The first report of the formation of a carbon–nitrogen bond from the reaction of metal-bound dinitrogen involved the reaction of organic acid chlorides with $W(N_2)_2(dppe)_2$ (**14**) to produce 2-acyl- and 2-aroylhydrazido(2−)-*N* complexes of the type $[WCl_2(N_2HCOR)(dppe)_2]$.[3] Hydrogen chloride can be removed by base to form the corresponding neutral 2-acyl- or 2-aroyldiazenido-*N* complexes ($-N_2COR$).

Subsequently, it has been shown that alkyl bromides and iodides react with **1** and **14** to produce 2-alkyldiazenido-*N* derivatives of the type $MX(N_2R)(dppe)_2$, where M = Mo or W, X = Br or I, and R = alkyl (eq 1).[4-6]

$$M(N_2)_2(dppe)_2 + RX \rightarrow MX(N_2R)(dppe)_2 + N_2 \quad (1)$$

An X-ray structure determination was carried out on yellow-orange single crystals of $MoI(N_2C_6H_{11})(dppe)_2\cdot{}^1/_2C_6H_6$.[6,7] The singly bent cyclohexyldiazenido and iodide ligands occupy trans positions in the octahedral-coordination polyhedron.

Simple alkyl chlorides such as methyl chloride, benzyl chloride, and triphenylmethyl chloride react with **1** to form $MoCl_2(dppe)_2$ (eq 2).[2a,5,8] However, ethyl chloroacetate does

$$Mo(N_2)_2(dppe)_2 + 2C_6H_5CH_2Cl \rightarrow MoCl_2(dppe)_2 + C_{14}H_{14} + 2N_2 \quad (2)$$

react with **1** to give a mixture from which $MoCl(N_2CH_2COOC_2H_5)(dppe)_2$ and $MoCl_2(dppe)_2$ can be isolated.[10]

The carbon-bound nitrogen atom of the alkyldiazenido ligand can be protonated by strong aqueous or anhydrous acid to give the corresponding alkylhydrazido complex (eq 3).[5,10,11]

$$MoX(N_2R)(dppe)_2 + HBF_4 \rightarrow [MoX(N_2HR)(dppe)_2]BF_4 \quad (3)$$

The crystal structures of $[MoI(N_2HC_8H_{17})(dppe)_2]I$ (**10**)[11] and $[WBr(N_2HCH_3)(dppe)_2]Br$ (**14**)[12] have been reported, and in the former case the unique hydrogen atom was located. Aryldiazenido (or aryldiazo) metal complexes have been known for some time, and the ligand coordinates in either a singly bent[13] or doubly bent fashion,[14] or somewhere between the two extremes.[15] Protonation of these complexes may occur at the metal, at either nitrogen atom, or not at all, depending upon factors such as metal oxidation state and coordination number and the coligands present.[16] So far, protonation of alkyldiazenido complexes has always occurred at the carbon-bound nitrogen, based upon the chemical shift of the N–H hydrogen atom in the proton NMR spectrum. However, while many alkyldiazenido complexes are known, they are almost exclusively of the type $MX(N_2R)(dppe)_2$, where M = Mo or W, X = Cl, Br, or I, and R = alkyl. The exceptions are $(\eta^5\text{-}C_5H_5)M(CO)_2N_2CH_2Si(CH_3)_3$ (M = Mo or W) and $(\eta^5\text{-}C_5H_5)W(CO)(P(C_6H_5)_3)N_2CH_2Si(CH_3)_3$,[17] $[(C_4H_9)_4Bu][(\eta^5\text{-}C_5H_5)(CO)_2MN_2(COOC_2H_5)COH]$ (M = Mo or W),[18] $(\eta^5\text{-}C_5H_5)W(CO)_2N_2CH_3$,[19] and $Li[(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2CH_3]$.[20] The latter compound and its phenyl analogue are prepared by the reaction of $(\eta^5\text{-}C_5H_5)Mn(CO)_2N_2$ with LiR. In the resulting anion the organic moiety is attached to the metal-bound nitrogen. The other compounds were prepared by reactions not involving coordinated di-

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[8] Previously, we had reported[6] the formation of $MoX(N_2)(dppe)_2$ where X = Cl or Br as products from the reaction of methyl chloride and methyl bromide with **1**. We also believed these compounds to be products from the reaction of benzyl chloride and bromide, triphenylmethyl chloride and bromide, and α-bromo-*p*-xylene with **1**.[2a] Our conclusions were based upon the elemental analyses, infrared spectra, and magnetic susceptibilities (one unpaired electron observed; $\mu_{eff} \simeq 1.8\ \mu_B$). It has been shown that these compounds are identical with a 1:1 cocrystallized mixture of **1** and $MoX_2(dppe)_2$.[9]

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nitrogen. Where studied, monoprotonation in these complexes occurs on the metal-bound nitrogen atom.[18,20]

Reactions of *α*,*ω*-dibromoalkanes with **1** or **14** afford dialkylhydrazido complexes of the type $[MBr(N\overline{N(CH_2)_3CH_2})(dppe)_2]Br$ in which the alkylene group has its ring closed on the terminal nitrogen atom to form a heterocycle.[21a] A dialkylhydrazido complex, $WBr_2(N_2(CH_3)_2)(dppe)_2$, was isolated from the reaction of excess methyl bromide and **14**.[5] *gem*-Dibromides react with **1** or **14** to give diazoalkane complexes of the type $[MBr(NNCHR)(dppe)_2]Br$.[21b]

