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Supplementary Material Available: Procedure for the preparation of **4**, listings of crystal and positional parameters, bond lengths, angles, van der Waals contacts, and torsional angles, and ORTEP diagrams (28 pages). Ordering information is given on any current masthead page.

Cleavage of the N–N Bond in a High-Oxidation-State Tungsten or Molybdenum Hydrazine Complex and the Catalytic Reduction of Hydrazine

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In spite of a vast amount of research on nitrogenases[1] and isolable transition-metal dinitrogen complexes,[2] few details are known about how the N–N bond of dinitrogen is cleaved to give ammonia. Explanations involving enzymes focus on bound diazene and hydrazine as intermediates.[1] Synthetic and mechanistic studies on low-oxidation-state "Chatt-type" complexes, $M(N_2)_2L_4$ (M = Mo or W; L = a phosphine), and related derivatives suggest that (i) a single metal center is sufficient for reducing dinitrogen stoichiometrically to ammonia if an open coordination site is available; (ii) a hydrazido(2−) complex ($M{=}NNH_2$) is a key intermediate; and (iii) the N—N bond is cleaved either in a $M{=}NNH_3$ or $M{=}NHNH_3$ intermediate to give a $M{\equiv}N$ or $M{=}NH$ species, respectively.[3] We report here some results which suggest that the N–N bond is cleaved in coordinated hydrazine in relatively high oxidation state complexes having the MCp^*Me_3 core.

Complexes of the type $MCp^*Me_3(OTf)$ (M = Mo[4] or W;[5] OTf = OSO_2CF_3; Cp* = η^5-C_5Me_5) react with 1 equiv of hydrazine to give what are postulated to be η^2-hydrazine complexes (**1a** and **1b**; eq 1).[6] A monomeric structure containing η^2-hydrazine is proposed on the basis of the following: (i) the structure of $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$ is similar to the structure shown in eq 1;[7] (ii) ^{15}N NMR studies suggest that the hydrazine ligand in $[WCp^*Me_4(NH_2NH_2)]^+$ is bound in an η^2 fashion;[8] (iii) two η^2-NH_2NRR' complexes have been structurally characterized;[9] and (iv) conductivity studies on **1b** in nitromethane suggest that it is a 1:1 electrolyte analogous to $[WCp^*Me_4(\eta^2\text{-}NH_2NH_2)]^+$.[10,18]

Table I. Stoichiometric Reductions To Give Ammonia

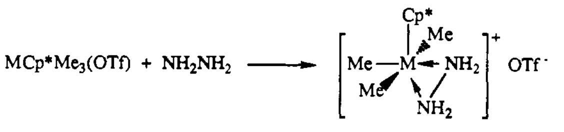
complex	NH_3 yield, equiv	conversion, %
$[Mo](N_2H_4)^{+\,b,c}$	1.80 (3)^d	90^e
$[W](N_2H_4)^{+\,c}$	1.84 (2)	92
$N_2H_4{}^{a-c}$	0.12 (4)	6
$[Mo](OTf)^c$	0.05 (2)	<3
$[W](OTf)^c$	0.05 (2)	<3
$[W](NNH_2)^{a,b}$	1.80 (3)	90

[a] Zn/Hg with base distillation. [b] Zn/Hg without base distillation. [c] $CoCp_2$ with base distillation. [d] Number of experiments. [e] Variation ±3% between experiments.

Table II. Catalytic Reductions of Hydrazine to Ammonia

complex	added N_2H_4, equiv	NH_3 yield, equiv	conversion, %
$[Mo](N_2H_4)^+$	2 (2)^a	5.70 (6)^b	95
	3 (4)	6.88 (8)	86
	4 (3)	8.70 (10)	87
$[W](N_2H_4)^+$	2 (2)	5.88 (6)	98
	3 (4)	7.28 (8)	91
	4 (3)	8.30 (10)	83
$[W](NNH_2)$	3 (2)	6.72 (8)	84
	6 (1)	10.92 (14)	78

[a] Number of experiments. [b] Maximum yield possible.



