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Homogeneous Reductions of Nitrogen-Containing Substrates Catalyzed by Molybdenum(IV) Complexes with μ-Sulfido Ligands

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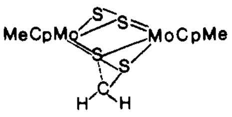
Molybdenum(IV) complexes of composition $[MeCpMo(\mu\text{-}S)]_2S_2CH_2$ (I) and $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ (II), where MeCp = $CH_3C_5H_4$, serve as homogeneous catalysts for the reduction of a series of nitrogen-containing substrates under 2–3 atm of hydrogen at mild temperatures. Phenyl azide is converted to aniline and azo compounds to hydrazines. The C=N bonds in imines, isothiocyanates, and isocyanates are selectively hydrogenated. Nitrobenzenes and phenylhydroxylamines are catalytically reduced to form anilines, while azoxybenzene and nitrosobenzene are reduced to 1,2-diphenylhydrazine. Reaction conditions and turnover numbers are presented. Some mechanistic features of the catalytic reduction of azobenzene are discussed.

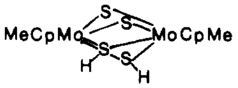
Introduction

We have reported that alkynes, allenes, and ketenes react with the bridging sulfido ligands in the molybdenum dimer $[MeCpMo(\mu\text{-}S)]_2S_2CH_2$ (I) to form stable 1,2-dithiolate ligands. Under mild conditions the dithiolate bridges are reduced by hydrogen to produce the corresponding alkenes or aldehydes and to regenerate I.[2] One characteristic of these reactions is that an excess of the unsaturated reactant inhibits the reduction. As a result, catalytic cycles for these substrates are maintained only at relatively high hydrogen pressures and low substrate concentrations.

More recently we have studied the potential reactivity of I and the related dimer $[MeCpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$[3] (II) with a variety of small molecules which contain heteroatoms at the unsaturated sites. Very few sulfur-coordinated adducts have been detected in these studies.[4] However we have found that both complexes I and II serve as homogeneous catalysts for the reduction of a series of such unsaturated molecules under a hydrogen atmosphere. Reaction conditions and product characterizations are reported here for the reduction of N=N bonds in azides and azocompounds, of C=N bonds in imines, isocyanates, and isothiocyanates, and of N—O bonds in nitrobenzenes, phenylhydroxylamines, nitrosobenzene, and azoxybenzene. Unlike the previously reported alkyne hydrogenations catalyzed by I,[2] these reactions proceed under mild conditions in the presence of large molar excesses of substrate.



I



II

In a few cases the reactions provide selectivity which is not readily achieved with other catalytic reducing systems. An additional feature of interest in these systems is the identification of well-defined molybdenum sulfido complexes which catalyze a wide range of hydrogenation and hydrogenolysis reactions. The complexes may model aspects of the reactivity of heterogeneous hydrotreating catalysts which are believed to contain molybdenum sulfide phases.[5] In addition the reactions of many synthetic sulfur-ligated molybdenum complexes and clusters with unsaturated nitrogen compounds have been of interest because of their possible relevance to the enzyme nitrogenase.[6-24] However, relatively few examples of catalytic reactivity have been identified in the studies of these previous systems.

Results and Discussion

The results of our investigation of the scope of the catalytic activity of I and II are summarized in Table I. Hydrogenations were carried out by stirring a 10–50-fold molar excess of substrate with catalyst in an organic solvent at 25 or 60 °C under a large molar excess of hydrogen (2–3 atm of pressure). Reaction conditions have not been

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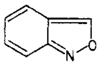
Table I. Data for the Reduction of Nitrogen-Containing Substrates by Hydrogen Catalyzed by Soluble Molybdenum(IV) Dimers with Sulfido Ligands

