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Reactions of Coordinated Dinitrogen. 14.[1] Formation of Carbon–Nitrogen Bonds from Bis(dinitrogen) Complexes of Molybdenum

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Received September 24, 1984

The single diastereomer *trans*-$Mo(N_2)_2((S,S)\text{-Chiraphos})_2$, where (*S,S*)-Chiraphos is (−)-(2*S*,3*S*)-bis(diphenylphosphino)butane, reacted with racemic 2-bromooctane to form $MoBr(NNCH(CH_3)C_6H_{13})((S,S)\text{-Chiraphos})_2$, in which there was a ca. 10% excess of one enantiomer over the other, on the basis of the ^1H NMR spectra at 100, 200, and 396 MHz. The 1,4-dihaloalkanes 1-bromo-4-chloro- and 1,4-dibromobutane and 1,4-dibromopentane reacted with *trans*-$Mo(N_2)_2(dppe)_2$, where dppe is bis(diphenylphosphino)ethane, to form the corresponding cyclic hydrazido(2−) complex. In the first example bromine rather than chlorine bonded to molybdenum. In the last example cyclization resulted in a nitrogen atom becoming bonded to primary and secondary carbon atoms. Methyl fluorosulfonate and iodomethane alkylated $MoBr(NNC_4H_9)(dppe)_2$ to form the unsymmetrically substituted hydrazido(2−) complex $[MoBr(NN(CH_3)C_4H_9)(dppe)_2]^+$. Primary alkyl bromides did not undergo this reaction.

The first report of the formation of a carbon–nitrogen bond in reactions of stable, well-defined dinitrogen complexes appeared in 1972. Chatt and co-workers[2] reported the formation of an alkylhydrazido(2−) complex in reactions of acyl halides with *trans*-$M(N_2)_2(dppe)_2$, where M = Mo, W and dppe = $Ph_2PCH_2CH_2PPh_2$ (eq 1). Since that time many similar reactions

$$M(N_2)_2(dppe)_2 + RCOX \xrightarrow{HX} [MX(NNCOR)(dppe)_2]X + N_2 \quad (1)$$

have been reported leading to alkyldiazenido(1−) (NNR), alkylhydrazido(2−) (NNHR), dialkylhydrazido(2−) (NNRR′), and diazoalkane (NN=CRR′) complexes. A second method for the formation of carbon–nitrogen bonds involves the condensation of aldehydes and ketones with hydrazido(2−) (NNH_2) complexes first reported by Hidai and co-workers.[3] These and other carbon–nitrogen bond-forming reactions have been reviewed recently.[4-6]

It has been shown previously that dihaloalkanes such as 1,4-dibromobutane react with $Mo(N_2)_2(dppe)_2$ to form dialkylhydrazido complexes (eq 2) wherein two carbon–nitrogen bonds are formed.[7] These results prompted us to investigate the synthesis

$$Mo(N_2)_2(dppe)_2 + BrCH_2CH_2CH_2CH_2Br \rightarrow N_2 + [MoBr(\overbrace{NNCH_2CH_2CH_2CH_2}^{\text{cyclic}})(dppe)_2]Br \quad (2)$$

of unsymmetrical dialkylhydrazido complexes by the alkylation of alkyldiazenido complexes and study the mechanism of such a reaction. While work was in progress a report of the mechanism of the alkylation of alkyldiazenido complexes appeared.[8]

In view of the facile reactivity of haloalkanes with $Mo(N_2)_2(dppe)_2$, efforts have been made to prepare optically active bis(dinitrogen) complexes of molybdenum and react them with racemic organic halides as a route to enantioselective carbon–nitrogen bond formation.

This paper reports our work involving these last two areas, some of which has appeared in preliminary communications.[9]

Experimental Section

Synthesis. General Procedures. All reactions and crystallizations were carried out under a dinitrogen atmosphere or in vacuo (vapor pressure of solvent) with use of standard techniques for the manipulation of air- and moisture-sensitive compounds. Organic solvents were reagent grade and were dried by distillation from the drying agent indicated: benzene, heptane, and dichloromethane (calcium hydride); tetrahydrofuran (sodium benzophenone ketyl or calcium hydride); methanol and ethanol (corresponding magnesium alkoxide). Organic halides were purchased from commercial sources or prepared by standard literature procedures.

All solvents were bubbled with dinitrogen for at least 0.5 h before use. Usually, once the reagents had been added to the reaction vessel, the mixture was taken through three freeze-pump–thaw cycles.

