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Characterization of Reversible Reactions of Isocyanides with Molybdenum Dithiolate Complexes[1]

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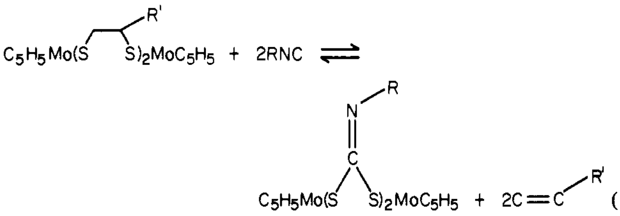
Abstract: Dimeric molybdenum complexes with bridging dithiocarbonimidate ligands of the formula $[C_5H_5MoS_2CNR]_2$ (where R = CH_3, $CH_2C_6H_5$, C_6H_{11}, and n-C_4H_9) have been synthesized and characterized. The syntheses involve the room-temperature reactions of excess isocyanides with solutions of the dimeric complex $[C_5H_5MoSC_3H_6S]_2$. During the course of these reactions, propene is displaced from the sulfur atoms of the bridging dithiolate ligands. Addition of excess alkene reverses the above reactions. Equilibrium constants have been calculated for the following reactions by integration of NMR resonances: $[CH_3C_5H_4MoSC_2H_4S]_2 + RNC \rightleftharpoons (CH_3C_5H_4Mo)_2(SC_2H_4S)(S_2CNR) + C{=}C$, $K_1 = 2.9 \pm 0.2$; $(CH_3C_5H_4Mo)_2(SC_2H_4S)(S_2CNR) + RNC \rightleftharpoons [CH_3C_5H_4MoS_2CNR]_2 + C{=}C$, $K_2 = 0.7 \pm 0.1$ (R = $CH_2C_6H_5$). The dithiocarbonimidate complexes react cleanly with the electrophiles CH_3OSO_2F and $HOSO_2CF_3$ to form $[C_5H_5MoS_2CNRR']_2^{2+}$ where R′ = H or CH_3. These products have been characterized by spectral and conductivity methods. The reactions of the dithiocarbonimidate complexes with reducing agents and with carbon monoxide are discussed.

Introduction

In a recent paper we identified unusual reactions of dimeric dithiolate bridged molybdenum complexes with alkenes and alkynes.[2] These unsaturated molecules react with the coordinated sulfur atoms in the dimers to displace an olefin and form new dithiolate bridges. In the case of alkenes, this exchange reaction is a reversible one. We report in this paper that isocyanides also react reversibly with these molybdenum complexes displacing an olefin from the sulfur atoms and forming bridging dithiocarbonimidate ligands (reaction 1). Mononuclear complexes



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containing this chelating ligand (S_2CNR^{2-}) have been prepared previously by the abstraction of sulfur from excess alkyl isothiocyanates in the presence of a metal ion.[3-5] Complexes with a similar ligand where R = CN have also been characterized.[6-8] However, the reactions reported here are significant because they represent the first examples of reversible interactions of isocyanides with coordinated sulfur ligands. The new complexes have been characterized by a number of physical techniques. Their reactions with electrophiles have also been investigated.

Table I. ^1H NMR Data for $[C_5H_5MoS_2CNR]_2$, $[C_5H_5MoS_2CN(CH_3)R]_2{}^{2+}$, and $[C_5H_5MoS_2CN(H)R]_2{}^{2+}$