cat. (concn, M)[a]	substr (concn, M)	[substr]/[cat.]	temp, °C	intermed product	final product	mol of prod[b]/mol of cat.	
						1 H	24 H
I (2.3×10^{-2})	$C_6H_5N{=}NC_6H_5$ (1.1)	48	room		$C_6H_5NHNHC_6H_5$	13	
II (2.3×10^{-2})	$C_6H_5N{=}NC_6H_5$ (1.1)	48	room		$C_6H_5NHNHC_6H_5$	9	
II (2.6×10^{-2})	$EtCO_2N{=}NCO_2Et$ (1.6)	62	room		$EtCO_2NHNHCO_2Et$	27	
II (4.2×10^{-3})	(p-$H_2NC_6H_4N)_2$ (0.036)[c]	9	room		p-$NH_2C_6H_4NH_2$	0.6	
I (2.7×10^{-2})	$C_6H_5N(O){=}NC_6H_5$ (0.56)	21	room		$C_6H_5NHNHC_6H_5$	8	
I (2.8×10^{-2})	$C_6H_5N_3$ (0.46)	16	room		$C_6H_5NH_2$		4
I (2.8×10^{-2})	$C_6H_5NO_2$ (0.97)	35	room	C_6H_5NHOH		2	
					$C_6H_5NH_2$	2	
II (3.0×10^{-2})	$C_6H_5NO_2$ (1.5)	50	room		$C_6H_5NH_2$		22
I (2.8×10^{-2})	C_6H_5NHOH (0.60)	21	room		$C_6H_5NH_2$	2	
II (2.8×10^{-2})	C_6H_5NHOH (0.60)	21	room		$C_6H_5NH_2$	2	
I*[d] (1.7×10^{-2})	$C_6H_5NO_2$ (0.33)	19	room	C_6H_5NHOH		2[e]	
I* (1.6×10^{-2})	p-$BrC_6H_4NO_2$ (0.33)	21	room	p-BrC_6H_4NO[f]		4[e]	
					p-$BrC_6H_4NH_2$	1[e]	
I* (1.7×10^{-2})	p-$H_2NC_6H_4NO_2$ (0.33)[g]	19	room		p-$NH_2C_6H_4NH_2$		6
I* (1.6×10^{-2})	p-$(NO_2)_2C_6H_4$ (0.35)[g]	22	room	p-$NO_2C_6H_4NHOH$		5[h]	
				p-$NO_2C_6H_4NH_2$		*h*	
					p-$NH_2C_6H_4NH_2$	*h*	
I* (1.7×10^{-2})	o-$(CHO)C_6H_4NO_2$ (0.33)	19	room			6[e]	
I* (1.6×10^{-2})	C_6H_5NO (0.33)	21	room	$C_6H_5N(O){=}NC_6H_5$		2[e]	
					$C_6H_5NHNHC_6H_5$	8[e]	
I (5.3×10^{-2})	CH_3NCO (0.98)	18	room		$CH_3N(H)CHO$		1
I (5.5×10^{-2})	C_6H_5NCO (0.92)	16	room		$C_6H_5N(H)CHO$		2
I (2.7×10^{-2})	CH_3NCS (2.2)	81	room		$CH_3N(H)CHS$[i]		29
I (5.8×10^{-3})	$C_6H_5CH{=}NC_6H_5$ (0.09)[c]	16	60		$C_6H_5CH_2N(H)C_6H_5$	2	
II (4.8×10^{-3})	$C_6H_5CH{=}NC_6H_5$ (0.09)[c]	19	60		$C_6H_5CH_2N(H)C_6H_5$	2	
II (5.0×10^{-3})	$C_6H_5CH{=}NCH_3$ (0.081)[c]	16	60		$C_6H_5CH_2N(H)CH_3$		3

[a] The solvent was $CDCl_3$ unless otherwise noted. [b] Product to substrate ratios were determined by NMR. [c] Solvent was THF. [d] The asterisk denotes complex I with C_5H_5 ligands. [e] Turnover frequencies were averaged from data taken after a 2- or 3-h reaction period. [f] Tentatively identified by mass spectral data which shows highest mass at m/e 185 and 183. [g] Substrate was not completely soluble in initial solution. [h] See ref 38. [i] A 6:1 E:Z isomer ratio is formed.[59]

optimized for catalytic activity, and turnover numbers in the table are reported for a relatively early stage in each of the reactions. Although each reaction proceeds to ultimately form a single product, in some cases intermediates have been detected, and these are also indicated in the table. The products were identified by comparison of spectral data with that of authentic samples. The pure product could generally be separated from the molybdenum catalyst by extraction into pentane or diethyl ether. Some notable features of the catalytic reactions are discussed here.