The following compounds were prepared according to literature methods: *trans*-$Mo(N_2)_2(dppe)_2$,[10] $MoBr(NNC_4H_9)(dppe)_2$,[11] $MoCl_3(THF)_3$,[12] (−)-(2*S*,3*S*)-bis(diphenylphosphino)butane ((*S,S*)-Chiraphos),[13] and $[WF(NNH_2)(dppe)_2]BF_4$.[14,15]

***trans*-$Mo(N_2)_2((S,S)\text{-Chiraphos})_2$.** $MoCl_3(THF)_3$ (1.13 g, 2.70 mmol) was added to a THF (80 mL) solution of (*S,S*)-Chiraphos (2.0989 g, 4.9214 mmol) containing a 0.7% sodium amalgam (0.93 g, 40.5 mmol Na) in a round-bottom flask. After it was stirred (12 h) under N_2, the suspension was allowed to settle before it was filtered through Celite. Solvent was removed from the filtrate with use of a rotary evaporator. The residue was dissolved in toluene (50 mL) and filtered. The flash and frit were washed with toluene (25 mL). To the combined filtrate was added methanol (175 mL). Large crystals began to form after about 2 h. After 24 h the product was collected as large (2 cm long) orange-red needle-shaped crystals by filtration, washed with pentane, and dried in vacuo. The yield was 1.2774 g (52%): $[\alpha]^{25}_{589}(C_6H_6) = +671°$. IR ($cm^{-1}$, CsI): 1962 ($\nu$(NN)).

Reaction of $Mo(N_2)_2((S,S)\text{-Chiraphos})_2$ with Racemic 2-Bromooctane. 2-Bromooctane (0.1720 g, 0.8906 mmol) and $Mo(N_2)_2((S,S)\text{-Chiraphos})_2$ (0.4803 g, 0.4779 mmol) were dissolved in benzene (22 mL). After the mixture was stirred, (48 h), volatiles were removed in vacuo and collected. The residue was dissolved in benzene (10 mL) and heptane (35 mL) added. The solution was filtered and volume reduced to 5 mL. Red crystals of $MoBr(NNC_8H_{17})((S,S)\text{-Chiraphos})_2$ were filtered off, washed with pentane, and dried in vacuo: yield 78%; $[\alpha]^{25}_{589}(C_6H_6) = +323°$. ^1H NMR (396 MHz, C_6D_6): δ 0.23, 0.32 (d, J = 6.0 Hz, $CH(CH_3)$).

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0020-1669/85/1324-1129$01.50/0

In three separate experiments the volatiles, removed after reaction, containing unreacted 2-bromooctane showed a small positive optical rotation: $[\alpha]^{25}_D = +0.75-1.10°$.

$MoBr(NNCH_2CH_2CH_2CH_2OOCCH_3)(dppe)_2$. An excess of 4-bromobutyl acetate was added to $Mo(N_2)_2(dppe)_2$ (0.76 g, 0.80 mmol) in benzene (0.18 L). The mixture was stirred in vacuo for 12 h under fluorescent lights. Methanol (0.10 L) was added to the red solution. Over a period of 2 h the solution become yellow. The solvent was removed with use of a rotary evaporator. The yellow residue was extracted with ethanol (2 × 20 mL). The extracts were filtered through a fine frit, and the red filtrate was allowed to stand. After 12 h red crystals were collected by filtration and dried in vacuo to yield 0.27 g (34%) of product: mp 220 °C dec; $\Lambda = 0.96\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{62}H_{59}BrMoN_2O_2P_4$: C, 61.35; H, 5.32; N, 2.51. Found: C, 61.26; H, 5.17; N, 2.25. IR (cm^{-1}, KBr): 1735 (ν(C=O)), 1540 (ν(N=N), 1316 (ν(C—N), 1230, 1090 (ν(C—O), ester). Visible–UV (C_6H_6; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): λ_{max} 433 (370), 368 (7750). ^1H NMR (100 MHz, C_6D_6): δ 0.40–1.42 (m), 1.71 (s, 3), 1.90 (t, 2, J = 6.5 Hz), 2.08–3.06 (b, 8), 3.91 (t, 2, J = 6.5 Hz). ^{13}C NMR (50.4 MHz, $CDCl_3$) δ 20.9 (s, CH_3), 25.3 (s, CH_2), 25.8 (s, CH_2), 29.1 (m, PCH_2), 48.3 (s, NCH_2), 64.4 (s, OCH_2), 126–140 (m, Ph), 170.9 (s, CO).

