$[(NH_3)_5Ru]^{n+}$ to $[(CN)_5Fe]^{n-}$ to $[(bpy)_2Ru]^{n+}$, is understandable. Thus, it seems, one could conveniently modify the metal–metal interaction by choosing the appropriate nonbridging "spectator ligands". This will have a large impact on the biological electron-transfer processes where the driving force (a function of redox asymmetry) plays an important role.[36]

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(37) One of the reviewers has suggested that this could be a trans isomer on the basis of IR spectral evidence presented in a manuscript that is under editorial consideration. However, we feel IR spectral evidence alone would prove insufficient for the correct assignment of the isomer. ^1H NMR spectral study for this compound, which is presently being undertaken in our laboratory, might solve this problem, and this will form the basis for a future paper.

Acknowledgment. We thank Dr. H. D. Bist, Department of Physics, IIT, Kanpur, India, for the emission and resonance Raman measurements and Dr. O. K. Medhi, Department of Chemistry, Gauhati University, Assam, India, for some of the electrochemical measurements. V.P. acknowledges the financial assistance (Senior Research Fellowship) by the CSIR, New Delhi, India.

Registry No. $[(bpy)_2Ru(NCSe)_2]$, 115794-05-3; $[(bpy)_2Ru(NCSe)Cl]$, 115704-98-8; $[(bpy)_2Ru(SeCN)Cl]$, 115704-99-9; $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$, 115705-03-8; $[(bpy)_2Ru(NCSe)Cl]BPh_4$, 115705-01-6; $[(bpy)_2Ru(NCSe)(SeCN)]BPh_4$, 115731-26-5; $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)_3$, 115705-05-0; $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)_2$, 115705-07-2; $[(bpy)_2Ru(NO)Cl](PF_6)_2$, 58575-12-5; *cis*-$[(bpy)_2RuCl_2]$, 19542-80-4; potassium azide, 20762-60-1.

Contribution from the Department of Chemistry, 6-331,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Preparation and Characterization of Two Unsubstituted Hydrazido(1–) Complexes, $W(\eta^5\text{-}C_5Me_5)Me_4(\eta^2\text{-}NHNH_2)$ and $[W(\eta^5\text{-}C_5Me_5)Me_3(\eta^2\text{-}NHNH_2)]^+[SO_3CF_3]^-$

R. R. Schrock,* A. H. Liu, M. B. O'Regan, W. C. Finch, and J. F. Payack

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The reaction between $[WCp^*Me_4]^+$ and 4 equiv of hydrazine (2-equiv excess) yields thermally unstable $WCp^*Me_4(NHNH_2)$. Crystals of $WCp^*Me_4(NHNH_2)$ obtained from a mixture of pentane and THF retain 1 equiv of THF per metal at low temperature, the THF being bonded to two NH_2 protons in a symmetrically bound η^2-$NHNH_2$ ligand in one of the two $WCp^*Me_4(NHNH_2)$ molecules in each asymmetric unit. Evaluation of the potential hydrogen bonds between the two molecules in the asymmetric unit allows us to conclude that the lone pair on the pyramidal NH nitrogen atom is pointing toward the Cp* ligand. (Crystal data: $a = 15.100$ (7) Å, $b = 16.551$ (6) Å, $c = 8.860$ (8) Å, $\alpha = 97.26$ (6)°, $\beta = 100.92$ (5)°, $\gamma = 66.08$ (4)°, $V = 1984.4$ Å^3, space group $P\bar{1}$, $Z = 4$, $M_r = 410.31$, ρ(calcd) = 1.564 g cm^{-3}, $\mu = 55.4$ cm^{-1}. Final $R_1 = 0.0973$ and $R_2 = 0.1153$.) ^1H and ^{15}N NMR studies show that two of the three hydrazido(1–) protons equilibrate first, probably by a shift to the lone pair on the NH nitrogen atom of the NH_2 proton that points toward the Cp* ligand. $WCp^*Me_4(NHNH_2)$ loses methane in an apparent first-order decomposition reaction to give $WCp^*Me_3(NNH_2)$ in high yield. Protonation of $WCp^*Me_3(NNH_2)$ yields $[WCp^*Me_3(NHNH_2)]^+$, a structure study of which showed it also to contain an η^2-$NHNH_2$ ligand, but one that is unsymmetrically bound with the NH nitrogen atom being sp^2 hybridized. (Crystal data for the triflate derivative: $a = 23.619$ (4) Å, $b = 8.486$ (2) Å, $c = 21.921$ (6) Å, $\beta = 100.40$ (2)°, $V = 4321$ (3) Å^3, space group $C2/c$, $Z = 8$, $M_r = 544.28$, ρ(calcd) = 1.78 g cm^{-3}, $\mu = 57.9$ cm^{-1}. Final $R_1 = 0.049$ and $R_2 = 0.059$.) $WCp^*Me_4(NHNH_2)$ is protonated to give what is postulated to be an η^2-hydrazine complex, $[WCp^*Me_4(NH_2NH_2)]^+$, with a structure closely related to that of $WCp^*Me_4(NHNH_2)$.