Reduction of Nitrogen–Nitrogen Bonds. Complex I catalyzes the reduction of phenyl azide to aniline and, presumably, dinitrogen. No intermediates or side products are detected when the reaction is followed by NMR. The catalytic reduction of azides to primary amines is usually accomplished by hydrogenation over group VIII (8–10[60]) heterogeneous catalysts.[25] We have not found previous examples of the reduction of the azido group catalyzed by a discrete transition-metal complex in solution.

Complexes I and II function comparably as homogeneous catalysts for the hydrogenation of azocompounds. The products of the reductions are generally the corresponding hydrazines. No benzidine rearrangement products are detected under these mild nonaqueous conditions; and 4,4′-azodianiline is the only azo system in which a further reduction (to 1,4-phenylenediamine) has been observed at 25 °C. We have detected no evidence for catalyst decomposition during the hydrogenations, and azo compounds in molar excesses of 10^4 have been completely reduced to the respective hydrazines. The reduction of azoxybenzene to 1,2-diphenylhydrazine in the presence of I occurs at a rate fairly comparable to that of azobenzene.

A number of catalysts for the reductions of azo compounds, either by hydrogen or by non-transition-metal hydrides, have been reported previously. Simple metal chlorides, including $MoCl_5$,[26] dithiocarbamate complexes of molybdenum,[13] and $[Rh(CO)_2Cl]_2$[27] have been found to catalyze the reduction of azo compounds by $NaBH_4$ or $LiAlH_4$. Bis(dimethylglyoximate)cobalt(II)[28] and a $(py)_3RhCl_3$–$NaBH_4$ system[29] are known homogeneous systems which catalyze the reduction by hydrogen; a number of heterogeneous catalysts are known as well.[30–32] The molybdenum complexes reported here result in turnover frequencies which are comparable to or larger than many of the metal-based systems previously reported.[28,31,32]

Reduction of Nitrogen–Oxygen Bonds. Nitrobenzenes are catalytically reduced to anilines under mild conditions with these molybdenum systems. Previous work has shown that a number of metal carbonyl complexes serve as catalysts for the reduction of nitrobenzenes by a mixture of CO and H_2O.[33] Some of these systems

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also catalyze the reduction by molecular hydrogen.[33c] Relatively few non-carbonyl catalysts are known for the homogeneous conversion of nitro compounds to amines,[29,34] and in most of the previously studied systems, relatively high pressures have been required in order to achieve reduction.[33,34]

During the course of nitrobenzene reduction with I as the catalyst, the formation of phenylhydroxylamine is observed. Although nitrosobenzene might be expected to also be an intermediate in the nitrobenzene to aniline reduction (eq 1), significant concentrations do not build up during the reaction. In separate experiments, we have established that excess nitrosobenzene is reduced rapidly in the presence of I to diphenylhydrazine. Azoxybenzene, a product resulting from the condensation of nitrosobenzene and phenylhydroxylamine,[35] is detected as an intermediate in this reaction (eq 2).[36]

$$\mathrm{PhNO_2} \xrightarrow[\mathrm{I}]{\mathrm{H_2}} \mathrm{PhNO} + \mathrm{H_2O} \xrightarrow[\mathrm{I}]{\mathrm{H_2}} \mathrm{PhNHOH} \xrightarrow[\mathrm{I}]{\mathrm{H_2}} \mathrm{PhNH_2} + \mathrm{H_2O} \qquad (1)$$

$$\mathrm{PhNO} \xrightarrow[\mathrm{I}]{\mathrm{H_2}} \mathrm{PhNHOH} \xrightarrow{\mathrm{PhNO}} \mathrm{PhN(O){=}NPh} + \mathrm{H_2O} \xrightarrow[\mathrm{I}]{\mathrm{H_2}} \mathrm{PhN(H)N(H)Ph} + \mathrm{H_2O} \qquad (2)$$

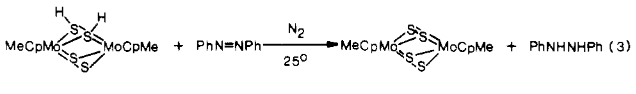
The relative rates of reduction for a series of substituted nitrobenzenes have been compared by using complex I as a catalyst,[37] and the results are included in Table I. Electron-withdrawing substituents at the para position of the substrate appear to result in some enhancement of the rate of nitro reduction, and vice versa. The reduction of *p*-dinitrobenzene proceeds in a stepwise fashion, and both *p*-$\mathrm{NO_2C_6H_4NHOH}$ and *p*-$\mathrm{NO_2C_6H_4NH_2}$ are observed as intermediates.[38] The reduction of *o*-nitrobenzaldehyde in the presence of I resulted in the clean formation of anthranil rather than the expected amino derivative.