Mechanistic data consistent with a free-radical process for the formation of alkyldiazenido complexes of molybdenum and tungsten from alkyl halides and **1** or **14** have been reported.[9] The rate-determining step in the overall reaction is loss of one dinitrogen ligand. In benzene solution when R is relatively stable, e.g., $C_6H_5CH_2\cdot$ and $(C_6H_5)_3C\cdot$, no diazenido complex is observed. When R is less stable, e.g., $CH_3\cdot$ and $C_6H_{11}\cdot$, high yields of the alkyldiazenido complex are formed. However, when the reaction is carried out above room temperature, increasing quantities of the dihalide are formed.[2a]

Alkyldiazenido complexes of the type reported in this paper can be converted into equimolar amounts of primary amine and ammonia upon treatment with strong base, e.g., sodium methoxide.[4] In this paper, we report the preparation and physical properties of alkyldiazenido and alkylhydrazido complexes derived from reactions of **1** with alkyl iodides in benzene solution. Recently, a comprehensive and critical review of the chemistry of coordinated dinitrogen has been published.[22]

Experimental Section

All preparations and crystallizations were carried out under a dinitrogen atmosphere with use of standard vacuum-line, drybox, or glovebag techniques unless otherwise specified. Irradiation of solutions in Pyrex vessels was accomplished with the use of either a 100-W, 100-A Blak-Ray lamp (Ultra-Violet Products, Inc.), a xenon arc lamp (Hanovia Chemical and Mfg. Co.), or three Sylvania 100-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.

All solvents were reagent grade and were dried and distilled under a dinitrogen atmosphere from an appropriate drying agent. 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. Methyl iodide was purchased from commercial sources while butyl iodide,[23] cyclohexyl iodide,[24] and octyl iodide[25] were prepared by published procedures. All iodides were distilled and stored in the dark at 0 °C over mercury or copper wire. $Mo(N_2)_2(dppe)_2$ (**1**) was prepared according to literature procedures,[26,27] except that in the latter method sodium amalgam was used in place of magnesium metal and the product was recrystallized from benzene–methanol solution rather than tetrahydrofuran–diethyl ether solution.

Infrared spectra were recorded with use of a Perkin-Elmer 621 spectrophotometer. Proton NMR spectra were obtained on a Varian A-60D or XL-100 spectrometer. Ultraviolet and visible spectra were recorded on a Cary 14 spectrophotometer. The mass spectra of gaseous products were recorded on a Perkin-Elmer Hitachi RMUI-6D double-focusing mass spectrometer or a Varian ICR-9 spectrometer; we thank Dr. M. L. Gross for the latter data. Melting points or decomposition points were taken in sealed capillary tubes with use of a Mel-Temp melting point apparatus and are uncorrected. All conductivity measurements were made at 25 °C in nitrobenzene solution at a concentration of 1.0×10^{-3} M by employing a Beckman Model RC16B2 conductivity bridge using a platinum-enclosed conductivity cell.

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory or Micro-Tech Laboratories, Inc.

Syntheses. Bis[ethylenebis(diphenylphosphine)]iodo(2-methyldiazenido-*N*)molybdenum (2). A. Into a solution of 0.50 g (0.53 mmol) of **1** in benzene (90 mL) was condensed 0.68 mmol of methyl iodide by using a vacuum line. After two freeze–pump–thaw cycles, the reaction mixture was sealed by means of a vacuum stopcock while under vacuum at −196 °C. Upon reaching ambient temperature, the solution was irradiated (Blak-Ray lamp) at 24 °C for 64 h. At the end of this period, the noncondensable (−196 °C) gases were identified as N_2, CH_4, and C_2H_6. The reaction suspension was filtered through a medium-porosity frit to yield a yellow solid. The filtrate contained a mixture of **1** and **2**. The yellow solid was crystallized from a dichloromethane–diethyl ether (1:1) solution to give yellow-orange crystalline **2** (0.32 g, 57%), mp 221 °C dec. Anal. Calcd for $MoI(N_2CH_3)(dppe)_2\cdot CH_2Cl_2$, $C_{54}H_{53}Cl_2IMoN_2P_4$: C, 56.51; H, 4.66; N, 2.44; Cl, 17.23. Found: C, 54.70; H, 4.51; N, 2.33; Cl, 16.67. Large single crystals of **2** were grown by slow evaporation of the above solvent mixture. The crystals were triclinic, P_1, with $a = 10.371$ (1) Å, $b = 10.628$ (1) Å, $c = 12.699$ (2) Å, $\alpha = 103.81$ (1)°, $\beta = 95.34$ (1)°, $\gamma = 118.12$ (1)°, $Z = 1$, $D_{calcd} = 1.52$ g cm^{-3}, and $D_{measd} = 1.54$ g cm^{-3}.

B. Under similar conditions, except that all operations were conducted under a red lamp in a darkroom, **1** (0.60 g, 0.63 mmol) and CH_3I (0.77 mmol) in benzene (200 mL) were stirred together in total darkness for 108 h at 25 °C. Comparable yield of product was obtained.