complex	δ (R)[a] (multiplicity, rel area)[b]	δ Cp	δ electrophile
$[C_5H_5MoS_2CNCH_3]_2$	2.99 (s, 6)	5.50 (s, 10)	
$[C_5H_5MoS_2CNCH_2C_6H_5]_2$	4.39 (s, 4) 7.30 (m, 10)	5.35 (s, 10)	
$[C_5H_5MoS_2CNC_6H_{11}]_2$	1.29 (m, 20) 3.22 (s, br, 2)	5.50 (s, 10)	
$[C_5H_5MoS_2CNC_4H_9]_2$	0.90 (m, 6) 1.37 (m, 8) 3.22 (t, 4)	5.48 (s, 10)	
$[C_5H_5MoS_2CN(CH_3)_2]_2{}^{2+}$ [c]	3.33 (s, 12)	5.98 (s, 10)	see δ_R
$[C_5H_5MoS_2CN(CH_3)C_4H_9]_2{}^{2+}$ [c]	0.95 (m, 6) 1.45 (m, 8) 3.62 (t, 4)	5.94 (s, 10)	3.31 (s, 6)
$[C_5H_5MoS_2CN(H)CH_3]_2{}^{2+}$ [d]	3.07 (s, 6)	5.94 (s, 10)	9.09 (br, 2)
$[C_5H_5MoS_2CN(H)C_4H_9]_2{}^{2+}$ [d]	0.93 (m, 6) 1.42 (m, 8) 3.43 (t, 4)	5.94 (s, 10)	9.41 (br, 2)

[a] Parts per million relative to Me_4Si in $CDCl_3$. [b] s = singlet; m = multiplet; t = triplet; br = broad. [c] SO_3F^- salt in CD_3CN. [d] $SO_3CF_3^-$ salt in CD_3CN.

Table II. Proton Decoupled ^{13}C NMR Data for $[C_5H_5MoS_2CNR]_2$

complex	δ (R)[a]	δ -S_2*C*N-	δ C_5H_5
$[C_5H_5MoS_2CNCH_3]_2$	37.98	180.86	92.04
$[C_5H_5MoS_2CNCH_2C_6H_5]_2$	55.21 138.94 128.44 128.02 127.17	181.53	91.98
$[C_5H_5MoS_2CNC_6H_{11}]_2$	60.18 33.67 25.42 24.63	178.37	92.04
$[C_5H_5MoS_2CNC_4H_9]_2$	51.09 32.40 20.26 13.77	179.71	91.98

[a] Parts per million downfield from Me_4Si in $CDCl_3$.

Results and Discussion

Preparation and Characterization of Complexes. The addition of excess isocyanide to a chloroform solution of $[C_5H_5MoSC_3H_6S]_2$ at 25 °C results in the displacement of propylene and the formation of the dimeric compound $[C_5H_5MoS_2CNR]_2$. A series of complexes of this formula have been isolated in analytically pure form with R = CH_3, $CH_2C_6H_5$, C_6H_{11}, and n-C_4H_9. The ^1H NMR spectra of the products show in each case a single cyclopentadienyl resonance and evidence for equivalent alkyl groups (Table I). In the infrared spectra the C–N stretches occur in the range 1605–1618 cm^{-1}. These frequencies are consistent with the reduction of bond order resulting from a bridging interaction of the

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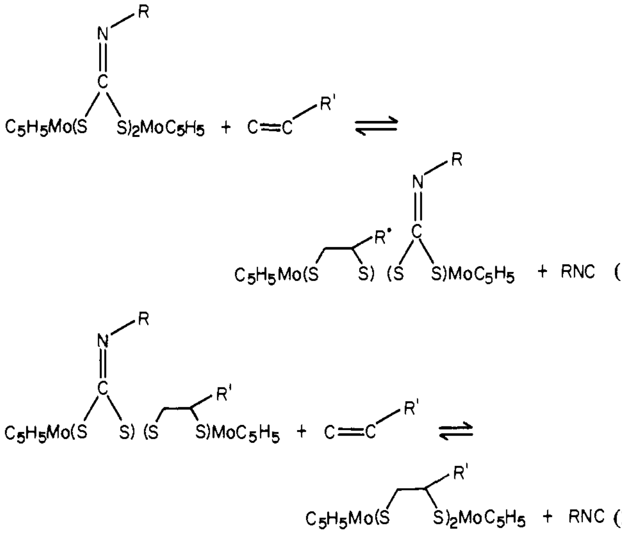
isocyanide carbon atom.[3-5,9-13] In this case the metal ions appear to remain coordinatively saturated by sulfur ligation, and a bridging interaction between two coordinated sulfur atoms is postulated. In the infrared spectra of the new complexes weak infrared bands occur between 910 and 940 cm^{-1} which can be attributed to C–S stretches.[3,4] In addition the ^{13}C NMR spectra of the products show resonances for the $>C{=}N$ carbon atoms between 178 and 182 ppm (Table II). These chemical shifts are very similar to those observed previously for the C atom in chelating ligands of the type S_2CNR^{2-}.[14,15]