Reduction of Carbon–Nitrogen Bonds. Methyl and phenyl isocyanate and methyl isothiocyanate are hydrogenated slowly in the presence of I at 60 °C. The reactions selectively produce *N*-methylformamide, formanilide, and *N*-methylthioformamide, respectively. Under these conditions, no evidence for further reductions or coupling reactions between reduced product and substrate were observed. The stoichiometric reduction of isocyanates and isothiocyanates by non-transition-metal hydrides leads to *N*-alkylamines.[39] Although examples of the stoichiometric insertion of a heterocumulene into a metal–hydride bond[40,41] and into the S–H bond of a coordinated mercaptide ligand[42] have been reported, we have not found previous examples of the selective hydrogenation of the C=N bond in these molecules catalyzed by a discrete transition-metal complex.

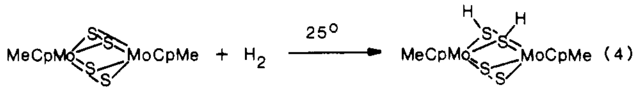
The reduction of phenyl isothiocyanate is more complex than the reactions discussed above. In the hydrogenation of a 30-mol excess of substrate at 60 °C, the final major products, observed after several days, are hydrogen sulfide and *N*-methylthiocarbanilide ($\mathrm{PhN(H)C({=}S)N(CH_3)Ph}$). At this stage, the molybdenum catalyst I is largely converted to the thioformaldehyde adduct of I[4] and $[\mathrm{CpMoS_2CH_2}]$.[2] The *N*-methylthiocarbanilide is believed to result from the initial formation of *N*-methylaniline and its addition to the starting cumulene.[43,44]

Although slow hydrogenatins of *N*-benzylidenemethylimine and -benzylimine to the corresponding amines have been observed with catalysts I and II, neither nitriles nor isonitriles were found to be hydrogenated under the conditions studied here.

Mechanistic Considerations. The mechanisms of the catalytic reductions are of interest because of the possible role of sulfur ligands in both the hydrogen activation and the hydrogen transfer process. For example, in the reaction of II with azobenzene in the absence of hydrogen, no adduct formation was observed, as mentioned above. However, a different type of reaction was characterized which involved the stoichiometric dehydrogenation of the hydrosulfido ligands, as shown in eq 3. The reaction proceeds quantitatively to form III which has been isolated and characterized by spectral methods.[45] Complex III was found to react cleanly with an atmosphere of hydrogen at 25 °C to reform II (eq 4). The reversible dissociation of hydrogen from II does not appear to be a facile process.[47] Solutions of complex II obey Beer's law over a concentration range of 2×10^{-6} to 2×10^{-4} M and are stable under reduced pressure. Reactions 3 and 4 define a room-temperature catalytic cycle for the reduction of azo com-



II III



III II

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(36) Significant amounts of aniline were not observed in reaction 2. Nitrosobenzene is known to react with aniline to form azobenzene: March, J. "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure"; McGraw Hill: New York, 1968; p 908.

(37) The complex with unsubstituted cyclopentadienyl rings, denoted as I*, was used in these studies.

(38) When the reaction is monitored by 90-MHz NMR, a new set of resonances (AA'BB'), assigned to intermediate A, is observed centered at 7.56 ppm. For example, after a reaction time of 3.5 h at 25 °C, the starting substrate is completely converted to intermediate A (~80%) and *p*-$\mathrm{NO_2C_6H_4NH_2}$, B (~20%). After 6.5 h, the distribution of A/B is approximately 40%/60%. When the reaction was heated at 60 °C for 12 h, complete conversion to 1,4-phenylenediamine was observed. Electron-impact mass spectral data (*m*/*e*) for A: 154 (parent for $\mathrm{O_2NC_6H_4NHOH^+}$, relative intensity 14), 152 ($\mathrm{O_2NC_6H_4NO^+}$, 38), 138 ($\mathrm{ONC_6H_4NHOH^+}$, 100). The data indicate either that $\mathrm{O_2NC_6H_4NO}$ and $\mathrm{O_2NC_6H_4NHOH}$ are components of A or that the former is produced in the mass spectrometer.