Bis[ethylenebis(diphenylphosphine)]iodo[2-methylhydrazido(2−)-*N*]molybdenum Tetrafluoroborate (3). Upon formation of **2** by procedure A or B, the crude product mixture dissolved in dichloromethane was treated with an excess of a 48% aqueous HBF_4 solution in ethanol solvent. After the solution had been stirred for 1.5 h, a yellow solid was removed by filtration and the filtrate volume reduced until a brown material precipitated. The brown solid collected by filtration was crystallized from an ethanol–heptane (1:1) solution to yield $[MoI(N_2HCH_3)(dppe)_2]BF_4$, mp 206 °C dec.

A benzene solution (100 mL) of $(C_2H_5)_3N$ (1.0 mL) was added to a stirred suspension of **3** (0.26 g, 0.23 mmol) in a small volume of benzene. There was an immediate color change to orange-yellow. After filtration, the solvent volume was reduced to about 50 mL and an equal volume of heptane added to precipitate an orange-yellow product. The solid was collected by filtration, washed with ethanol and heptane, and dried under vacuum to yield **2** (0.22 g, 89%), mp 221 °C dec. Anal. Calcd for $MoI(N_2CH_3)(dppe)_2\cdot{}^1/_2C_6H_6$, $C_{56}H_{54}IMoN_2PO_4$: C, 61.04; H, 4.95; N, 2.54; I, 11.52. Found: C, 61.18; H, 4.97; N, 2.50; I, 11.55.

Bis[ethylenebis(diphenylphosphine)](2-*n*-butyldiazenido-*N*)iodomolybdenum (4). *n*-Butyl iodide (0.37 mL, 3.2 mmol) was added to a solution of **1** (2.78 g, 2.90 mmol) in benzene (150 mL). The solution was evacuated at −196 °C and sealed by means of a vacuum stopcock. Upon reaching ambient temperature, the solution was irradiated (three 100-W light bulbs) for 7 h with stirring. The solution had noticeably darkened during this time. The solution was filtered and the volume reduced to about 100 mL. Methanol (160 mL) was added. After having been allowed to stand for 3 h, the solution was filtered and solvent evaporated to dryness, yielding a yellow solid which was washed with heptane and dried. This material was dissolved in a minimum volume of 2-propanol, and the solution was allowed to stand overnight. The orange crystals were filtered off, washed with 2-propanol, and dried in vacuo to yield pure **4** (1.32 g, 41%), mp 188 °C dec. Anal. Calcd for $MoI(N_2C_4H_9)(dppe)_2$, $C_{56}H_{57}IMoN_2P_4$: C, 60.88; H, 5.20; N, 2.54; I, 11.49. Found: C, 60.26; H, 5.24; N, 2.39; I, 11.35. We thank Molly Chang for preparing this compound.

Bis[ethylenebis(diphenylphosphine)](2-cyclohexyldiazenido-*N*)iodomolybdenum (5). A benzene (220 mL) solution of **1** (3.01 g, 3.17 mmol) and cyclohexyl iodide (0.74 g, 3.52 mmol) was stirred at 18 °C for 84 h in vacuo under irradiation (Blak-Ray lamp). After

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filtration, the solvent was removed and the orange-yellow solid was crystallized from a benzene–heptane (1:1) solution to yield **5** (2.88 g, 80%), mp 204 °C dec. Anal. Calcd for $MoI(N_2C_6H_{11})(dppe)_2 \cdot {}^1/_2C_6H_6$, $C_{61}H_{62}IMoN_2P_4$: C, 62.62; H, 5.35; N, 2.40; I, 10.85. Found: C, 62.59; H, 5.29; N, 2.25; I, 10.89.

Bis[ethylenebis(diphenylphosphine)][2-cyclohexylhydrazido(2–)-*N*]iodomolybdenum Tetrafluoroborate (6). To 0.74 g (0.65 mmol) of **5** dissolved in benzene (200 mL) was added an ethanol (200 mL) solution containing 1.0 mL of a 48% aqueous HBF_4 solution. After being stirred for 5 min, during which time the color changed from orange-brown to green-brown, the suspension was filtered. The filtrate volume was reduced to ca. 100 mL and an equal volume of heptane added to precipitate greenish tan $[MoI(N_2HC_6H_{11})(dppe)_2]BF_4$ (0.54 g, 63%), mp 211 °C dec. Anal. Calcd for $C_{58}H_{60}BF_4IMoN_2P_4$: C, 57.19; H, 4.97; N, 2.30; F, 6.24. Found: C, 57.22; H, 5.06; N, 2.15; F, 6.13.

Bis[ethylenebis(diphenylphosphine)](2-cyclohexylhydrazido(2–)-*N*)iodomolybdenum Hydrogen Dichloride (7). A mixture of anhydrous hydrogen chloride (5.70 mmol) and **1** (0.64 g, 0.57 mmol) was stirred in benzene (250 mL) solution for 12 h at 23 °C. The green-yellow solid formed was collected by filtration and was crystallized from a THF–heptane (1:1) solution. The beige first fraction was not characterized. Upon reduction of the volume in vacuo, a green-yellow second fraction, shown to be $[MoI(N_2HC_6H_{11})(dppe)_2]HCl_2$ (0.11 g, 16%), mp 132 °C dec, was obtained. Anal. Calcd for $C_{58}H_{61}Cl_2IMoN_2P_4$: C, 57.86; H, 5.12; N, 2.33; I, 10.54; Cl, 5.89. Found: C, 57.98; H, 5.29; N, 2.24; I, 10.53; Cl, 4.36.