In the mass spectra of the complexes no parent ions are observed, but the envelope corresponding to the $[C_5H_5MoS_2]_2$ unit and its previously reported fragmentation pattern are present.[16] The cyclic voltammetry of $[C_5H_5MoS_2CNC_4H_9]_2$, which is the only complex of the series with appreciable solubility in acetonitrile, shows a reversible oxidation at +0.61 V vs. SCE.[17] The complex is significantly more difficult to oxidize than the dithiolate bridged derivatives.[2] The displacement of propene in these syntheses and pertinent spectral data for the product complexes suggest that the new compounds should be formulated as dimers with two dithiocarbonimidate ligands. Reactions of these compounds with unsaturated molecules also support this formulation.

Reactions with Alkenes and Alkynes. In the presence of excess alkene (total pressure 1–2 atm) at 25 °C, isocyanide is displaced from the complexes $[C_5H_5MoS_2CNR]_2$, and the equilibria shown in reactions 2 and 3 are established. The analogous forward reactions are also observed with acetylene. The products of these reactions have been identified by NMR. The NMR spectrum of a mixture of $C_6H_5CH_2NC$ and $[CH_3C_5H_4MoSC_2H_4S]_2$ in $CDCl_3$ in a sealed tube permits the measurement of concentrations of all species in solution (Figure 1). Equilibrium concentrations have been measured at 35 °C for reactions 2 and 3, and values for K_1 and K_2 for the reactions as written above have been found to be 1.4 ± 0.1 and 0.3 ± 0.05, respectively.



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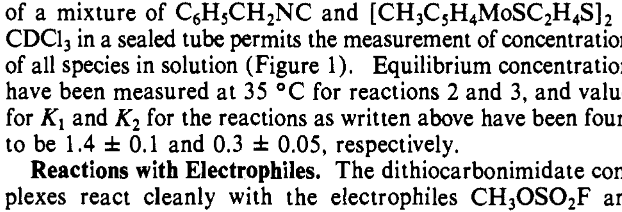

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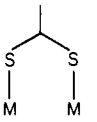
Reactions with Electrophiles. The dithiocarbonimidate complexes react cleanly with the electrophiles CH_3OSO_2F and $HOSO_2CF_3$ to form dimeric complexes in which the nitrogen atom of each ligand has been alkylated or protonated. Analogous reactions of coordinated dithiocarbonimidate ligands with other electrophiles have been reported previously.[3,4] The products of the reactions reported here, which have been characterized for the *N*-methyl and *N*-butyl derivatives, are dications in which the bridging ligands can be formally described as dithiocarbamate anions.[7] To our knowledge, these complexes provide the first examples of molybdenum complexes with bridging dithiocarbamate ligands. Two different types of bridging interactions have been characterized for these ligands in dimeric complexes of other metal ions: I and II.[18-21] A third bonding mode, III, is possible for the present systems, and we are continuing our efforts to isolate crystals suitable for an X-ray diffraction study.