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(44) The reductive cleavage of a C=S moiety has been catalyzed previously by complex I in the reaction of hydrogen with carbon disulfide.[4]

(45) The pentamethylcyclopentadienyl analogue of III has been reported.[46] Spectral characterization of III is included in the Experimental Section.

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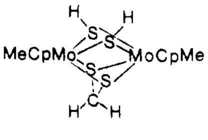
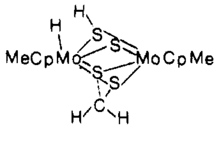
(47) The facile elimination of $\mathrm{H_2}$ from II is observed, however, in the presence of unsaturated molecules such as alkenes and alkynes.[3]

pounds.[48] However analogous stoichiometric hydrogen transfer from II to the other types of nitrogen-containing substrates in Table I is not generally observed.

In contrast to the reactivity of III, no spectral evidence is observed for the reaction of I with hydrogen. Nor does I undergo a detectable interaction with the substrates in the absence of hydrogen. On the basis of reactions 3 and 4, it seems reasonable to postulate that activation of hydrogen by I to form an intermediate such as IV[49] occurs prior to interaction of the catalyst with the substrate. The catalytic hydrogenation of azo compounds, for example, is inhibited by the presence of excess alkene which is known to interact with the sulfido ligands of I, thereby blocking the proposed site of hydrogen activation. However, in view of the documented ability of metal ions in organometallic complexes to activate molecular hydrogen, intermediates with metal hydrides, e.g., V, cannot be ruled out.



IV



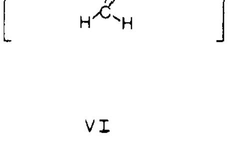
V

Several pathways for the transfer of hydrogen from such intermediates to the substrate can be considered. In our discussion here, we will focus on the azobenzene reduction catalyzed by I (reaction 5). It should be noted that

$$\mathrm{PhN{=}NPh} + \mathrm{H_2} \xrightarrow[\mathrm{(MeCpMoS)_2S_2CH_2}]{} \mathrm{PhN(H)N(H)Ph} \quad (5)$$

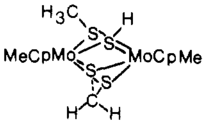
mechanistic features appear to vary significantly with different substrates. The turnover frequency of reaction 5 is not markedly affected by the presence of acid (trifluoroacetic) or base (triethylamine) present in a 25 mol % ratio with the molybdenum catalyst. Typical turnover frequencies/h in THF are 17 (acid), 20 (blank), and 24 (base). The differences observed here are near the limit of experimental error. (See Experimental Section.) A larger effect might be expected if the major pathway were acid or base catalyzed, and we conclude that the reaction of an ionic intermediate does not constitute a major pathway for the azo reduction. The observed insensitivity of the catalytic reaction to increased solvent polarity is also consistent with this conclusion.[50]

Another mechanistic possibility for reaction 5 is a radical chain reaction which might be initiated by the cleavage of an S–H bond in IV (or V) to form a dimer with a thiyl radical ligand. A model for this type of intermediate has been synthesized recently, VI.[51] In experiments which were monitored by EPR and NMR spectroscopy, we have detected no evidence for an interaction between this derivative and azobenzene at room temperature or at 60 °C. Moreover, the turnover frequency for Reaction 5 is not decreased by the presence of hydroquinone (25 mol %/mol of catalyst) which is expected to inhibit a radical chain process.



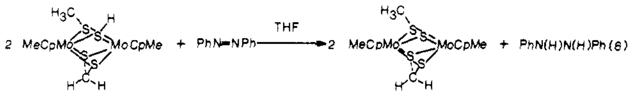
VI

The latter result does not rule out a hydrogen atom transfer mechanism for the reduction reaction. We have recently synthesized a molybdenum(III) dimer with a bridging hydrosulfido ligand, VII, which closely models



VII

the electronic and structural properties of the proposed intermediate IV.[52] The hydrosulfido complex VII reacts rapidly with azobenzene in THF to form the known mixed-valence dimer VI and diphenylhydrazine (reaction 6).