Introduction

It is generally believed (although there is no direct evidence) that dinitrogen is activated by and reduced at a molybdenum center in nitrogenase, with the possible assistance of a second metal (most likely Fe).[1] For this reason the coordination of molecular nitrogen to one or more transition metals and its reduction to ammonia have been the subject of a great deal of research in the past 2 decades.[1d] The long-term goals are to understand the inorganic chemistry at metal centers in nitrogenases[1f] and to design a nonbiological catalytic system for the reduction of dinitrogen under mild conditions, ideally 25 °C and 1 atm.

One of the possible intermediates in a sequence of steps that could lead to reduction of dinitrogen at a single metal center (eq 1) is a hydrazido(1–) complex, M–NHNH$_2$. A complex that

$$M{-}N_2 \xrightarrow[2e^-]{2H^+} M{-}N_2H_2 \xrightarrow[e^-]{H^+} M{-}NHNH_2 \xrightarrow[e^-]{H^+(N_\beta)} M{=}NH + NH_3 \quad (1)$$

almost certainly contains the hydrazido(1–) ligand has been reported,[2] but unfortunately it could not be characterized fully. In contrast, there are a great many reports of complexes that contain substituted hydrazido(1–) ligands, M–NRNR′R″.[1d] We reported in a preliminary communication[3] that the reaction between $[WCp^*Me_4]^+$ and hydrazine yielded what was believed to be $WCp^*Me_4(NHNH_2)$, a species that readily loses methane to give $WCp^*Me_3(NNH_2)$, from which $[WCp^*Me_3]_2(\mu\text{-}N_2)$[3,4] could be prepared by addition of $[WCp^*Me_4]^+$. Since then we have found that both $WCp^*Me_4(NHNH_2)$ and $WCp^*Me_3(NNH_2)$ can be protonated, the former to give $[WCp^*Me_4(NH_2NH_2)]^+$ and the latter to give a second example of a hydrazido(1–) complex, $[WCp^*Me_3(NHNH_2)]^+$. The results of these studies are reported here.

Results

Preparation and Characterization of $WCp^*Me_4(NHNH_2)$. Addition of $[WCp^*Me_4]^+$ ($Cp^* = \eta^5$-C_5Me_5; the anion is usually PF_6^-) to an excess (4 equiv) of hydrazine in diethyl ether results