(1)

1a (Mo); **1b** (W)

Both **1a** and **1b** are reduced by zinc amalgam or cobaltocene in THF in the presence of 2,6-lutidine hydrochloride (lutHCl) to give ammonia in >90% yield (Table I).[11] Since $[WCp^*Me_3(\eta^2\text{-}NH_2NH_2)]^+$ is reduced by sodium amalgam in the absence of lutHCl to give $WCp^*Me_3(NH)$[12] and ammonia in at least 70% yield, we propose that the N–N bond is cleaved in $WCp^*Me_3(NH_2NH_2)$. In the absence of added protons, an attractive mechanism for N–N cleavage is overall migration of an H_α proton to N_β, either in an η^1-hydrazine ligand (eq 2) or (equivalently) as shown in eq 3.[13] In the presence of protons, the N_β electron pair could be protonated in η^1-hydrazine (eq 2) or in one of the amido ligands in $WCp^*Me_3(NH_2)_2$. In all scenarios, ammonia would be formed smoothly since the required two electrons are provided by the metal.

Hydrazine can be reduced catalytically to ammonia in high yield by $[WCp^*Me_3(NH_2NH_2)]^+$ or $[MoCp^*Me_3(NH_2NH_2)]^+$ under conditions analogous to those employed for stoichiometric reductions (Table II). Catalytic reduction of hydrazine to ammonia

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(1) (a) Orme-Johnson, W. H. *Annu. Rev. Biophys. Biophys. Chem.* **1985**, *14*, 419. (b) Veeger, C., Newton, W. E., Eds. *Advances in Nitrogen Fixation Research*; Dr. W. Junk/Martinus Nijhoff: Boston, 1984. (c) Leigh, G. J. *J. Mol. Catal.* **1988**, *47*, 363.

(2) (a) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Radiochem.* **1983**, *27*, 197. (b) Leigh, G. J. *Trans. Met. Chem.* **1986**, *11*, 118. (c) Hidai, M.; Mizobe, Y. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1989; Vol. 11. (d) George, T. A.; Tisdale, R. C. *Inorg. Chem.* **1988**, *27*, 2909.

(3) Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *J. Chem. Soc., Dalton Trans.* **1989**, 425.

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(5) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331.

(6) Experimental details, NMR or EPR data, and elemental analyses can be found in the supplementary material. Hydrazine was obtained from Aldrich and dried with CaH_2.

(7) Liu, A. H.; O'Regan, M. B.; Finch, W. C.; Payack, J. F.; Schrock, R. R. *Inorg. Chem.* **1988**, *27*, 3574.

(8) A −80 °C ^{15}N NMR spectrum of $[WCp^*Me_4(\eta^2\text{-}{}^{15}NH_2{}^{15}NH_2)]^+PF_6^-$, prepared by treating $[WCp^*Me_4]^+PF_6^-$ with $^{15}NH_2{}^{15}NH_2$, shows a single nitrogen resonance at δ 29.7 (vs liquid NH_3) with $J_{NH} = 80$ and 83 Hz and $J_{NW} < 5$ Hz.

(9) (a) Bultitude, J.; Larkworthy, L. F.; Povey, D. C.; Smith, G. W.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1748. (b) Bailey, N. A.; Frisch, P. D.; McCleverty, J. A.; Walker, N. W.; Williams, J. *J. Chem. Soc., Chem. Commun.* **1975**, 350.

(10) $[WCp^*Me_4(\eta^2\text{-}NH_2NH_2)]^+$ loses methane slowly in nitromethane to give $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$, which is stable in nitromethane. Λ_0 (units Ω^{-1} mol^{-1} cm^{-2}) was determined to be 83 for $[Cp^*WMe_3(\eta^2\text{-}NH_2NH_2)]OTf$ and 93 for $[Cp^*WMe_4(\eta^2\text{-}NH_2NH_2)]PF_6$.[6]

(11) (a) Reductions were carried out in THF at room temperature under N_2 using 12 equiv of Zn/Hg and 16 equiv of lutidine hydrochloride. The reaction mixture was stirred for approximately 15 h. See supplementary material for a complete description of the workup procedure. The ammonia was quantified by the indophenol method.[11b] (b) Chaney, A. L.; Marbach, E. P. *Clin. Chem.* (*Winston-Salem, N.C.*) **1962**, *8*, 130.