$MoBr(NNCH_2CH_2CH_2CH_2OH)(dppe)_2$. An excess of 4-bromobutanol was added to $Mo(N_2)_2(dppe)_2$ (0.565 g, 0.600 mmol) in benzene (50 mL) as described above. After 12 h, the red solution was taken to dryness and THF (100 mL) and solid $LiAlH_4$ (0.01 g, 0.26 mmol) were added. After the mixture was stirred for 2 h, deionized water (3–5 mL) was added very slowly. The solvent was removed with use of a rotary evaporator and the residue extracted with benzene (2 × 25 mL). The extract was filtered and the solvent evaporated. The red residue was extracted with Et_2O (2 × 20 mL), filtered, and allowed to stand. After 12 h, red crystals were collected by filtration and dried in vacuo to yield 0.039 g (6%) of product; mp 168 °C dec. Anal. Calcd for $C_{60}H_{57}BrMoN_2OP_4$: C, 62.62; H, 5.35; N, 2.6; Br, 7.4. Found: C, 62.61; H, 5.62; N, 2.46; Br, 7.14. IR (cm^{-1}, KBr): 3445 (ν(O—H)), 1527 (ν(N=N)). Visible–UV (C_6H_6; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): λ_{max} 500 (360), 363 (6930). ^1H NMR (200 MHz, C_6D_6): δ 0.76 (m, 2, CH_2), 1.21 (m, 2, CH_2), 1.94 (t, 2, NCH_2, $^2J_{HH}$ = 6.1 Hz), 2.59 (d, 8, PCH_2), 2.92 (s, 1, OH), 3.51 (t, 2, OCH_2, $^2J_{HH}$ = 5.8 Hz), 6.95–7.56 (m, Ph). ^{13}C NMR (50.4 Hz, C_6D_6): δ 26.8 (s, CH_2), 29.9 (m, PCH_2), 31.6 (s, CH_2), 50.26 (s, NCH_2), 65.9 (s, OCH_2), 127–140 (m, Ph).

$[MoBr(NNCH_2CH_2CH_2CH_2)(dppe)_2]BF_4$. 1,4-Dibromobutane (0.1495 g, 0.6291 mmol) was added to $Mo(N_2)_2(dppe)_2$ (0.5693 g, 0.6000 mmol) in benzene (180 mL). The orange solution was stirred in vacuo under fluorescent lights for 24 h. The green precipitate was filtered off and washed with pentane (50 mL). The yellow filtrate was discarded. The green solid was dissolved in the minimum volume of CH_2Cl_2 and filtered. To this solution was added a filtered solution of $NaBF_4$ (ca. 2 mmol) in 5% aqueous ethanol (50 mL). The combined solution was filtered. After 12 h green crystals were collected by filtration, washed with ethanol (10 mL), and dried in vacuo to yield 0.2351 g (34.4%) of product: mp 274 °C; $\Lambda = 43.0\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{56}H_{56}BBrF_4MoN_2P_4$: C, 58.81; H, 5.64; N, 2.44; Br, 6.98. Found: C, 59.04; H, 5.11; N, 2.38; Br, 7.15. Visible–UV (CH_2Cl_2; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): λ_{max} 588 (890), 425 (270), 291 (5370). ^1H NMR (100 MHz, $CDCl_3$): δ 0.88–2.00 (m, CH_2), 2.58–3.22 (m, PCH_2), 6.95–7.63 (m, Ph). ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 23.5 (s, 2, CH_2), 28.7 (t, 4, PCH_2), 50.0 (s, 2, NCH_2), 127–135 (m, Ph).

The above complex was also prepared from 1-bromo-4-chlorobutane with use of the same experimental procedure: yield 37.2%; $\Lambda = 45.0\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Found: C, 58.45; H, 5.03; N, 2.41; Br, 7.40.

$[MoBr(NNCH(CH_3)CH_2CH_2CH_2)(dppe)_2]BF_4$. This compound was prepared by the reaction of 1,4-dibromopentane (0.0104 g, 0.4522 mmol) and $Mo(N_2)_2(dppe)_2$ (0.4295 g, 0.4526 mmol) according to the above procedure: yield of green product 0.2151 g (41.3%); mp 216 °C dec; $\Lambda = 45.0\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{57}H_{58}BBrF_4MoN_2P_4$: C, 59.14; N, 5.05; N, 2.41; Br, 6.90. Found: C, 58.59; H, 5.27; N, 2.39; Br, 6.32. Visible–UV (CH_2Cl_2; λ, nm (ϵ, $M^{-1}\ cm^{-1}$)): λ_{max} 575 (866), 413 (266), 294. ^{13}C NMR (25.2 MHz, $CDCl_3$): δ 18.7 (s, CH_3), 21.6 (s, CH_2), 26.4 (d, PCH_2), 29.0 (d, PCH_2), 30.8 (s, CH_2), 51.1 (s, NCH_2), 58.4 (s, NCH), 127–136 (m, Ph).