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(1) (a) Coughlin, M., Ed. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: Elmsford, NY, 1980. (b) Hardy, R. W. F., Bottomley, F., Burns, R. C., Eds. *A Treatise on Dinitrogen Fixation*; Wiley-Interscience: New York, 1979. (c) Gibson, A. H., Newton, W. F., Eds. *Current Perspectives in Nitrogen Fixation*; Elsevier: Amsterdam, 1981. (d) Henderson, R. A.; Leigh, J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197. (e) For a discussion of the most recent theories see: Conradson, S. D.; Burgess, B. K.; Newton, W. E.; Mortenson, L. E.; Hodgson, K. O. *J. Am. Chem. Soc.* **1987**, *109*, 7507. (f) Recent genetic evidence implicates FeMo-co as the site of binding and reduction of dinitrogen.[1g] Nitrogenases that contain vanadium[1h] or tungsten[1i] are now known. (g) Hawkes, T. R.; McLean, P. A.; Smith, B. E. *Biochem. J.* **1984**, *217*, 317. (h) Morningstar, J. E.; Hales, B. J. *J. Am. Chem. Soc.* **1987**, *109*, 6854. (i) Hales, B. J.; Case, E. E. *J. Biol. Chem.* **1987**, *262*, 16205.

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(4) Churchill, M. R.; Li, Y. J. *J. Organomet. Chem.* **1985**, *301*, 49.

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Table I. Bond Distances (Å) and Angles (deg) in the Two Molecules of WCp*Me$_4$(NHNH$_2$) Labeled As Shown in Figure 1a[a]

Intramolecular Distances and Angles			
W(1)-N(11)	2.17 (3)	N(11)-W(1)-N(12)	37.9 (9)
W(1)-N(12)	2.12 (2)	N(11)-W(1)-C(11)	85.3 (11)
N(11)-N(12)	1.39 (3)	N(11)-W(1)-C(12)	149.8 (10)
W(1)-C(11)	2.21 (3)	N(11)-W(1)-C(13)	114.3 (11)
W(1)-C(12)	2.25 (2)	N(11)-W(1)-C(14)	74.2 (10)
W(1)-C(13)	2.20 (3)	N(12)-W(1)-C(11)	120.6 (12)
W(1)-C(14)	2.23 (4)	N(12)-W(1)-C(12)	145.5 (9)
W(1)-Cp(1)	2.40 (2)	N(12)-W(1)-C(13)	78.1 (10)
W(1)-Cp(2)	2.43 (2)	N(12)-W(1)-C(14)	75.2 (10)
W(1)-Cp(3)	2.47 (3)	C(11)-C(1)-C(12)	72.4 (12)
W(1)-Cp(4)	2.46 (2)	C(12)-W(1)-C(13)	73.5 (10)
W(1)-Cp(5)	2.40 (2)	C(11)-W(1)-C(13)	137.6 (10)
W(1)-Cp(cent)	2.12	C(11)-W(1)-C(14)	72.6 (11)
Cp(cent)-W(1)-C(11)	107.5	C(12)-W(1)-C(14)	79.7 (12)
Cp(cent)-W(1)-C(12)	103.3	C(13)-W(1)-C(14)	77.3 (13)
Cp(cent)-W(1)-C(13)	104.2	W(1)-N(11)-N(12)	69.2 (15)
Cp(cent)-W(1)-C(14)	176.9	W(1)-N(12)-N(11)	72.9 (14)
Cp(cent)-W(1)-N(11)	102.7		
Cp(cent)-W(1)-N(12)	102.3		
W(2)-N(21)	2.16 (2)	N(21)-W(2)-N(22)	36.8 (9)
W(2)-N(22)	2.10 (2)	N(21)-W(2)-C(21)	115.8 (8)
N(21)-N(22)	1.35 (3)	N(21)-W(2)-C(22)	148.3 (10)
W(2)-C(21)	2.25 (3)	N(21)-W(2)-C(23)	79.9 (9)
W(2)-C(22)	2.25 (3)	N(21)-W(2)-C(24)	78.1 (10)
W(2)-C(23)	2.22 (3)	N(22)-W(2)-C(21)	80.3 (8)
W(2)-C(24)	2.27 (3)	N(22)-W(2)-C(22)	147.9 (8)
W(2)-Cp(21)	2.42 (2)	N(22)-W(2)-C(23)	114.7 (10)
W(2)-Cp(22)	2.42 (2)	N(22)-W(2)-C(24)	76.1 (9)
W(2)-Cp(23)	2.39 (2)	C(21)-W(2)-C(22)	75.5 (10)
W(2)-Cp(24)	2.45 (2)	C(22)-W(2)-C(23)	75.4 (11)
W(2)-Cp(25)	2.47 (2)	C(21)-W(2)-C(23)	142.4 (9)
W(2)-Cp(centroid)	2.11	C(21)-W(2)-C(24)	74.3 (12)
Cp(cent)-W(2)-C(21)	105.0	C(22)-W(2)-C(24)	77.1 (10)
Cp(cent)-W(2)-C(22)	101.7	C(23)-W(2)-C(24)	76.4 (11)
Cp(cent)-W(2)-C(23)	103.9	W(2)-N(21)-N(22)	69.3 (12)
Cp(cent)-W(2)-C(24)	178.7	W(2)-N(22)-N(21)	73.8 (11)
Cp(cent)-W(2)-N(21)	103.2		
Cp(cent)-W(2)-N(22)	104.8		
Intermolecular Distances			
N(11)-N(21)	2.94 (4)	N(22)-O(1)	2.99 (3)
		N(22)-O(2)	3.01 (2)