Bis[ethylenebis(diphenylphosphine)]iodo(2-*n*-octyldiazenido-*N*)-molybdenum (8). *n*-Octyl iodide (1.10 g, 4.30 mmol) was added to a solution of **1** (3.95 g, 4.20 mmol) in benzene (300 mL). After three freeze–pump–thaw cycles, the reaction was allowed to reach ambient temperature and stirred for 20 h under room fluorescent lighting. A small amount of green solid was removed by filtration. The filtrate volume was reduced to 100 mL and heptane (150 mL) added. The yellow precipitate was removed by filtration and the filtrate volume further reduced to ca. 60 mL. The resulting bright orange solid was crystallized by dissolving in benzene (60 mL) and adding heptane (90 mL). When the volume was reduced to ca. 50 mL, the rich orange product was removed by filtration, washed with heptane, and dried in vacuo to yield $MoI(N_2C_8H_{17})(dppe)_2$ (3.41 g, 69%), mp 195 °C dec. Anal. Calcd for $C_{60}H_{65}IMoN_2P_4$: C, 62.08; H, 5.64; N, 2.41; I, 10.93. Found: C, 61.82; H, 5.59; N, 2.30; I, 11.17.

Bis[ethylenebis(diphenylphosphine)]iodo[2-*n*-octylhydrazido(2–)-*N*]molybdenum Tetrafluoroborate (9). To a benzene (5 mL) solution of **10** (0.28 g, 0.24 mmol) was added a 48% aqueous HBF_4 solution (0.25 mL) and ethanol (50 mL). The solution immediately changed from brown-orange to brown-green. After 0.2 h of stirring and after filtration, heptane (50 mL) was added and the solution chilled to –78 °C. From this solution were obtained large brown needles of $[MoI(N_2HC_8H_{17})(dppe)_2]BF_4$ (0.18 g, 60%), mp 224 °C. Anal. Calcd for $C_{60}H_{66}BF_4IMoN_2P_4$: C, 57.69; H, 5.39; N, 2.31; I, 10.80. Found: C, 57.71; H, 5.33; N, 2.24; I, 10.16.

Bis[ethylenebis(diphenylphosphine)]iodo[2-*n*-octylhydrazido(2–)-*N*]molybdenum Iodide (10). Hydrogen iodide was bubbled through a benzene (125 mL) solution of **8** (0.53 g, 0.45 mmol) for 0.25 h. After dinitrogen was bubbled through the solution for 0.25 h, the green suspension was filtered and diethyl ether (200 mL) added. Stirring was maintained for 0.25 h and a second filtration conducted. The green filtrate was reduced in volume to ca. 60 mL, and heptane was (100 mL) added slowly. The resulting green precipitate was filtered off, washed with heptane, and dried in vacuo to give 0.44 g (76%), mp 190 °C dec, of **10**. Further purification was accomplished by dissolving the product in warm benzene (ca. 50 °C, 100 mL) and adding heptane dropwise with swirling until the solution became just cloudy. Slow evaporation of solvent from the solution in a dinitrogen-flushed glovebag produced dark green crystals (24 h) that were filtered off, washed with heptane, and dried in vacuo. Anal. Calcd for $[MoI(N_2HC_8H_{17})(dppe)_2]I$, $C_{60}H_{66}I_2MoN_2P_4$: C, 55.92; H, 5.16; N, 2.17; I, 19.69. Found: C, 56.40; H, 5.20; N, 2.13; I, 20.39. $\Lambda = 23.17\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Bis[ethylenebis(diphenylphosphine)]iodo[2-*n*-octylhydrazido(2–)-*N*]molybdenum Chloride (11). Anhydrous hydrogen chloride was bubbled through a benzene (100 mL) solution of **8** (0.48 g, 0.41 mmol) for 0.33 h. After filtration, the green filtrate was reduced to 35 mL and heptane was added slowly with swirling until the solution became just cloudy. After the mixture was allowed to stand for 1.5 h, the green crystals that had formed were filtered off, washed with heptane, and dried in vacuo to yield 0.29 g (59%) of **11**, mp 150 °C dec. Anal. Calcd for $[MoI(N_2HC_8H_{17})(dppe)_2]Cl$, $C_{60}H_{66}ClIMoN_2P_4$: C, 60.19; H, 5.56; N, 2.34; Cl, 2.96. Found: C, 60.43; H, 5.63; N, 2.01; Cl, 3.01. $\Lambda = 19.38\ \Omega^{-1}\ cm^2\ mol^{-1}$.

Bis[ethylenebis(diphenylphosphine)](2-cyclohexyldiazenido-*N*)-hydroxomolybdenum (12). Compound **12** was prepared during an attempt to purify **5** by column chromatography using alumina (Fisher Scientific Co. alumina for chromatographic analysis, 80–200 mesh). Alumina was deoxygenated under vacuum at ambient temperature (12 h) and a column (2 × 27 cm) was prepared under dinitrogen. Addition of a benzene solution of a small quantity of **5** produced a yellow fraction that eluted with benzene. This compound was not satisfactorily characterized. Elution with tetrahydrofuran produced an orange fraction. Solvent was removed and the product crystallized from a tetrahydrofuran–heptane (1:2) solution to produce pure orange **12**, mp 149 °C dec. Anal. Calcd for $Mo(OH)(N_2C_6H_{11})(dppe)_2$, $C_{58}H_{60}ON_2P_4Mo$: C, 68.22; H, 5.94; N, 2.74. Found: C, 68.31; H, 6.27; N, 2.48.