(12) Addition of 1 or 2 equiv of ammonia to $MCp^*Me_3(OTf)$ yields $[MCp^*Me_3(NH_3)]^+OTf^-$ or $[MCp^*Me_3(NH_3)_2]^+OTf^-$, respectively (M = Mo or W). Each is deprotonated by excess NEt_3 to give $MCp^*Me_3(NH_2)$. In the presence of NEt_3, $WCp^*Me_3(NH_2)$ reacts with $FeCp_2{}^+PF_6{}^-$ to yield $WCp^*Me_3(NH)$ in high yield, we propose via $[WCp^*Me_3(NH_2)]^+$. So far $[WCp^*Me_3(NH_2)]^+$ has not been observed at room temperature by NMR.

(13) (a) We thank C. Cummins for this suggestion. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731. (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729.

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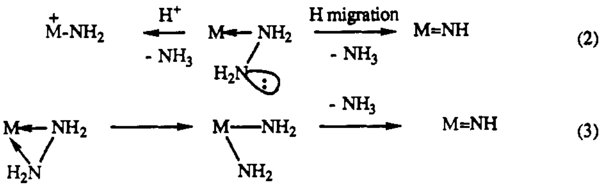

is rare,[14] although there are many examples of formation of dinitrogen and ammonia complexes from hydrazine, including $[Ru(NH_3)_5(N_2)]^{2+}$, the first dinitrogen complex.[15] The first four steps that are most plausible on the basis of the observed chemistry are shown in eq 4 (M = MCp^*Me_3). (In brackets are compounds that have not been observed and are believed to be unstable.) Steps that complete the cycle shown in eq 5 are based on the demonstrated reaction between $WCp^*Me_3(NH_2)$ and hydrazine to give $WCp^*Me_3(NNH_2)$ and $WCp^*Me_3(NH)$ as well as ammonia via disproportionation of $WCp^*Me_3(NHNH_2)$ in the absence of protons.[16] (The nature of the disproportionation in the absence of protons is still under investigation.) Support for the last step in eq 5 is protonation of $WCp^*Me_4(NHNH_2)$ to give $[WCp^*Me_4(NH_2NH_2)]^+$.[7] Note that the N-N bond in $WCp^*Me_3(NHNH_2)$ (d^1) in the absence of protons most likely is cleaved in a *disproportionation* reaction, while in $WCp^*Me_3(NH_2NH_2)$ (d^2) it most likely is cleaved *intramolecularly*. Note also that $WCp^*Me_4(NHNH_2)$, $[WCp^*Me_3(NHNH_2)]^+$, and $[WCp^*Me_4(NH_2NH_2)]^+$, all formally d^0 complexes, are relatively stable toward N-N cleavage.

$$M(N_2H_4)^+ \xrightarrow{e} [M(N_2H_4)] \xrightarrow{-NH_3} M{=}NH \xrightarrow{H^+} [M(NH_2)^+] \xrightarrow{e} M(NH_2) \quad (4)$$

$$M(NH_2) \xrightarrow[-NH_3]{N_2H_4} [M(NHNH_2)] \xrightarrow{H^+} M(N_2H_4)^+ \quad (5)$$

We believe that these findings are relevant to the reduction of dinitrogen. So far we known that $WCp^*Me_3(NNH_2)$, a likely intermediate in a dinitrogen reduction system based on complexes having the MCp^*Me_3 core,[17] can be reduced to give ammonia (Table I) and is a catalyst for reducing hydrazine (Table II). However, reduction of $MCp^*Me_3(OTf)$ complexes under dinitrogen gives little ammonia (Table I). Side reactions (most likely protonations) probably destroy the metal site before dinitrogen can bind and $WCp^*Me_3(NNH_2)$ can form.