[a] Cent = centroid.

in the formation of N$_2$H$_5^+$ and WCp*Me$_4$(NHNH$_2$) (**1**, eq 2) in good yield. Ivory-colored crystals of WCp*Me$_4$(NHNH$_2$) can

$$[\mathrm{WCp^*Me_4}]^+ + 4\mathrm{N_2H_4}\ (\text{excess}) \rightarrow \underset{\mathbf{1}}{\mathrm{WCp^*Me_4(NHNH_2)}} + \mathrm{N_2H_5}^+ \quad (2)$$

be obtained from a mixture of pentane and THF (1:3) at −30 °C, but these become a powder at 25 °C. The powder does not contain THF (by ^{1}H NMR), but the crystals obtained at low temperature contain one THF per metal. Therefore, we propose that crystalline "WCp*Me$_4$(NHNH$_2$)(THF)" loses THF readily at 25 °C. We provide evidence later that **1** forms when hydrazine deprotonates [WCp*Me$_4$(N$_2$H$_4$)]$^+$, the logical first-formed complex in the reaction shown in eq 2. **1** decomposes slowly to give WCp*Me$_3$(NNH$_2$) (**2**, eq 3) in solution and also decomposes to some extent in the solid state. This decomposition is discussed later.

$$\underset{\mathbf{1}}{\mathrm{WCp^*Me_4(NHNH_2)}} \rightarrow \underset{\mathbf{2}}{\mathrm{WCp^*Me_3(NNH_2)}} + \mathrm{CH_4} \quad (3)$$

A crystal of "WCp*Me$_4$(NHNH$_2$)(THF)" was selected from the mother liquor at −30 °C under dinitrogen and mounted on a fiber in a stream of cold nitrogen gas. Data were collected at −65 °C. Two molecules of **1** were found in each asymmetric unit along with two molecules of THF (Figure 1). Bond distances and angles can be found in Table I.