Results and Discussion

Syntheses and Characterization. Alkyldiazenido complexes of the type $MoX(N_2R)(dppe)_2$ where X = Br or I and R = alkyl have been prepared by the reaction of $Mo(N_2)_2(dppe)_2$ (**1**) with simple alkyl bromides and iodides.[4-6] The molecular structures of $MoI(N_2C_6H_{11})(dppe)_2$[6,7] and $MoI(N_2C_8H_{17})(dppe)_2$ have been determined, and the three-dimensional X-ray data will be reported in full detail in a subsequent publication.[28] Protonation of the carbon-bound nitrogen has been accomplished with strong acids to form alkylhydrazido complexes of the type $[MoI(N_2HR)(dppe)_2]Y$ where Y = Cl, Br, I, HCl_2, or BF_4. The molecular structure of $[MoI(N_2HC_8H_{17})(dppe)_2]I$ has been determined[11] by X-ray diffraction studies, and the data will be compared with those for the corresponding octyldiazenido complex in a forthcoming publication.[28] The coordinated iodide ion of the alkyldiazenido complexes can be displaced by hydroxide, azide, and thiocyanate ions, respectively. All of the compounds gave satisfactory elemental analyses. Infrared, proton NMR, and electronic absorption spectra (Table I) have been measured for the alkyldiazenido and alkylhydrazido complexes. Conductivity measurements indicate that the alkylhydrazido complexes are 1:1 electrolytes in nitrobenzene. All compounds reported are air stable and are relatively stable in solution, especially in the absence of dioxygen.

Alkyldiazenido Complexes. Methyl iodide reacts with **1** in benzene solution to form $MoI(N_2CH_3)(dppe)_2$ (**2**) (eq 4). The reaction occurs slowly in the dark but much more rapidly in the light. Normal room light is sufficient to provide a reasonable rate of reaction. Methane, ethane, and dinitrogen were identified by an ion cyclotron resonance spectral analysis of the noncondensable gases obtained after irradiating (366 nm) a benzene solution of **1** and methyl iodide in a Pyrex flask for 40 h with a 100-W 100-A Blak-Ray lamp (the reaction temperature was 39 °C). The highest yields of product were obtained when the temperature was maintained at room temperature. Compound **2** is significantly less soluble in nonpolar organic solvents than the higher homologues. This made it difficult to purify. The most satisfactory purification procedure involved adding aqueous ethanolic tetrafluoroboric acid to a dichloromethane solution of the crude product and isolating $[MoI(N_2HCH_3)(dppe)_2]BF_4$ (**3**) (eq 5). Compound **2** can be regenerated by deprotonation of **3** with triethylamine (eq 6). The main impurity is $MoI_2(dppe)_2$. Compound **2** crystallizes with a solvent molecule of dichloromethane from a dichloromethane–diethyl ether solution or half a molecule of benzene from a benzene–heptane solution.

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Table I. Spectral Data

	IR, cm^{-1} [a]				^{1}H NMR, τ (rel area)[b]						electronic abs data	
compd	ν(NN) (br)	ν(NH) (br)	other(s)	phase	solvent	alkyl	NH[c]	CH_2(P)	phenyl	other	solvent[d]	λ, nm (ϵ_{max} M^{-1} cm^{-1})
$MoI(N_2CH_3)(dppe)_2$ (2)	1542 vs		1355 vs	KBr	$CDCl_3$	8.30 (3) s		7.0–7.6 (8) d	2.4–3.0 m		C_6H_6	357 (6240), 505 (170)
$MoI(N_2C_4H_9)(dppe)_2$ (4)	1529 s, 1511 s		1347 m, 1294 s	KBr							C_6H_6	353 (6610), 500 (160)
$MoI(N_2C_6H_{11})(dppe)_2$ (5)	1550 vs		1345 m, 1289 s	KBr	CD_2Cl_2	6.94 (1) m, 8.5–9.4 (10) m		7.1–7.5 (8) m	2.3–3.0 m	2.64 s	C_6H_6	364 (6520), 506 (140)
$MoI(N_2C_8H_{17})(dppe)_2$ (8)	1535 vs		1353 vs	CsI	C_6D_6	7.90 t, 8.5–9.4 m		6.8–7.8 d	2.1–3.3 m			
$Mo(OH)(N_2C_6H_{11})(dppe)_2$ (12)	1475 vs		3600 w, 1348 w, 1332 m, 1284 m	CsI	CD_2Cl_2	7.90 (1) m, 8.5–9.4 (10) m		7.0–7.8 m	2.1–3.3 m	7.3 br s	C_6H_6	363 (5670), 510 (150)
$[MoI(N_2HCH_3)(dppe)_2]BF_4$ (3)	na	3290 m	1355 m	CsI								
$[MoI(N_2HC_6H_{11})(dppe)_2]BF_4$ (6)	na	3262 m	1390 sh, 1357 m, 1343 m	KBr	CD_2Cl_2	7.58 (1) m, 8.6–9.5 (10) m	6.52 (1) br s	6.6–7.4 d	2.3–2.9 m		C_6H_6	316 (11 130)
$[MoI(N_2HC_6H_{11})(dppe)_2]HCl_2$ (7)	na	3265 w	1355 m, 1340 m	CsI	CD_2Cl_2	7.58 (1) m, 8.6–9.5 (10) m	6.00 (1) br s	6.6–7.4 (8) d	2.3–3.0 m			
$[MoI(N_2HC_8H_{17})(dppe)_2]BF_4$ (9)	na	3260 w	1385 sh, 1330 m, 1309 m	KBr	$CDCl_3$	8.0–9.7 m	6.00 br s	6.4–7.4 d	2.2–3.0 m		THF	295 (12 800), 447 (580)
$[MoI(N_2HC_8H_{17})(dppe)_2]I$ (10)	na	3280 m	1330 m, 1308 m	CsI	$CDCl_3$	8.2 br m, 8.4–9.8 m	6.10 br d	6.4–7.6 d	2.5–3.1 m			
$[MoI(N_2HC_8H_{17})(dppe)_2]Cl$ (11)	na	3280 w	1330 m, 1305 m	CsI	$CDCl_3$	8.3 br m, 8.5–9.6 m	3.90 br s	6.2–7.8 s	2.3–3.1 m			
$[MoI(N_2HC_8H_{17})(dppe)_2]Br$ (13)[e]	na	3280 w	1332 m, 1310 m	CsI	$CDCl_3$	8.5–9.6 m, 8.0–9.6 m	5.00 br s	6.2–7.6 d	2.4–3.0 m			