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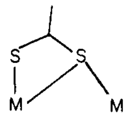

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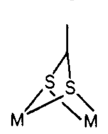

III

The spectral data for the alkylated products do not reveal the structural details of the complexes, but the data are consistent with their general formulation. The ^{1}H NMR spectrum of $[C_5H_5MoS_2CN(CH_3)_2]_2^{2+}$ confirms that the nitrogen atom is the site of methylation in this product. Two sharp singlets, assigned to cyclopentadienyl and methyl protons, are observed at 5.98 and 3.33 ppm, respectively (relative intensity 10:12). A single methyl carbon resonance is also observed in the ^{13}C NMR spectrum. Conductivity data support the formulation of the complexes as 2:1 electrolytes.[22]

The protonated complexes, which are also 2:1 electrolytes, have a sharp ν_{N-H} in the infrared spectra at 3300 cm^{-1}. The resonance of the N-substituted proton can only be observed in the NMR spectra of these complexes in rigorously dried solvents. Decoupling experiments with the derivative $[C_5H_5MoS_2CN(H)C_4H_9]_2^{2+}$ support the conclusion that the nitrogen atom is the site of protonation. At 30 °C the resonance of the methylene group adjacent to the nitrogen atom is a triplet. At 0 °C a complex splitting pattern is observed for this signal, but by decoupling the NH proton the splitting of the methylene resonance is reduced again to the triplet pattern. Addition of D_2O to the NMR tube at ~5 °C results in rapid exchange of the NH proton, and this also simplifies the splitting pattern of the methylene resonance. No resonance is observed for the NH proton in the presence of D_2O or H_2O.

The protonated complexes are air stable in the solid state but decompose in aprotic solutions, even under nitrogen, over a period of hours. The complexes are also subject to extensive decomposition through hydrolysis reactions. The bridging ligands in the cationic derivatives do not show the lability characteristics of the dithiocarbonimidate ligands. For example, no reaction is observed between $[C_5H_5MoS_2CN(CH_3)_2]_2^{2+}$ and excess olefin.

Reactions with Hydrogen and Other Reducing Agents. We have reported previously that the unsaturated ethenedithiolate ligands in $[C_5H_5MoSC_2H_2S]_2$ are reduced by 1–2 atm of hydrogen;[2] this reaction proved to be a step in the catalytic reduction of acetylene to ethylene. This cycle may have relevance to the mode of catalytic reduction of substrate by the molybdoenzyme nitrogenase.[23] It is of interest therefore to determine whether these dimeric molybdenum complexes, which interact with isocyanides, also participate in the reduction of this unsaturated species. The products

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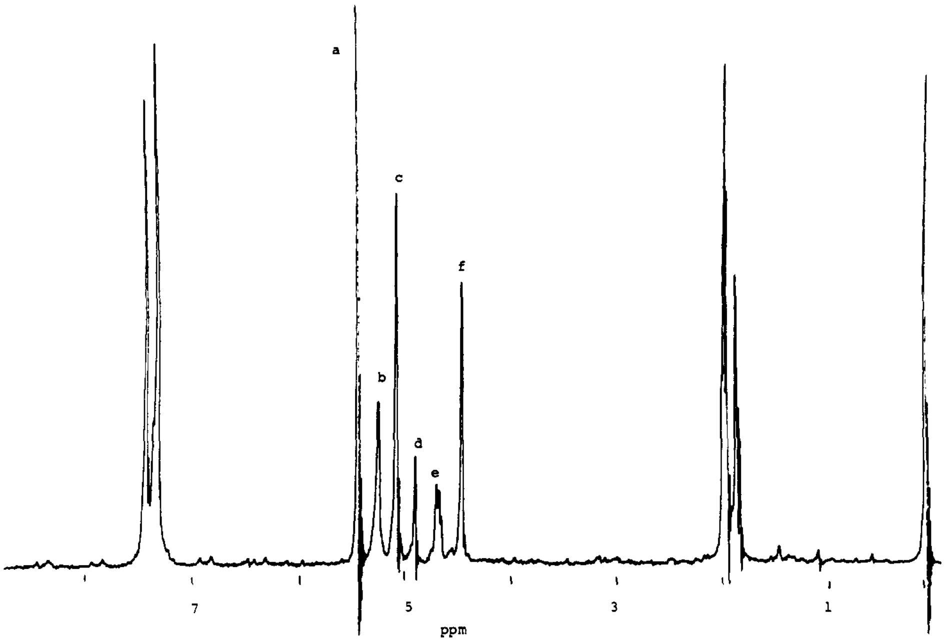