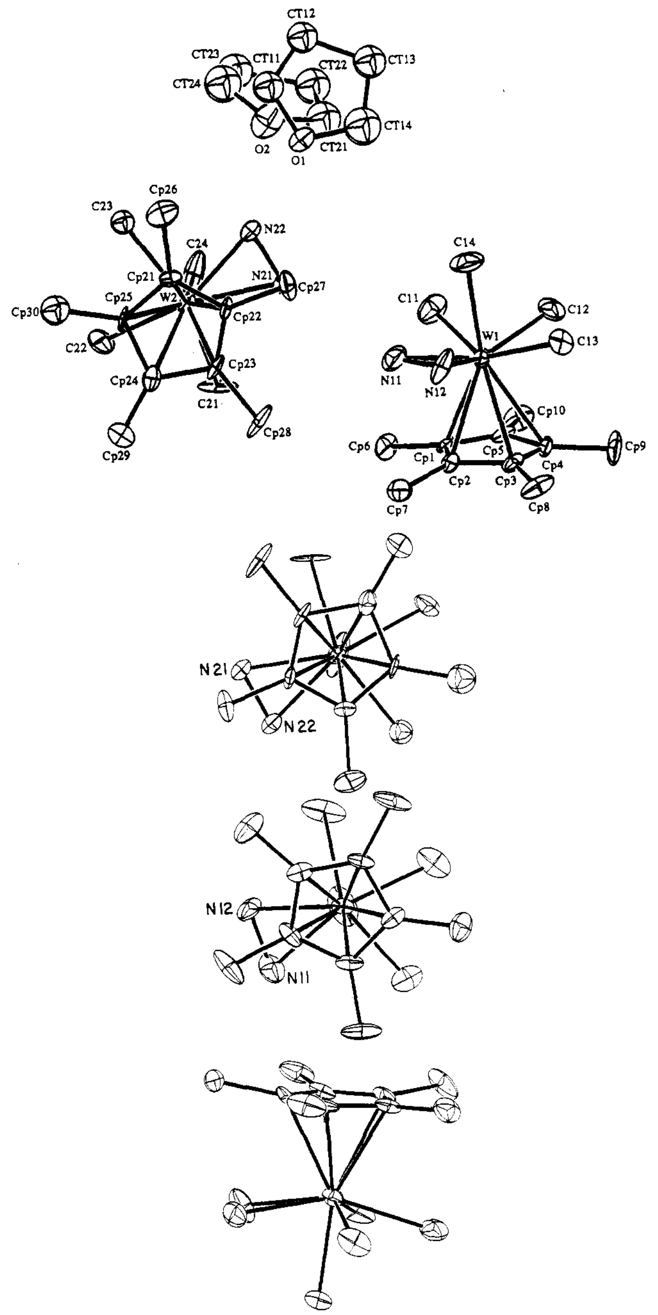

Figure 1. (a, Top) View of the two independent molecules of WCp*Me$_4$(NHNH$_2$) (**1**) and two molecules of THF. (b, Middle) View of each of the two molecules from above the Cp* ring. (c, Bottom) View of the molecule containing W(1) from the side.

The two molecules of WCp*Me$_4$(NHNH$_2$) are essentially identical, each being a distorted pentagonal bipyramid. The methyl groups of the Cp* ring are more or less staggered with respect to the three methyl groups and the two nitrogen atoms in the pseudo equatorial plane of the distorted pentagonal bipyramid (Figure 1b). The "equatorial" groups are bent away from the normal dish-shaped Cp* ring to a significant extent (Figure 1c), as shown by the Cp(cent)-W-X (X = C or N; cent = centroid) angles of 102-107° listed in Table I. The eight W-Me distances are virtually identical, as are the four W-N and two N-N distances in the η^2-hydrazido(1−) ligands in the two molecules. The latter data suggest that each nitrogen atom in each complex is only singly bound to the metal, i.e., that each is sp^3 hybridized and roughly pyramidal. (Distances and angles in the NHNH$_2$ ligands will be compared with those in another hydrazido(1−) complex, as well as with those in complexes containing a substituted hydrazido(1−) ligand, in the Discussion.)

The presence of two molecules of THF whose oxygen atoms (O(1) and O(2)) point in the general direction of N(22) strongly suggests that these oxygen atoms hydrogen bond to two protons on N(22). If two protons are replaced on N(22) (with an H-N-H