VII VI

It seems reasonable to propose that a similar type of hydrogen atom transfer occurs during the catalytic reaction 5.[53] It is apparently thermodynamically unfavorable for the diphenylhydrazyl radical to abstract a hydrogen atom from THF (C–H bond dissociation energy for THF = 92 kcal/mol),[54] and 2 mol of molybdenum dimer are necessary for the reduction of 1 mol of azobenzene. A similar stoichiometry for reaction 6 was observed in the presence of excess cyclohexadiene ($\mathrm{BDE_{C-H}}$ = 76 kcal/mol).[54] If the diene served as a major source of hydrogen for the diphenylhydrazyl radical, we would expect to observe a 1:1 stoichiometry in eq 6. Although we have not found reported quantitative data on the N–H bond energy of diphenylhydrazine, the above studies support the conclusion that hydrogen abstraction by the diphenylhydrazyl radical is quite selective. The abstraction of the second hydrogen atom could occur through a disproportionation of the hydrazyl radical (although present in very low concentration) (eq 7)[55] or by reaction with the molybdenum dimer

$$2\mathrm{PhNH\dot{N}Ph} \rightarrow \mathrm{PhN(H)N(H)Ph} + \mathrm{PhN{=}NPh} \quad (7)$$

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[48] However, under a hydrogen atmosphere additional reactive species may be formed in eq 3 and 4.

[49] Extended Hückel calculations on I have shown that the sulfido ligands should have acceptor properties favorable for interaction with hydrogen similar to those described previously for II.

[50] Average turnover numbers/h for reaction 5: toluene, 20; $\mathrm{CH_2Cl_2}$, 12.

(51) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119.

(52) Synthetic details and characterization data are included in the Experimental Section. A more complete study of the chemistry of this derivative will be reported. Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.*, in press.

(53) It is difficult to distinguish between hydrogen atom transfer and electron followed by proton transfer in reaction 6. Outer-sphere electron transfer from a related molybdenum(III) dimer $\mathrm{(MeCpMo)_2S_2CH_2(\mu\text{-}SCH_3)_2}$ to azobenzene does not occur in the presence of water as a proton donor. No diphenylhydrazine is detected after such a reaction is stirred for several hours. Use of a strong acid, such as $\mathrm{HBF_4}$ or $\mathrm{CF_3CO_2H}$, as a proton donor in the above reaction results in rapid one-electron oxidation of the molybdenum complex. No diphenylhydrazine is produced. The following reference provides data on the reduction potential of azobenzene as a function of acid strength and concentration: Boto, K. G.; Thomas, F. G. *Aust. J. Chem.* **1973**, *26*, 1669, 2409, 2417.

(54) (a) Benson, S. W.; Golden, D. M. *Chem. Rev.* **1969**, *69*, 125. (b) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976; p 299.

VII. These investigations of the source of the reducing hydrogen in eq 6 suggest that the S–H bond dissociation energy of complex VII is considerably less than those characteristic of organic thiols (~90 kcal/mol).[56,57]

As expected from these stoichiometric model studies, the molybdenum complex serves as the ultimate source of both reducing hydrogens in the catalytic reaction (reaction 5) as well. For example, when the reaction is carried out in THF under a deuterium atmosphere, PhN(D)N(D)Ph is the major product.[61] NMR integration of the isolated product shows <0.1 N–H/hydrazine molecule. It would be interesting to determine whether the solvent would serve as a source of hydrogen atoms as the reactivity of the intermediate substrate radical is increased or whether the nature of substrate–catalyst interaction precludes solvent involvement. Further mechanistic studies with other substrates are in progress.

Experimental Section

Materials. The molybdenum dimers $(\mathrm{MeCpMoS})_2\mathrm{S_2CH_2}$[2] (I), $[\mathrm{MeCpMo}(\mu\text{-S})(\mu\text{-SH})]_2$[3] (II), and $(\mathrm{MeCpMo})_2(\mathrm{S_2CH_2})(\mu\text{-S})(\mu\text{-SCH_3})$[51] (VI) and phenyl azide[58] were prepared as reported previously. Azo compounds, nitrobenzenes, phenylhydroxylamine, nitrosobenzene, isocyanates, isothiocyanates, and imines were purchased from commercial suppliers and used without purification for the hydrogenation studies. Tetrahydrofuran was distilled from $\mathrm{LiAlH_4}$, and dichloromethane was distilled from $\mathrm{P_4O_{10}}$ prior to use. In some cases deuteriochloroform was passed through basic alumina prior to use. Reagent grade hydrogen and deuterium (99.9%) were purchased from Matheson.