$[MoI(NNCH_2CH_2CH_2CH_2)(dppe)_2]I$. This compound was prepared similarly from 1,4-diiodobutane (0.2583 g, 0.830 mmol) and $Mo(N_2)_2(dppe)_2$ (0.7591 g, 0.800 mmol). The initial green precipitate was filtered off, dissolved in the minimum volume of CH_2Cl_2, and filtered. Ethanol (50 mL) was added and the solution filtered. After 12 h, the green crystals were collected by filtration and dried in vacuo to yield 0.3413 g (34.6%) of product: mp 193 °C dec; $\Lambda = 43.6\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd for $C_{56}H_{52}I_2MoN_2P_4$: C, 54.56; H, 4.58; N, 2.23; I, 20.62. Found: C, 54.51; H, 4.67; N, 2.27; I, 20.41.

Preparation of $[MoBr(NN(CH_3)(C_4H_9))(dppe)_2]SO_3F$. Methyl fluorosulfonate (0.12 mL, 1.4 mmol) in CH_2Cl_2 (10 mL) was added to Proton Sponge[16] (0.5098 g, 2.379 mmol) also in CH_2Cl_2 (50 mL) in a 250-mL three-necked flask to which a vacuum stopcock, a separatory funnel containing methanol (50 mL), and a side-arm tube containing solid $MoBr(NNC_4H_9)(dppe)_2$ were attached. The solution was taken through three freeze–pump–thaw cycles and the solid added at −23 °C. While the solution was stirred for 1 h at −23 °C, its color went from red to green. After 0.5 h of stirring at room temperature, all volatiles were removed in vacuo. The residue was dissolved in a 1:1 benzene/CH_2Cl_2 (15 mL) solvent mixture and filtered. The flask was rinsed with benzene (5 mL), which was filtered and combined with the other filtrate. Upon addition of heptane (5 mL), large brown crystals formed. The product was removed by filtration, washed with pentane, and dried in vacuo to yield 0.4984 g (92%). Anal. Calcd for $C_{57}H_{60}BrFMoN_2O_3P_4S$: C, 58.42; H, 5.16; N, 2.39. Found: C, 57.42; H, 5.35; N, 2.34. ^1H NMR (200 MHz, $CDCl_3$): δ 0.60 (m, 7, $CH_2CH_2CH_3$), 1.42 (s, 3, NCH_3), 1.81 (m, 2, NCH_2), 2.88 (d, 8, PCH_2), 6.8–7.7 (m, Ph). ^{13}C NMR (50.4 MHz, $CDCl_3$): δ 13.3 (s, 1, CH_3), 19.3 (s, 1, CH_2), 28.0 (m, 5, PCH_2 and NCH_3), 37.2 (s, 1, CH_2), 54.2 (s, 1, NCH_2), 127–135 (m, Ph).

Preparation of $[MoBr(NN(CH_3)(C_4H_9))(dppe)_2]I$. To a solution of proton sponge[16] (0.10 g, 0.5 mmol) in iodomethane (15 mL) was added $MoBr(NNC_4H_9)(dppe)_2$ (0.7454 g, 0.7046 mmol). The solution was stirred (17 h) before volatiles were removed in vacuo. The residue was dissolved in a 1:1 v/v benzene/CH_2Cl_2 solution and the solution filtered. Slow addition of heptane caused blue-green crystals for form. The yield of product was 0.5651 g (0.4710 mmol, 66.8%). ^1H NMR revealed a small amount of Proton Sponge, which was removed by recrystallization from a 1:1 benzene/CH_2Cl_2 solution followed by addition of heptane. Anal. Calcd for $C_{57}H_{60}BrIMoN_2P_4 \cdot CH_2Cl_2$: C, 54.20; H, 4.87; N, 2.18. Found: C, 54.40; H, 4.89; N, 2.13. ^1H NMR (200 MHz, $CDCl_3$): δ 0.60 (m, 7, $CH_2CH_2CH_3$), 1.42 (s, 3, NCH_3), 1.82 (m, 2, NCH_2), 2.90 (d, 8, PCH_2), 6.8–7.7 (m, Ph). ^{13}C NMR (50.4 NHz, $CDCl_3$): δ 13.2 (s, CH_3), 19.2 (s, CH_2), 28.1 (m, PCH_2 and NCH_3), 37.3 (s, CH_2), 54.2 (s, NCH_2), 127–135 (m, Ph).