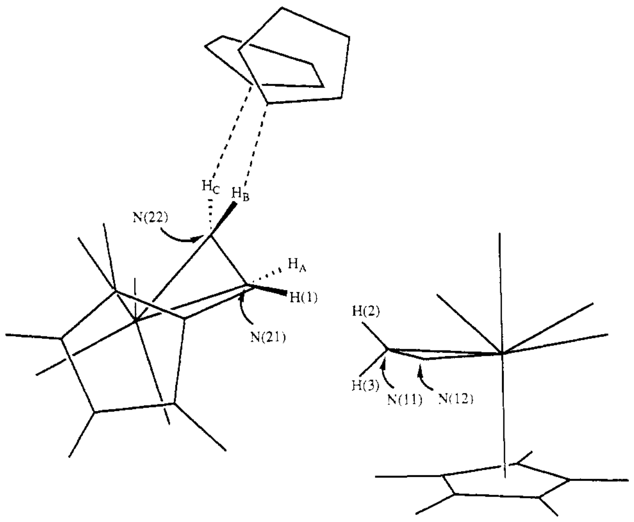

Figure 2. The two molecules of $WCp^*Me_4(NHNH_2)$ with six hydrogen atoms placed in symmetrical positions about three nitrogen atoms (N–H = 0.95 Å and H–N–H = 109.7°).

Table II. Comparison of Potential Hydrogen Bonds Involving the Hydrazido(1–) Ligands[a] with Known Hydrogen-Bond Distances and Angles

N–H···O unit	N–O, Å	N–H, Å	H···O, Å	NHO, deg
typical bond dist and angle[5]	3	1	2	160

N–H···X unit (X = N, O)	N–O, Å	H (N–H fixed at 0.95 Å)	H···X calcd, Å	NHX calcd, deg
NHO (THF)	2.99 (3)	H_B	2.14	148
	3.01 (2)	H_C	2.11	157
NHN (four possibilities)	2.94 (4)	H_A	2.74	93
		H(1)	2.33	122
		H(2)	2.12	144
		N(3)	3.00	77

[a] See Figure 2.

angle of 109.7°) in positions that are symmetric with respect to the N–N and N–W bonds, the distances and angles in the resulting $NH_2(THF)_2$ arrangement are close to what are found in other N–H···O systems (Table II and Figure 2).[5a] Therefore we can conclude that two protons are present on N(22), H_B pointing toward the Cp* ring ("up") and H_C pointing away ("down").

We examined the likelihood of four other potential hydrogen bonds between N(11) and N(21) using similar methods. In Figure 2 we show four hypothetical protons (H_A, H(1), H(2), H(3)) that could be involved. Since two protons are on N(22), only H_A or H(1) is bound to N(21) (confirmed by NMR studies to be discussed below); the other position is occupied by an electron pair that could be, but does not have to be, involved in bonding to H(2) or H(3) on N(11). We placed two hypothetical protons on N(21) and two on N(11) in symmetrical positions with respect to the N–N and N–W bonds (with an H–N–H angle of 109.7°) and calculated distances and angles for the four hypothetical hydrogen bonds. The results are listed in Table II. It is clear that H_A cannot be involved in hydrogen bonding to an electron pair on N(11) nor can H(3) be bonded to an electron pair on N(21). It is possible that H(1) is hydrogen bonded to an electron pair on N(11) according to the H(1)···N(11) distance (2.33 Å) and N(21)–H(1)···N(11) angle (122°), but the only truly satisfactory interpretation is that H(2) is hydrogen bonded to N(21) (H(2)···N(21) = 2.12 Å; N(11)–H(2)···N(21) = 144°). Therefore, we conclude that H_A is the proton present on N(21) and that H(2) interacts with the nonbonding electron pair on N(21); i.e., *the lone pair on N(21) points toward the Cp* ligand.* Since H(2) is pointed away from the Cp* ligand in the second molecule, we cannot tell if one or two protons are bound to N(11). Note that the Cp* ring is rotated slightly away from N(22) in molecule 2 (Figure 1b); *if* the same is true in molecule 1, then two protons must be bound to N(12).[5b] If so, packing considerations must prevent incorporation of two more THF molecules to hydrogen bond to the two protons on N(12). In any case, as a result of incorporation of two molecules of THF and the relative orientations of the two $WCp^*Me_4(NHNH_2)$ molecules, we have located all three protons in the $NHNH_2$ ligand in one of the two molecules in the asymmetric unit. We assume that the lone pair in the $NHNH_2$ ligand in the other molecule in the asymmetric unit also points toward the Cp* ligand, even though we have no other solid-state data that confirm that this is the case.