Instrumentation. Visible spectral data were recorded on a Cary 219 spectrophotometer. NMR spectra were recorded at 90 MHz on a Varian EM 390 or a JEOL FX-90-Q spectrometer and referenced to tetramethylsilane. Mass spectra were obtained on a Varian MAT CH-5 spectrometer or a VG 7070 EQ-HF tandem mass spectrometer.

Hydrogenation Reactions. In a typical procedure, 0.10 g (0.2 mmol) of molybdenum dimer I or II was dissolved in 10 mL of $\mathrm{CDCl_3}$ and 25–50 equiv of substrate was added. The solution was placed in a 200-mL reaction vessel equipped with a high vacuum valve and degased in two or three freeze–pump–thaw cycles. Hydrogen ($^3/_4$–1 atm) was added at −196 °C. After the flask was sealed, the solution was warmed to the reaction temperature and stirred throughout the reaction period. Solutions were analyzed by NMR after a time period of 1 or 24 h to determine percent conversion of substrate to product. Most turnover determinations were repeated several times and were found to be reproducible ±10%. In separate experiments, similar reactions were carried out for several days and then analyzed by NMR to determine final product purity. Organic products could usually be isolated by evaporation of the solvent and extraction with ether. Products were identified on the basis of NMR and mass spectral data. Under similar conditions no hydrogenation activity was observed for solutions of substrate and hydrogen in the absence of molybdenum complex.

Synthesis of $(\mathrm{CH_3C_5H_4Mo})_2(\mu\text{-S})_2(\mu\text{-S}_2)$ (III). The reaction of an equimolar ratio of II and azobenzene was monitored by NMR and found to proceed quantitatively. For a larger scale synthesis, the following procedure was followed. Complex II (0.30 g, 0.62 mmol) and azobenzene (0.37 g, 2.0 mmol) were dissolved in dichloromethane under nitrogen. After the reaction was stirred for 3–4 h, the solvent was rotoevaporated. The remaining solid was washed with ether until washings were nearly colorless to remove azo and hydrazo compounds. III is a brown solid which forms blue solutions in organic solvents: yield 70%; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 2.32 (s, 6, $\mathrm{CH_3}$), 6.24 (m, 8, Cp); IR (Nujol) 432 cm^{-1} (m); visible ($\mathrm{CH_2Cl_2}$) 525 nm (ϵ 9.7×10^2 M^{-1} cm^{-1}); 628 (2.1×10^3); 770 (1.6×10^3). Anal. Calcd for $\mathrm{C_{12}H_{14}Mo_2S_4}$: C, 30.13; H, 2.95; S, 26.81. Found: C, 30.16; H, 2.93; S, 26.70.

Reaction of $(\mathrm{MeCpMo})_2(\mu\text{-S})_2(\mu\text{-S}_2)$ (III) with Hydrogen. Complex III (0.048 g, 0.1 mmol) was dissolved in 100 mL of $\mathrm{CH_2Cl_2}$, and the solution was degassed in a freeze–pump–thaw cycle. One atmosphere of hydrogen was added at room temperature, and the solution was stirred. Monitoring of the visible absorption spectrum indicated that the formation of II was quantitative and complete within 90 min.

Synthesis of $(\mathrm{MeCpMo})_2(\mu\text{-SH})(\mu\text{-SCH_3})\mathrm{S_2CH_2}$ (VII). A THF solution of VI (0.16 mmol), which was prepared under $\mathrm{N_2}$, was degassed in one freeze–pump–thaw cycle, and 1 atm of hydrogen was added at −196 °C. The solution was stirred at 25 °C for 2–12 h. The resulting highly air-sensitive orange-brown product could be isolated under an inert atmosphere by evaporation of the solvent. ^{1}H NMR (THF-d_8) δ −1.3 (s, 1, SH), 1.52 (s, 3, $\mathrm{SCH_3}$), 2.00 (s, 6, $\mathrm{CH_3Cp}$), 5.41 (s, 8, Cp), 5.76 (s, 2, $\mathrm{S_2CH_2}$); the resonances are relatively broad; IR (mineral oil mull) 2380 cm^{-1} (ν_{SH}, vw). The identity of the complex was further confirmed by reactivity studies which will be described elsewhere.[52]