Reactions of $[WF(NNH_2)(dppe)_2]BF_4$ with Aldehydes. (i) Salicylaldehyde. To $[WF(NNH_2)(dppe)_2]BF_4$ (0.5598 g, 0.5014 mmol) was added salicylaldehyde (0.1862 g, 1.525 mmol), CH_2Cl_2 (20 mL), and 1 drop of 48% aqueous HBF_4. The solution turned green after stirring for 1 h. After 20 h, the solution was filtered and the volume of filtrate reduced to ca. 10 mL. Pentane was added until a dark green oil formed. The supernatant was decanted off and the oil redissolved in CH_2Cl_2 (ca. 3 mL). Et_2O was added until the solution became turbid and the solution was stored at 0 °C. After 1 day, green crystals of $[WF(NNCHC_6H_4\text{-}2\text{-}OH)(dppe)_2]BF_4$ were filtered off, washed with Et_2O, and dried in vacuo. A second crop of crystals was obtained to yield a total of 0.4937 g (81%). Anal. Calcd for $C_{59}H_{54}BF_5N_2OP_4W$: C, 58.06; H, 4.46; N, 2.29. Found: C, 57.31; H, 4.64; N, 2.13. ^1H NMR (90 MHz, $CDCl_3$): δ 9.2 (s, −OH), 5.7 (s, NNCH−). IR (cm^{-1}, KBr): 1529, 1520 sh (ν(C=N)), 3380 (ν(OH)).

(ii) 2-Hydroxy-1-naphthaldehyde. This reaction was carried out in an analogous manner to give green crystals of $[WF(NNCHC_{10}H_6\text{-}2\text{-}OH)(dppe)_2]BF_4$ in 42% yield. Anal. Calcd for $C_{63}H_{56}BF_5N_2OP_4W \cdot {}^1/_2CH_2Cl_2$: C, 58.08; H, 4.38; N, 2.13. Found: C, 58.58; H, 4.88; N, 1.98. ^1H NMR (90 MHz, $CDCl_3$): δ 10.8 (s, −OH), 6.0 (s, NNCH−, poorly resolved). IR (KBr): ν(C=N) not assigned.

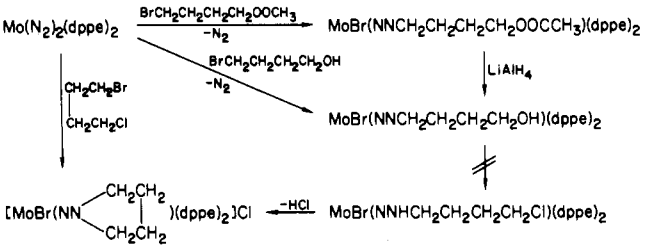
Spectra and Characterization. The ^1H and ^{13}C NMR spectra were recorded on a Varian XL-100 FT spectrometer unless otherwise noted with chemical shifts referenced to internal Me_4Si (δ 0.0). $^{31}P\{^1H\}$ NMR spectra were recorded on a Nocolet NMC 360 (146.17 MHz) spectrometer with chemical shifts relative to 85% H_3PO_4 (external), with positive chemical shifts being downfield. The IR spectra were recorded as KBr or CsI dispersions with use of a Perkin-Elmer 283 spectrometer. Visible–UV spectra were recorded in 1.0-cm cuvettes with a Hewlett-Packard 8450A spectrometer. Conductivities were measured in pyridine solutions (ca. 1.0×10^{-3} M) with use of a standard cell thermostated at 25 °C. Melting points were obtained in sealed capillary tubes and are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, or Galbraith Laboratories, Inc., Knoxville, TN.

Results

A single diastereomeric bis(dinitrogen) complex, *trans*-$Mo(N_2)_2((S,S)\text{-Chiraphos})_2$, was prepared with use of the diastereomeric bidentate phosphine (*S,S*)-$[Ph_2PCH(CH_3)CH(CH_3)PPh_2]$. This phosphine when complexed to rhodium has been shown to be very effective in the asymmetric hydrogenation of

(16) 1,8-Bis(dimethylamino)naphthalene: Aldrich Chemical Co., Inc.