Figure 1. The 90-MHz ^{1}H NMR spectrum of $[CH_3C_5H_4MoSC_2H_4S]_2 + 2C_6H_5CH_2NC$ at equilibrium (solvent $CDCl_3$). The resonances between 6.0 and 4.0 ppm were used in the equilibrium calculations. Assignments are as follows: a, C_5H_4 in $[CH_3C_5H_4MoS_2CNR]_2$; b, C_2H_4; c, C_5H_4 in $CH_3C_5H_4Mo(S_2CNR)(SC_2H_4S)MoC_5H_4CH_3$; d, C_5H_4 in $[CH_3C_5H_4MoSC_2H_4S]_2$; e, $-CH_2-$ in free $C_6H_5CH_2NC$; f, $-CH_2-$ in intermediate and final products.

of the nitrogenase-catalyzed reduction of isocyanides are amines and alkanes.[23] Under an atmosphere of hydrogen the complexes $[C_5H_5MoS_2CNR]_2$ undergo extensive decomposition above ~60 °C. No molybdenum-containing products from this reaction could be characterized, nor were any hydrogenated products (namely, amines) detected. Similar observations were made for analogous reactions carried out in the presence of excess isocyanide at 80 °C, for reactions with hydrogen at 500–1000 psi, and for reactions with sodium borohydride in THF solutions.

Reactions with Carbon Monoxide. In many cases isocyanides undergo reactions with metal ions which are similar to those of the isoelectronic molecule carbon monoxide.[24] The interaction of carbon monoxide with the sulfur ligands in these molybdenum complexes to form bridging dithiocarbonate ligands would be an interesting extension of the present systems. It is possible that such a coordination would activate the molecule for further reduction. However, no CO-containing products could be isolated from solutions of $[C_5H_5MoS_2CNCH_2C_6H_5]_2$ which had been stirred under a carbon monoxide purge or under carbon monoxide pressures ranging from 15 to 800 psi. No evidence for CO reduction was observed in systems with $[C_5H_5MoS_2CNCH_2C_6H_5]_2$ under CO/H_2 pressures up to 900 psi.

Experimental Section

Materials. Benzyl, cyclohexyl, and *n*-butyl isocyanides, methyl fluorosulfonate (97%), and trifluoromethanesulfonic acid were purchased from Aldrich and used without purification. Methyl isocyanide was synthesized according to a published procedure.[25] Chloroform and dichloromethane were purified immediately before use by passing them through a column of alumina. Tetrahydrofuran was distilled from $LiAlH_4$. All solvents were either distilled under an atmosphere of nitrogen or degassed by bubbling nitrogen through them. $[C_5H_5MoSC_3H_6S]_2$ and $[C_5H_5MoSC_2H_4S]_2$ were prepared according to procedures in a previous paper.[2]

Physical Measurements. ^{1}H NMR spectra were measured at 90 MHz on a Varian 390 spectrometer. The 25-MHz ^{13}C NMR spectra were obtained with a JEOL PFT-100 spectrometer with a Nicolet Model 1080 data system. ^{1}H and ^{13}C chemical shifts were measured relative to tetramethylsilane. Infrared spectra of Nujol mulls were recorded on a Perkin-Elmer 337 spectrophotometer. Mass spectra were obtained at 70-eV electron energies with a Varian MAT CH-5 spectrometer. Elemental analyses were provided by Spang Laboratories. Experimental details for the cyclic voltammetry and conductivity measurements have been described in a previous paper.[2]

Syntheses. Except where noted all reactions were carried out under a nitrogen atmosphere.