[a] na = not assignable; vs = very strong, s = strong, m = medium, w = weak. [b] Relative to $Si(CH_3)_4$; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. [c] Resonances disappeared upon addition of D_2O. [d] THF = tetrahydrofuran. [e] Not analytically pure; 8 + HBr(g); Λ = 23.17 Ω^{-1} cm^{-1} mol^{-1}.

$$Mo(N_2)_2(dppe)_2 + CH_3I \rightarrow MoI(N_2CH_3)(dppe)_2 + N_2 \quad (4)$$

$$MoI(N_2CH_3)(dppe)_2 + HBF_4 \rightarrow [MoI(N_2HCH_3)(dppe)_2]BF_4 \quad (5)$$

$$[MoI(N_2HCH_3)(dppe)_2]BF_4 + N(C_2H_5)_3 \rightarrow MoI(N_2CH_3)(dppe)_2 + [N(C_2H_5)_3H]BF_4 \quad (6)$$

Cyclohexyl iodide similarly produced $MoI(N_2C_6H_{11})(dppe)_2$ (**5**) when reacted with **1**. Purification was accomplished by forming the corresponding hydrazido complex **6**, followed by deprotonation with triethylamine. Compound **5** crystallized with half a molecule of benzene from a benzene–heptane solution. The presence of the solvent of crystallization was supported by its observation in the proton NMR spectrum of **5** (τ 2.64 (s); Table I) and was confirmed by the single-crystal X-ray diffraction analysis of **5**. Compounds **2** and **5** are both diamagnetic as determined by the Faraday method.[29]

n-Butyl and *n*-octyl iodides reacted with **1** to form $MoI(N_2C_4H_9)(dppe)_2)$ (**4**) and $MoI(N_2C_8H_{17})(dppe)_2$ (**8**), respectively. Both can be purified directly by recrystallization: **4** from 2-propanol and **8** from a benzene–heptane solution, respectively.

The single most distinctive feature of the infrared spectra (Table I) of the alkyldiazenido complexes **2**, **4**, **5**, and **8** is the strong to very strong band at 1510–1550 cm^{-1} assignable to ν(NN). It is a well-defined absorption for the methyldiazenido complex **2** but is broader in the other complexes, with some structure to the band. This broadness persists in solution and mull spectra. The assignment of ν(NN) is supported by ^{15}N labeling showing a shift of ca. 45 cm^{-1} to lower energy. However, there are no other clearly discernible changes in the spectra that may be attributed to ν(CN), for example. Compound **2** shows the characteristic symmetric methyl bend associated with NCH_3 at 1355 cm^{-1}. Although peaks in the region 1200–1300 cm^{-1} are listed in Table I, no assignment is made. A number of bands appear in the 1500–1350-cm^{-1} region of the long-chain-alkyl derivatives in addition to the bands assignable to coordinated dppe.

The proton NMR spectra (Table I) of the alkyldiazenido complexes exhibit a broad multiplet between about τ 2.1 and 3.3 due to the aromatic protons, a broad multiplet (usually a doublet) between about τ 6.8 and 7.8 arising from the phosphine methylene protons, and resonance(s) due to the alkyl protons. Compound **2** exhibits a singlet at τ 8.30 due to the methyl protons. The α-hydrogen atom of the cyclohexyl group of compound **5** appears as a multiplet centered at τ 6.94 just downfield from the phosphine methylene protons. A benzene solvate molecule appears as a sharp singlet (τ 2.64) among the aromatic multiplet.