Scheme I



prochiral olefins.[13,17] In three separate reactions a twofold excess of racemic 2-bromooctane was reacted with $Mo(N_2)_2((S,S)$-Chiraphos$)_2$ in benzene solution to produce the corresponding (1-methylheptyl)diazenido complex $MoBr(NNCH(CH_3)C_6H_{13})((S,S$-Chiraphos$)_2$ in high yield, together with some $MoBr_2((S,S)$-Chiraphos$)_2$. The ^1H NMR spectra of the alkyldiazenido complex were recorded at 100, 200, and 396 MHz. All three spectra showed the two resonances due to the α-methyl group ($NNCH(CH_3)$–) of the two diastereomers, $MoBr((S)$-$NNC_8H_{17})((S,S)$-Chiraphos$)_2$ and $MoBr((R)$-$NNC_8H_{17})((S,S)$-Chiraphos$)_2$. In addition all three spectra indicated that one diastereomer was in excess by about 10%.[18] In the 396-MHz ^1H NMR spectrum each methyl group appeared as a doublet at δ 0.23 and 0.32, respectively, with $J_{H-H}(CHCH_3) = 6.0$ Hz.

At the completion of the reaction solvent and unreacted 2-bromooctane were removed in vacuo and collected. The 2-bromooctane in this solution showed a small positive optical rotation corresponding to an excess of the (+)-(*S*)-2-bromooctane enantiomer.

No bis(dinitrogen) complex of molybdenum could be formed with use of (+)-DIOP.

Primary bromo- and iodoalkanes react with $Mo(N_2)_2(dppe)_2$ to form alkyldiazenido complexes. Chloroalkanes react instead to form $MoCl_2(dppe)_2$ with the loss of 2 mol of N_2. Only activated chloroalkanes such as ethyl chloroacetate produce alkyldiazenido complexes.[19] However, 1-bromo-4-chlorobutane reacted with $Mo(N_2)_2(dppe)_2$ to form the dialkylhydrazido complex as a result of both C–Br and C–Cl bond cleavage. After the counterion was exchanged with BF_4^-, an elemental analysis showed bromine but no chlorine present. Therefore, the original product is formulated as $[MoBr(NNCH_2CH_2CH_2CH_2)(dppe)_2]Cl$. 1,4-Dibromopentane reacted with $Mo(N_2)_2(dppe)_2$ to produce the corresponding dialkylhydrazido complex.

The complex $MoBr(NNC_4H_9)(dppe)_2$ was reacted with a series of alkylating agents (RX) in order to prepare dialkylhydrazido complexes (eq 3). Magic Methyl rapidly alkylated the butyl-

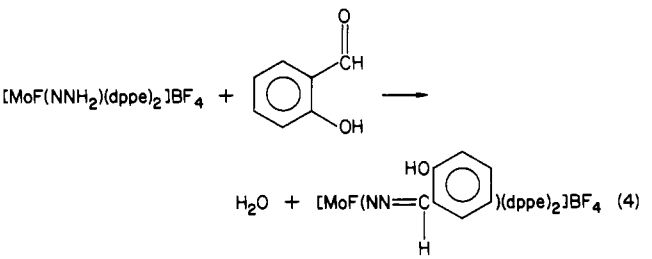
$$MoBr(NNC_4H_9)(dppe)_2 + RX \rightarrow [MoBr(NN(R)C_4H_9)(dppe)_2]X \quad (3)$$

diazenido complex in almost quantitative yield. Magic Methyl was stirred with Proton Sponge first to remove any acid present (to avoid formation of the butylhydrazido complex) before the reaction was carried out. As a result trace quantities of Proton Sponge were present in the product. The [NN–CH_3] group was observed in the ^1H NMR spectrum at δ 1.42. The same complex, as the iodide salt, was synthesized by reacting $MoBr(NNC_4H_9)(dppe)_2$ with a large excess of iodomethane with no solvent. The yield was significantly lower than in the Magic Methyl reaction. No reaction occurred with iodomethane when a solvent (benzene or THF) was used. Reaction with methyl tosylate resulted in decomposition of the butyldiazenido complex.