$[C_5H_5MoS_2CNCH_3]_2$. $[C_5H_5MoSC_3H_6S]_2$ (2.17 g, 4.0 mmol) was dissolved in 100 mL of THF and methyl isocyanide (~2.5 mL, 46 mmol) was added. After the solution was stirred at 25 °C for 3 days, the resulting tan precipitate was filtered, yield 60%. The product was also formed from $[C_5H_5MoSC_2H_4S]_2$ by adding a large (30:1) molar excess of methyl isocyanide to the molybdenum complex in $THF/CHCl_3$. The solution was heated at 60 °C in a valve-sealed flask for 6 days. After cooling, the solution volume was reduced and the precipitate, which was ~85% the expected product, was filtered, yield 33%. The remaining product was the derivative in which only one dithiolate bridge had exchanged with the isocyanide. IR: 1613 (strong, ν_{N-C}), 926 cm^{-1} (weak, ν_{C-S}). Anal. Calcd for $C_{14}H_{16}N_2S_4Mo_2$: C, 31.58; H, 3.03; S, 24.09. Found: C, 31.76; H, 3.19; S, 24.06.

$[C_5H_5MoS_2CNCH_2C_6H_5]_2$. Benzyl isocyanide (0.7 g, 6.0 mmol) was added to $[C_5H_5MoSC_3H_6S]_2$ (1.0 g, 1.9 mmol) in a procedure similar to that described above. The tan product was recrystallized from $CHCl_3$, yield 44%. IR: 1610 (s, ν_{C-N}), 910 cm^{-1} (w, ν_{C-S}). Anal. Calcd for $C_{24}H_{24}N_2S_4Mo_2$: C, 45.61; H, 3.51; S, 18.71. Found: C, 45.47; H, 3.34; S, 18.64.

$[C_5H_5MoS_2CNC_6H_{11}]_2$. $[C_5H_5MoSC_3H_6S]_2$ (0.27 g, 0.51 mmol) was dissolved in 80 mL of THF, and cyclohexyl isocyanide (0.6 mL, ~5 mmol) was added. The solution was stirred for 4 days. The solvent was then flash evaporated, and the flesh-colored solid was recrystallized from chloroform and heptanes, yield 30%. IR: 1605 (s, ν_{C-N}), 920 cm^{-1} (w, ν_{C-S}). Anal. Calcd for $C_{24}H_{32}H_2S_4Mo_2$: C, 43.11; H, 4.82; S, 19.18. Found: C, 42.97; H, 4.82; S, 19.22.

$[C_5H_5MoS_2CNC_4H_9]_2$. $[C_5H_5MoSC_3H_6S]_2$ (2.29 g, 4.29 mmol) was dissolved in 100 mL of chloroform and *n*-butyl isocyanide (~6.8 mL, ~65 mmol) was added. The solution was stirred for 6 days. At this time 60 mL of hexanes were added. Filtration through a medium-porosity frit removed a brown precipitate which was discarded. The filtrate was reduced in volume in vacuo until a slurry of flesh-colored material was produced. This material was filtered, yield 36%. IR: 1618 (s, ν_{C-N}), 938 cm^{-1} (w, ν_{C-S}). Anal. Calcd for $C_{20}H_{28}N_2S_4Mo_2$: C, 38.96; H, 4.58; S, 20.80. Found: C, 39.05; H, 4.52; S, 20.66.

$[C_5H_5MoS_2CNR(CH_3)]_2(SO_3F)_2$. The neutral dithiocarbonimidate complex (R = CH_3 or C_4H_9) was slurried or dissolved in dichloromethane, and ~2.5 equiv of methyl fluorosulfonate was added via syringe. After 2 h of stirring, the resulting orange solid was filtered. R = CH_3: yield 90%; IR 1582 (s, ν_{C-N}), 1265, 582 cm^{-1} (SO_3F); Λ_M (CH_3CN) = 276 $cm^2/\Omega\cdot mol$. R = C_4H_9: yield 82%; IR 1556 (s, ν_{C-N}), 1280, 580 cm^{-1} (SO_3F); Λ_M (CH_3CN) = 267 $cm^2/\Omega\cdot mol$.