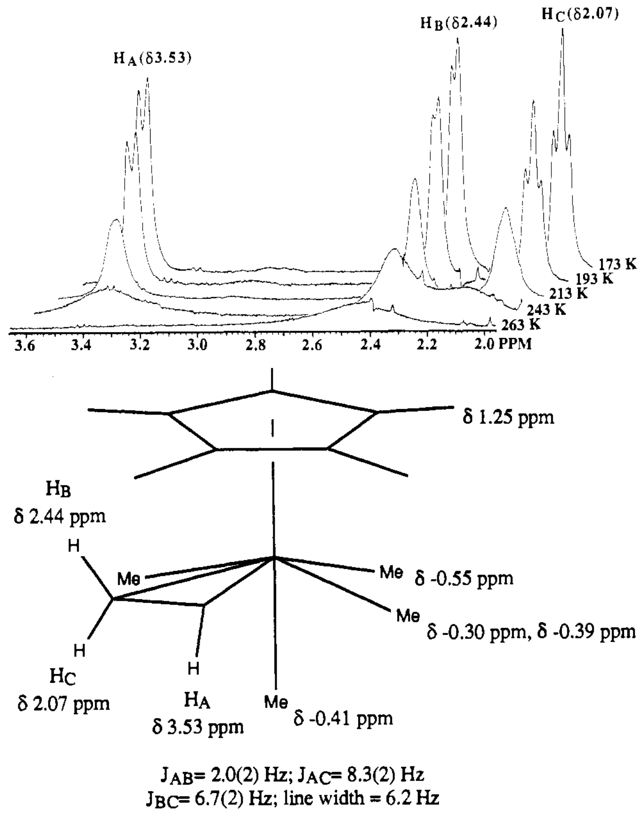

Figure 3. (a, Top) Variable-temperature ^1H NMR spectra of the $NHNH_2$ protons in $WCp^*Me_4(NHNH_2)$ in CD_2Cl_2. (b, Bottom) Chemical shifts and coupling constants in $WCp^*Me_4(NHNH_2)$.

^1H NMR studies of **1** (THF-free) show that the three $NHNH_2$ protons are inequivalent (Figure 3a) as are the four methyl groups (Figure 3b) at low temperatures.[6a] Simulation of the $NHNH_2$ portion of the spectrum taken at 173 K (Figure 3a) yields the coupling constants shown in Figure 3b. On the basis of chemical shifts, we assign the two high-field resonances to the NH_2 protons (H_B and H_C in Figure 3b). We assign the small coupling to that between H_A and H_B (as a result of the nearly 90° dihedral angle between them), which implies that the resonance at 2.44 ppm can be assigned to H_B. A complete listing of chemical shifts and coupling constants can be found in Figure 3b.

Difference NOE studies at low temperature confirm our assignments and allow us to conclude that the arrangement of

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(5) (a) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids, Methods of Molecular Structure Determination*; Benjamin: New York, 1968; pp 260–265. (b) We thank a reviewer for suggesting this comparison. There are no intermolecular distances involving N(12) that would indicate hydrogen bonding to another molecule, and the distances of the two nitrogen atoms from the mean plane of the Cp* ligand in each molecule are too similar to allow us to determine conclusively how many protons are on N(11) and N(12).

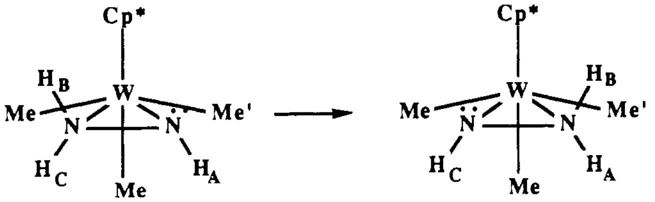
(6) (a) Spectra of $WCp^*Me_4(NHNH_2)$ always show resonances due to $WCp^*Me_3(NNH_2)$ that result from decomposition of $WCp^*Me_4(NHNH_2)$. None of these resonances, however, overlaps with any of **1** in the low-temperature spectra in question. (b) Chatt, J.; Fakley, M. E.; Richards, R. L.; Mason, J.; Stenhouse, I. A. *J. Chem. Res., Synop.* **1979**, 3701. (c) Unpublished results.