Primary bromoalkanes (e.g., 6-bromo-1-hexene) did not react with $MoBr(NNC_4H_9)(dppe)_2$ at room temperature. When these were heated together at 60 °C in the absence of solvent, a small amount of secondary alkylation occurred (detected by ^1H NMR spectroscopy) although significant decomposition was observed with the formation of phosphonium salts. Heating with secondary bromoalkanes resulted in the formation of the butylhydrazido complex $[MoBr(NNHC_4H_9)(dppe)_2]Br$. In order to study the mechanism of secondary alkylation leading to formation of cyclic dialkylhydrazido complexes, an attempt was made to synthesize $[MoBr(NNHCH_2CH_2CH_2CH_2Cl)(dppe)_2]Cl$ (see Scheme I). Deprotonation of the (4-chlorobutyl)hydrazido complex should lead to cyclization at the carbon-bound nitrogen atom. The (4-hydroxybutyl)diazenido complex was prepared (i) by $LiAlH_4$ reduction of the (4-acetylbutyl)diazenido complex (60% yield), (ii) by the direct reaction of 4-bromobutanol with $Mo(N_2)_2(dppe)_2$ (by which method product was never isolated pure), and (iii) in situ $LiAlH_4$ reduction of the (4-acetylbutyl)diazenido complex (6% yield).

Attempts to convert the alcohol into a halide and tosylate resulted in formation of the (4-hydroxybutyl)hydrazido complex and decomposition, respectively. The reaction of 4-hydroxybutyl tosylate with $Mo(N_2)_2(dppe)_2$ led to decomposition.

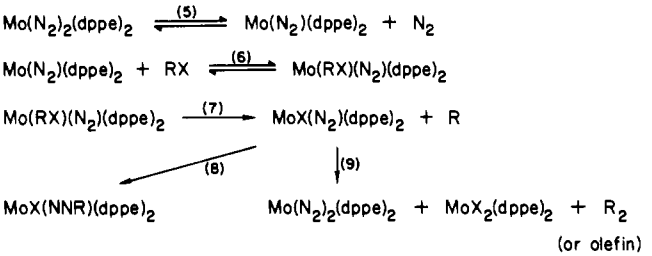
The condensation reaction of aldehydes and ketones with hydrazido complexes provides an alternate method of introducing organic moieties containing functional groups. For example, reactions of $[WF(NNH_2)(dppe)_2]BF_4$ with salicylaldehyde (eq 4) and 2-hydroxy-1-naphthaldehyde led to the formation of hydroxy-substituted diazoalkane complexes. These complexes were prepared in variable yield as air-stable green crystalline solids.



Discussion

The mechanism of monoalkylation of dinitrogen coordinated to molybdenum and tungsten by haloalkanes has been studied in detail by Chatt and co-workers.[20] Their results are summarized in Scheme II. The rate-determining step is loss of N_2 (eq 5).[20,21]

Scheme II



The interesting results obtained from the reaction of racemic 2-bromooctane (R′X) with *trans*-$Mo(N_2)_2((S,S)$-Chiraphos$)_2$ (eq 10) can be accounted for by the mechanism shown in Scheme II.

$$[Mo(N_2)_2((S,S)\text{-Chiraphos})_2] + 2R'X \rightarrow [MoBr(NNR')((S,S)\text{-Chiraphos})_2] + N_2 + R'X \quad (10)$$

The recovery of unreacted 2-bromooctane (eq 10) in which there is an excess of the *S* enantiomer suggests that $\Delta G^{\ddagger}$ for the reaction of $Mo(N_2)((S,S)$-Chiraphos$)_2$ with the *R* enantiomer to form $Mo((R)$-R′X$)(N_2)((S,S)$-Chiraphos$)_2$ is less than with the *S* enantiomer. Therefore, there is kinetic resolution at this stage

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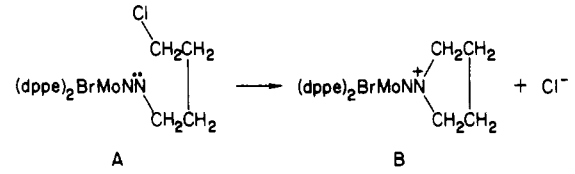
of the reaction (eq 6). Formation of the (2-methylheptyl)diazenido complex involves reaction between the 2-octyl radical and the molybdenum(I) complex $MoBr(N_2)((S,S)$-Chiraphos$)_2$ (eq 8). That this step in the reaction is slow has been shown by studies of the reaction of 6-bromo-1-hexene with $Mo(N_2)_2(dppe)_2$.[11,20] Therefore, the 2-octyl radical will have completely equilibrated before alkylation occurs (eq 8). Again kinetic resolution is observed. Excess of one diastereomeric product over the other (we cannot say which predominates from these data) arises because ΔG^* is different for the interaction of each of the two faces of the prochiral trigonal carbon radical with the chiral molybdenum(I) radical (asymmetric synthesis[22]).