During an attempt to purify **5** by column chromatography, elution with tetrahydrofuran (after benzene failed to remove the major component) produced the hydroxo analogue **12**. This compound exhibits the lowest ν(NN) (1475 cm^{-1}) of all the molybdenum diazenido complexes that we have investigated, being 75 cm^{-1} lower in energy than the parent iodide, **5**. The ν(OH) stretch appears as a needle-sharp absorption at 3600 cm^{-1}. The proton NMR spectrum of **12** is similar to that of **5** except in two respects: (a) the α-hydrogen resonance appears at τ 7.90 (cf. τ 6.94 for **5**) and (b) the OH proton appears as a broad singlet at τ 7.3 (alongside the phosphine methylene protons) and disappears upon the addition of D_2O to the methylene-d_2 chloride solution. Attempts have been made to prepare **12** on a larger scale by alternative routes but without success. Direct metathesis with hydroxide ion in mixed solvents and/or with 18-crown-6 ether has not been successful. If a hydroxo derivative is formed under these basic conditions,

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[29] We thank E. R. Domb for the magnetic susceptibility measurements.

it would probably be rapidly deprotonated and the resulting anion may be unstable and decompose. However, **12** could be prepared consistently, on a small scale, by eluting from an alumina column after **5** had been absorbed onto the support. It would appear that the alumina provides a sufficient concentration of hydroxide ion for metathesis without being too basic.

It has been possible to replace the iodide ion of **4** with chloride ion (ν(NN) = 1522 cm^{-1}; $[(C_6H_5)_3P]_2NCl/C_6H_6/$acetone, 25 °C), azide ion (ν(NN) = 1523 cm^{-1}, $\nu(N_3)$ = 2092 cm^{-1}; $NaN_3/C_6H_6/C_2H_5OH$/18-crown-6 ether, 25 °C), and thiocyanate ion (ν(NN) = 1629 cm^{-1}, ν(NCS) = 2080 (vs) and 2000 (s) cm^{-1}; $KNCS/C_6H_6$/acetone, 25 °C). However, these compounds have been studied in more detail by preparation from $MoBr(N_2C_4H_9)(dppe)_2$.[4]

The electronic absorption spectra of the alkyldiazenido complexes in benzene solution show a maximum at about 360 nm with an extinction coefficient of about 6000 M^{-1} cm^{-1} and a low-intensity (ca. ϵ = 155) shoulder at about 505 nm. The latter absorption may be due to a d–d transition. Above the 360-nm absorption, the spectra rise steeply into the ultraviolet where the dppe ligands absorb strongly.

Alkylhydrazido Complexes. Simple alkyldiazenido complexes of molybdenum are protonated at the carbon-bound nitrogen by strong protic acids such as HCl, HBr, HI, and HBF_4. The resulting alkylhydrazido complexes are produced by the addition of excess of either an aqueous–ethanolic or aqueous solution of the acid or an anhydrous acid to a solution (benzene or methylene chloride) of the alkyldiazenido complex. The resulting alkylhydrazido complexes are air-stable, green, greenish yellow, or brown solids that show good solubility in polar and nonpolar organic (except paraffin) solvents. Compounds **10**, **11**, and **13** are 1:1 electrolytes in nitrobenzene.

In all these compounds, ν(NH) appears ca. 3270 cm^{-1} in the infrared spectra (Table I) whether they were taken as KBr or CsI pellets or as mulls. This assignment agrees very closely with those made for some similar tungsten complexes reported recently, e.g., $[WBr(NNHR)(dppe)_2]Br$ where R = $(CH_2)_4OCH_3$, $(CH_2)_2CHCH_2$, and $(CH_2)_3CO_2CH_3$.[21b] On the other hand, the same authors in an earlier article assigned ν(NH) in the 3080–2820-cm^{-1} region of some similar tungsten and molybdenum complexes (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, and t-C_4H_9).[5] This latter work was supported by deuterium-labeling experiments (ν(ND) 2320–2180 cm^{-1}). However, we have prepared the bromide and tetrafluoroborate salts of $MoBr(N_2HCH_3)(dppe)_2$, and ν(NH) appears at 2780 and 3260 cm^{-1}, respectively.[4] The X-ray structure of $[MoI(N_2HC_8H_{17})(dppe)_2]I$ shows clearly hydrogen bonding between the nitrogen-bound hydrogen and the iodide anion.[11] Hydrogen bonding is known to increase in the order H---I < H---Br < H---Cl.[30] We see no change though in ν(NH) (3280 cm^{-1}) upon changing the anion of **10** to bromide (**13**) and chloride (**11**). The bromide, **13**, has not been prepared analytically pure but its physical properties are similar to those of **10** and **11**. This large variation in the position of ν(NH) noted among alkylhydrazido complexes of molybdenum and tungsten may be the result of a number of factors, among them being (1) conformational effects of the alkyl group, (2) solvent of crystallization, (3) variation in anion, (4) differences between molybdenum and tungsten, and (5) the effect of variations in the ligand trans to the alkylhydrazido group on the basicity of the carbon-bound nitrogen. In fact, we have observed this latter effect not in the infrared spectra but in the proton NMR spectra of a series of complexes $[MoX(N_2HR)(dppe)_2]BF_4$, where R = $CH_2COOC_2H_5$ and X = Cl, Br, or I, the only variable being the trans ligand. The N–H chemical shifts in deuteriochloroform are τ 5.35 (I), 5.98 (Br), and 6.10 (Cl), respectively.[10] However, no change in ν(NH) is observed among this series.[10]