Reaction of $(\mathrm{MeCpMo})_2(\mu\text{-SH})(\mu\text{-SCH_3})\mathrm{S_2CH_2}$ with Azobenzene. A THF solution of VII (0.17 mmol) was added to 45 mg (0.25 mmol) of azobenzene. An immediate color change to the characteristic pink color of VI was observed. After the solution was stirred for 30–60 min, the solvent was removed in vacuo. An NMR sample in $\mathrm{CDCl_3}$ was prepared in the glovebox. By integration of the phenyl resonances the relative ratio of diphenylhydrazine/azobenzene was determined. In three separate runs, yields corresponding to ~0.4–0.5 mol of the hydrazine/mol of molybdenum dimer were found. The reaction was repeated with the addition of 50 equiv of cyclohexadiene to the THF solvent. A yield of ~0.4 mol of hydrazine/mol of dimer was found.

In contrast no reaction was observed between compound VI and azobenzene. An EPR spectrum of VI and excess azobenzene in THF under $\mathrm{N_2}$ was identical with the EPR spectrum of the control solution of VI.

Acknowledgment. Support by the National Institutes of Health (to M.R.D. for C.J.C. and L.L.W.) and the Department of Energy, Office of Basic Energy Science (to M.R.D. for W.K.M.) and in part by the National Science Foundation (for D.E.C.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged. M.R.D. is grateful for a fellowship from the John Simon Guggenheim Foundation, 1984–1985.

Registry No. I, 85565-70-4; I*, 100791-17-1; II, 77480-01-4; III, 100791-15-9; VI, 99510-48-2; VII, 100791-16-0; $\mathrm{C_6H_5N{=}NC_6H_5}$, 103-33-3; $\mathrm{C_6H_5NHNHC_6H_5}$, 122-66-7; $\mathrm{EtO_2CN{=}NCO_2Et}$, 1972-28-7; $\mathrm{EtO_2CNHNHCO_2Et}$, 4114-28-7; $p\text{-}\mathrm{H_2NC_6H_4N{=}NC_6H_4NH_2}\text{-}p$, 538-41-0; $p\text{-}\mathrm{H_2NC_6H_4NH_2}$, 106-50-3; $\mathrm{C_6H_5N(O){=}NC_6H_5}$, 495-48-7; $\mathrm{C_6H_5N_3}$, 622-37-7; $\mathrm{C_6H_5NH_2}$, 62-53-3; $\mathrm{C_6H_5NO_2}$, 98-95-3; $\mathrm{C_6H_5NHOH}$, 100-65-2; $p\text{-}\mathrm{BrC_6H_4NO_2}$, 586-78-7; $p\text{-}\mathrm{BrC_6H_4NO}$, 3623-23-2; $p\text{-}\mathrm{BrC_6H_4NH_2}$, 106-40-1; $p\text{-}\mathrm{H_2NC_6H_4NO_2}$, 100-01-6; $p\text{-}\mathrm{NO_2C_6H_4NO_2}$, 100-25-4; $o\text{-}\mathrm{OHCC_6H_4NO_2}$, 552-89-6; $\mathrm{C_6H_5NO}$, 586-96-9; $\mathrm{H_3CNCO}$, 624-83-9; $\mathrm{H_3CNHCHO}$, 123-39-7; $\mathrm{C_6H_5NCO}$, 103-71-9; $\mathrm{C_6H_5NHCHO}$, 103-70-8; (E)-$\mathrm{H_3CNHCHS}$, 79297-85-1; (Z)-$\mathrm{H_3CNHCHS}$, 79297-84-0; $\mathrm{C_6H_5CH{=}NC_6H_5}$, 538-51-2; $\mathrm{C_6H_5CH{=}NCH_3}$, 622-29-7; $\mathrm{C_6H_5CH_2NHCH_3}$, 103-67-3; 2,1-benzisoxazole, 271-58-9.

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(57) A similar conclusion was suggested by our reported observation that complex VI does not abstract a hydrogen atom from cyclohexadiene.[51]

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(60) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III 3 and 13.)

(61) **Note Added in Proof.** Control experiments have established that the NH protons of diphenylhydrazine exchange with deuterium gas to a measurable extent under the conditions of reaction 5. Thus, labeling studies cannot rule out solvent as a minor source of hydrogen in reaction 5, since the NH product so formed could undergo further exchange with $\mathrm{D_2}$.