Hydrogenolysis of the mixture of diastereomeric alkyldiazenido complexes ($NaBH_4/C_6H_6/CH_3OH$, 100 °C)[11] resulted in the formation of 2-aminooctane that was totally racemized.

There is an interesting contrast between the difficulty of alkylating $MoBr(NNC_4H_9)(dppe)_2$, for example, and the apparent ease with which cyclization occurs to form cyclic dialkylhydrazido complexes. The reaction of 1-bromo-4-chlorobutane with $Mo(N_2)_2(dppe)_2$ is assumed to involve first alkylation of coordinated N_2 by the alkyl bromide end of the molecule and second an intramolecular alkylation of the carbon-bound nitrogen atom resulting in cleavage of the carbon–chlorine bond. This order of alkylation is supported by previous work[20] and the occurrence of chloride rather than bromide (or a mixture) as the counterion. It seems clear that the facile cyclization of A to B is the result of anchiomeric assistance with the transition state being stabilized by



the chelating effect of the five-membered ring. The presence of four of the phenyl groups of the two dppe ligands around the $NNCH_2$–group will cause considerable steric hindrance toward intermolecular secondary alkylation. This can be demonstrated by comparing the reactions of $Mo(N_2)_2(dppe)_2$ and $Mo(N_2)_2(Et_2PCH_2CH_2PEt_2)_2$ with bromomethane. Under similar conditions, the former complex produces the methyldiazenido complex $MoBr(NNMe)(dppe)_2$ whereas the latter directly forms the dimethylhydrazido complex $[MoBr(NNMe_2)(Et_2PCH_2CH_2PEt_2)_2]Br$.[8] A more dramatic effect of anchiomeric assistance is demonstrated by the rapid cyclization of 1,4-dibromopentane to form a product in which both a primary and a secondary carbon atom are attached to the same nitrogen atom.

Acknowledgment. This work was supported in part by the National Science Foundation and the University of Nebraska Research Council. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. The 396-MHz ^1H NMR spectra were obtained in the Fourier transform mode on an instrument designed and constructed by Professor F. A. L. Anet of the Department of Chemistry, University of California, Los Angeles. We thank Dr. D. C. Busby for recording the 200- and 396-MHz spectra.

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New Multidentate Ligands. 23. Chelating Tendencies of Octadentate Diamido Diamino Tetraacetic Acids

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Received January 20, 1984

Protonation constants and metal ion binding constants are reported for five octadentate chelating ligands: *N,N'*-bis(2-aminoethyl)oxalamide-*N'',N''',N'''',N''''*-tetraacetic acid (BAOTA), *N,N'*-bis(2-aminoethyl)malonamide-*N'',N''',N'''',N''''*-tetraacetic acid (BAMTA), *N*-(glycylglycyl)-1,2-diaminoethane-*N',N'',N''',N''''*-tetraacetic acid (GGENTA), *N,N'*-diglycyl-1,2-diaminoethane-*N'',N''',N'''',N''''*-tetraacetic acid (DGENTA), and *N,N'*-diglycyl-1,4-diaminobutane-*N'',N''',N'''',N''''*-tetraacetic acid (DGBNTA). Synthetic procedures for the four new ligands (BAOTA, BAMTA, GGENTA, and DGBNTA) are described. All of these ligands, including the one previously reported (DGENTA), contain two amido groups and two terminal iminodiacetate groups and differ mainly in the arrangement and spacing of the amido groups. Differences in protonation constants and metal ion binding constants are interpreted in terms of constitutional and steric effects resulting from differences in ligand structures. The tendencies of the amide groups to coordinate metal ions through proton displacement are sensitive to the steric arrangements of these groups and to the participation of iminodiacetate groups in metal coordination. Microscopic information on metal ion binding sites of the ligands are inferred from visible and infrared absorption spectra of the ligands and metal complexes in aqueous solution. Potentiometric results with iron(III) ion suggest amide proton displacement with BAOTA and GGENTA, but results with zinc ion are less conclusive.

Introduction

Amide groups in polypeptides have been extensively studied, and their metal-binding tendencies are greatly increased by proton displacement.[1] Direct evidence for this was obtained from infrared spectra for the Cu(II) and Ni(II) complexes in aqueous solution[2-4] and from X-ray crystallographic studes for Cu(II)–polyglycines in the solid state.[5,6] Few coordination chemists have taken advantage of the coordination tendencies of deprotonated amide groups in the design of selective multidentate ligands. Several reports have been published on the chelating tendencies of diglycylethylenediamine and its derivatives.[7-11] Several reports have described the incorporation of the oxalamido linkage with ad-

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