We have not been able to make an assignment for ν(NN) despite nitrogen-15 labeling. Upon protonation, the absorption bands in the 1400–1500-cm^{-1} region broaden noticeably in the low-intensity area. This may be due to the nitrogen hydrogen affecting the methylene deformation modes of the neighboring alkyl methylene groups or the asymmetric methyl bending of the methyl group. A strong band at ca. 1435 cm^{-1} has been assigned as being associated with the N_2HR ligand.[5] We find that this band appears in the parent compound **1** and all the other compounds **2**–**13** that contain the dppe ligand. There is very little change in its position or intensity irrespective of the particular molybdenum complex. It has been attributed to a planar ring-deformation vibration of the phenyl group by others.[31]

The proton NMR spectra (Table I) of the alkylhydrazido complexes exhibit a broad multiplet between about τ 2.2 and 3.1 due to the aromatic protons, a broad doublet, except in the case of **11** (a broad singlet), arising from the phosphine methylene protons, resonances due to the alkyl protons, and an N–H resonance. The assignment of the N–H resonance was based upon its disappearance when D_2O was added to a solution of the individual complex. The N–H chemical shift varied considerably. Within the octyl series in which only the anion is changing, the N–H resonance values are τ 3.90 (Cl), 5.00 (Br), 6.10 (I), and 6.00 (BF_4). Although the iodide, bromide, and chloride salts are 1:1 electrolytes in nitrobenzene, it is likely that in deuteriochloroform or methylene-d_2 chloride they exist as ion pairs, and hence the influence of hydrogen bonding causing a downfield shift is observed (certainly in **11** and **13**).[32] The change in N–H resonance is in the correct order for decreasing hydrogen bonding ($Cl^- > Br^- > I^-$) with decreasing electronegativity of the anion. This large observed change is in direct contrast to the invariance of ν(NH) to changes in anion. However, the infrared spectra were recorded in the solid phase where crystal packing will dominate, and although hydrogen bonding is observed in the iodide **10**, it may not be occurring in the bromide or chloride complexes in the solid state. On the other hand, in solvents of low dielectric constant, the formation of an ion pair may involve strong hydrogen bonding with the nitrogen-bound hydrogen atom. The proton NMR data support the latter contention.

A dramatic change in the absorption spectrum arises upon protonation, resulting in loss of the 360-nm band.[33] The absorption maximum at ca. 300 nm slowly tails into the visible region, showing a discernible maximum at ca. 450 nm. Interestingly, spectra of alkyldiazenido complexes run in 1:1 benzene–methanol solution are identical with the spectra of the corresponding alkylhydrazido complexes. The effect is not as dramatic in benzene–ethanol and benzene–2-propanol solutions. Spectra of the alkyldiazenido complexes in 1:1 benzene–dimethylformamide solution are identical with those in benzene solution. Clearly, hydrogen bonding between methanol (and to a lesser extent ethanol and 2-propanol) is causing electronic changes in the alkyldiazenido complexes equivalent to protonation.

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Poly(pyridyl)ruthenium(II) Complexes of Poly(4-vinylpyridine). Synthesis, Characterization, and Investigation of Optical and Electrochemical Properties

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A series of metallopolymers have been prepared by the reaction between poly(4-vinylpyridine) ($M_n \approx 3900$) and $[Ru(trpy)(bpy)(OH_2)]^{2+}$ (trpy is 2,2′,2″-terpyridine and bpy is 2,2′-bipyridine). The synthetic procedure allows for the degree of metalation of the polymer to be controlled in a systematic and reproducible way. The degree of metalation in a series of samples was determined by ^1H NMR, UV–vis spectroscopy, elemental analysis, and ESCA. The redox properties of materials as thin films on electrode surfaces were investigated electrochemically. The results of UV–visible absorption and emission studies in solution suggest that, in samples where the degree of metalation is low, the optical properties of the polymer-bound sites are essentially those of the related monomer $Ru(trpy)(bpy)py^{2+}$, but at high degrees of metalation, evidence for interactions between sites has been obtained.

Introduction

In the search for new chemical materials, one of the most attractive areas in chemistry is the development of metallopolymers. This relatively new class of materials has promise for applications in a number of diverse areas including heterogeneous catalysis[1] and electrode modifications,[2] in biomimetic chemistry[3] and possibly for device applications.

Our interest in the area originated with the idea of combining the potential advantages offered by polymeric materials with the extensive ground- and excited-state chemistry which has been established for poly(pyridyl) complexes of ruthenium. Similar monomeric and dimeric ruthenium complexes have proven to be of value in the development of redox catalysts,[4] for the existence of exploitable excited states,[5,6a] and as model compounds for the study of electron-transfer processes.[6]

Metallopolymers in which ruthenium–bipyridyl complexes are chemically bound to poly(4-vinylpyridine) (4-PVP) have been reported whose preparations are based on the substitutional chemistry of $Ru(bpy)_2Cl_2$.[7] In this paper we report our results on the attachment of the group $(trpy)(bpy)Ru^{II}$ (trpy is 2,2′,2″-terpyridine and bpy is 2,2′-bipyridine) to 4-PVP. The metallopolymers prepared in this manner are of interest because of the synthetic control and reproducibility available in the preparations and the high degree of definition which results from their characterization. However, the most important feature of these materials is the carryover of properties from the monomer to polymers, in terms of both electrochemical redox properties in thin films on electrode surfaces and excited-state properties of the bound chromophoric sites. Ultimately, both properties may be exploitable in a number of applications.

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