We believe that the chemistry of dinitrogen and N_2H_x and NH_y ligands bound to a single Mo or W in a high oxidation state is extensive and will offer further insight into the mechanism of dinitrogen reduction, especially if the metal site can be stabilized toward protons. Efforts in this direction are under way.

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Supplementary Material Available: Synthetic procedures, NMR and EPR data, and elemental analyses for **1a**, **1b**, and $WCp^*Me_3(NH)$, reduction procedures (stoichiometric and catalytic), and conductivity measurements (4 pages). Ordering information is given on any current masthead page.

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(16) (a) Similar results are observed in the reaction between $WCp^*Me_3(OTf)$ and LiN_2H_3, the reduction of $WCp^*Me_3(NHNH_2)^+$ with Na/Hg, and the deprotonation of $WCp^*Me_3(NH_2NH_2)^+$. The role of disproportionation reactions in Chatt-type compounds and derivatives has been addressed recently.[16b] (b) Kaul, B. B.; Hayes, R. K.; George, T. A. *J. Am. Chem. Soc.* **1990**, *112*, 2002.

(17) $WCp^*Me_3(OTf)$ is reduced under dinitrogen (no added H^+) to give $Cp^*Me_3W{=}NN{=}WCp^*Me_3$ in >90% yield.[5] The key proposed reaction is electrophilic attack on intermediate $WCp^*Me_3(\eta^1\text{-}N_2)$ by $WCp^*Me_3(OTf)$.

(18) Note added in proof: The proposed structure of **16** (eq 1) has now been proven in an X-ray study.

Bis(oxazolines) as Chiral Ligands in Metal-Catalyzed Asymmetric Reactions. Catalytic, Asymmetric Cyclopropanation of Olefins

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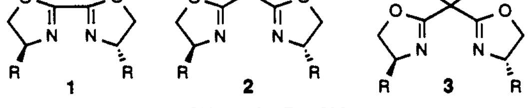
The design of catalytic, asymmetric reactions that proceed with high enantioselectivity is an important goal in chemical synthesis.[1] As a consequence of our continuing interest in asymmetric synthesis, we have been evaluating the potential utility of chiral 4,4′-disubstituted bis(oxazolines) such as **1**–**3** as bidentate ligands for several transition-metal-catalyzed reactions. In order to examine the stereodifferentiating ability of these ligands, and because of the importance of cyclopropanes of defined absolute stereochemistry,[2] we have studied the catalyzed asymmetric cyclopropanation of olefins.[3]



a, R = $CHMe_2$; b, R = CMe_3

Recently, chiral oxazoline ligands have been employed in metal-catalyzed asymmetric reactions.[4] Such ligands are attractive as a consequence of their topography and ease of synthesis from readily available chiral amino alcohols. We have constructed a number of such ligands, including the illustrated examples, **1**–**3**. One of these, the neutral ligand **3**, resembles the charged semicorrin ligand recently reported by Pfaltz, who has demonstrated that derived copper(I) complexes deliver high levels of enantioselection in the cyclopropanation of monosubstituted olefins by menthyl diazoacetate esters.[5] The purpose of this communication is to report a Cu(I) complex derived from ligand **3b** and copper(I) triflate which is an attractive catalyst for the cyclopropanation of mono- and 1,1-disubstituted olefins with achiral diazo esters at ambient temperatures. Asymmetric induction in excess of 99% and 1000-fold catalyst turnover are appealing attributes of these processes.

Initially, a search was made for a copper complex to catalyze the cyclopropanation of styrene with ethyl diazoacetate (eq 1). Complexes of chiral bis(oxazolines)[6,7] **1**–**3** with copper(I) triflate[8] were found to be highly effective catalysts for the reaction, which proceeds rapidly at 25 °C. The products were isolated as trans/cis mixtures of the cyclopropyl esters **5** and **6** whose absolute stereochemistry is as shown.[9] Copper(II) triflate complexes do not

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