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$[C_5H_5MoS_2CN(CH_3)_2]_2(PF_6)_2$. The fluorosulfonate salt was slurried in MeOH, and NH_4PF_6 was added. The slurry was stirred for 1 h in an open beaker, and the solid was filtered off. This was carried out twice. The final solid was recrystallized from acetonitrile/methanol in the presence of NH_4PF_6, yield 80%. IR: 1585 (s, ν_{C-N}), 845, 560 cm^{-1} (PF_6). $\Lambda_M(CH_3CN) = 288\ cm^2/\Omega\cdot mol$. ^{13}C NMR (CD_3CN): δ 97.32 (CH_3), 118.31 (C_5H_5), S_2CN- not observed. Anal. Calcd for $C_{16}H_{22}N_2S_4Mo_2P_2F_{12}$: C, 22.54; H, 2.60; S, 15.04. Found: C, 22.57; H, 2.58; S, 15.12.

$[C_5H_5MoS_2CN(H)R]_2(X)_2$ ($X = SO_3CF_3$ or PF_6). The neutral dithiocarbonimidate complex ($R = CH_3$, C_4H_9) was dissolved in THF, and trifluoromethanesulfonic acid (~2.5 equiv) was added. After stirring for 2.5 h, the yellow-brown precipitate was filtered. $R = CH_3$: yield 85%. $R = C_4H_9$: yield 70%; IR 1565 cm^{-1} (s, ν_{C-N}); $\Lambda_M(CH_3CN) = 247\ cm^2/\Omega\cdot mol$. Each derivative was dissolved in MeOH, and the addition of excess NH_4PF_6 resulted in the precipitation of the bronze-colored PF_6^- salt. For $R = CH_3$: IR 3300 (m, ν_{N-H}), 2463 (w, ν_{H-H}), 1595 (s, ν_{C-N}), 845, 560 cm^{-1} (s, PF_6^-); $\Lambda_M(CH_3CN) = 284\ cm^2/\Omega\cdot mol$. Anal. Calcd for $C_{14}H_{18}N_2S_4Mo_2P_2F_{12}$: C, 20.40; H, 2.20; S, 15.56. Found: C, 20.62; H, 2.35; S, 15.51.

Reactions of $[C_5H_5MoS_2CNCH_3]_2$ with Ethene or Propene. $[C_5H_5MoS_2CNCH_3]_2$ (0.25 g, 0.47 mmol) was dissolved in 25 mL of $CHCl_3$, and ~2 atm of the appropriate gas was added to a 100-mL reaction tube equipped with a vacuum valve. The solution was stirred for 8 days at 25 °C. The solution was then filtered, the filtrate was reduced in volume, and the resulting solid was analyzed by NMR. For the ethene case, ~74% of the product was $[C_5H_5MoSC_2H_4S]_2$; ~26% of a mixed-bridge derivative $(C_5H_5)_2Mo_2(S_2CNCH_3)(SC_2H_4S)$ was present. Yields of the dithiolate bridged species may be increased by exhausting the atmosphere of the reaction tube and recharging with the appropriate gas.

Determination of Equilibrium Constants. Samples of $[C_5H_4CH_3MoSC_2H_4S]_2$ (0.025 g) were dissolved in 0.70 mL of $CDCl_3$ in three NMR tubes, and 1, 2, and 3 equiv of $C_6H_5CH_2NC$ were added, respectively. The solutions were degassed in three freeze–pump–thaw cycles and the tubes were flame sealed. The systems were allowed to reach equilibrium for 10–14 days at 25 °C and for 6–24 h in the probe. NMR spectra were obtained at 35 °C. Averages of integration values were determined from several scans of each sample.

Reactions with Reducing Agents. A. $[C_5H_5MoS_2CNR]_2$ ($R = CH_3$ or $C_6H_5CH_2$) was dissolved in $CHCl_3$ and 1–2 atm of H_2 was added. The solution was stirred at 60–80 °C for 24 h. The dark brown products of low solubility which were formed were not characterized. No amines were detected by NMR or GC.

B. The above reaction was repeated with the addition of excess RNC. Similar results were observed.

C. $[C_5H_5MoS_2CNR]_2$ was dissolved in $CDCl_3$ in a bomb reactor and 800–900 psi H_2 was added. The solution was stirred for 36 h at 25 °C. Largely insoluble products were formed; no amines were detected by NMR.

D. The reaction in C was repeated with the addition of excess RNC. No decomposition occurred in this case; no amines were detected by NMR.

E. $[C_5H_5MoS_2CNCH_2C_6H_5]_2$ (0.06 mmol) was slurried in THF under a nitrogen atmosphere and $NaBH_4$ (0.6 mmol) was added. The solution was refluxed for 36 h. Most of the dithiocarbonimidate complex was recovered; no amines were detected by NMR.

Attempted Reactions with CO. A. $[C_5H_5MoS_2CNCH_2C_6H_5]_2$ was dissolved in $CDCl_3$ and 1–2 atm CO was added. The solution was stirred at 70 °C for 48 h. The NMR spectrum of the solution indicated that no free isocyanide was present and the spectrum of the starting complex was unchanged. Similar results were observed with 800 psi CO at 25 °C and after purging a solution with CO for 48 h.

B. The reaction in A was repeated in a bomb reactor with 900 psi CO/H_2 (1:3 molar ratio). The solution was stirred for 48 h at 25 °C. No pressure change occurred and no hydrogenated products were detected by GC. Dark, insoluble molybdenum-containing products were not characterized.

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Low-Temperature Crystal and Molecular Structure of Tetracarbonyl[2-bromoheptahydrotriborato(1−)]manganese, $(CO)_4MnB_3H_7Br$, and a ^1H NMR Study of the Kinetics of Its Intramolecular Hydrogen Exchange in Solution

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Abstract: The −100 °C X-ray-determined structure of $(CO)_4MnB_3H_7Br$ shows the bidentate B_3H_7Br ligand (in which the Br atom is attached to the unique B atom in an exo position) bound by two Mn–H–B bridge bonds to the octahedrally coordinated manganese in molecules of C_s molecular symmetry. The orthorhombic crystals, of space group *Pmcn*, have unit cell parameters $a = 7.658$ (3) Å, $b = 9.084$ (3) Å, $c = 15.426$ (5) Å, $V = 1073$ (1) Å^3, and $Z = 4$. The X-ray structure was solved by heavy-atom methods and refined to $R_1 = 0.0536$ and $R_2 = 0.0652$ for 1473 independent θ–2θ observed reflections. The boron-bound hydrogen atoms in $(CO)_4MnB_3H_7Br$ undergo internal exchange in solution at rates amenable to study by NMR. Kinetic activation parameters for the intramolecular hydrogen-exchange process in $(CO)_4MnB_3H_7Br$, based on an analysis of $^1H\{^{11}B\}$ variable-temperature NMR spectra, are $\Delta G^{\ddagger}(23\ °C) = 12.2 \pm 0.1$ kcal/mol, $\Delta H^{\ddagger} = 10.7 \pm 0.7$ kcal/mol, and $\Delta S^{\ddagger} = -5.1 \pm 2.7$ eu. Mechanistic proposals for the intramolecular hydrogen-exchange processes in $(CO)_4MnB_3H_7Br$ and the related molecules $(CO)_3MnB_3H_8$ and $(CO)_4MnB_3H_8$ are discussed.

Introduction

Tetracarbonyl[bromoheptahydrotriborato(1−)]manganese, $(CO)_4MnB_3H_7Br$, is a moderately air-stable, light yellow solid (mp 48–49 °C, dec) which can be prepared by direct halogenation of tetracarbonyl[octahydrotriborato(1−)]manganese, $(CO)_4MnB_3H_8$.[1] The room-temperature ^{11}B NMR spectrum of $(CO)_4MnB_3H_7Br$ indicates that the B_3H_7Br ligand is bidentate and is halogenated at the unique boron atom B(2). In addition, a rapid intramolecular hydrogen exchange among the boron-bound hydrogens is indicated by the ^1H NMR spectrum, while the hy-

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