protons on the $\mathrm{NHNH_2}$ ligand is the same in solution as in the solid state. Irradiation of the Cp* methyl groups at 193 K did not enhance the 2.07 and 3.53 ppm resonances but did significantly enhance the 2.44 ppm resonance, a fact that suggests that the 2.44 ppm resonance can be assigned to the only proton that points toward the Cp* ring (H_B), as we proposed above. We also found that three of the methyl resonances became ~25% more intense than the fourth at −0.41 ppm. Therefore, we assign the resonance at −0.41 ppm to the methyl group trans to the Cp* ligand.

^{1}H NMR spectra at several temperatures are shown in Figure 3a. The resonances at 2.07 ppm (H_C) and 3.53 ppm (H_A) broaden and disappear into the base line at ~253 K. The resonance at 2.44 ppm (H_B) also broadens, but more slowly. The spectrum at 243 K shows most clearly that H_A and H_C are exchanging with each other marginally faster than H_B is exchanging with either H_A or H_C. Eventually (at ~263 K) all three resonances coalesce to give a broad peak at ~2.4 ppm. From coalescence temperatures, ΔG^* for the interconversion of H_A and H_C is estimated to be 11.3 (3) kcal mol^{-1} at 253 K, and for the interconversion of all three protons $\Delta G^* = 12.7$ (4) kcal mol^{-1} at 263 K. The two methyl resonances at −0.30 and −0.39 ppm at low temperature broaden and coalesce at 228 K to a single peak of area 6. The value for ΔG^* (11.4 (3) kcal mol^{-1}) calculated from these data suggests that these two methyl groups exchange in the same process in which H_A and H_C exchange. Since the spectra of two samples that differ by a factor of 10 in concentration (5 and 50 mM) at 243 K are identical, we can propose that two *intra*molecular fluxional processes are taking place; one interconverts H_A and H_C, and a slightly slower one interconverts all three protons. This proposal is supported by spin-saturation-transfer experiments. At 193 K, irradiation of the 2.44 ppm resonance does not affect the intensities of the 2.07 and 3.53 ppm resonances, while irradiation of the 3.53 ppm resonance significantly decreases the intensity only of the 2.07 ppm resonance.

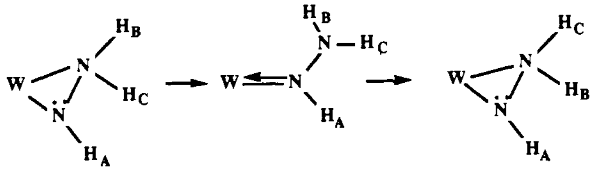
The ^{15}N NMR spectrum of **1**-$^{15}N_2$ (prepared by analogous methods; see Experimental Section) at 193 K shows the expected NH doublet ($J_{NH} = 58$ Hz) 88.18 ppm downfield of $^{15}\mathrm{NH_3}$ and the $\mathrm{NH_2}$ triplet ($J_{NH} = 84$ Hz) 39.95 ppm downfield of $^{15}\mathrm{NH_3}$. Spectra obtained at 223, 243, 273, and 298 K show that the two resonances broaden and collapse to one at approximately an averaged position of 65 ppm at 273 K. The 65 ppm resonance does not show significant structure at higher temperatures, in part because decomposition of the sample at higher temperatures made it virtually impossible to obtain a spectrum with a good signal to noise ratio. From the coalescence temperature for the two ^{15}N resonances we estimate $\Delta G^* = 11.1$ (2) kcal mol^{-1} at 263 K. Therefore the nitrogen atoms must exchange in the same process that interconverts H_A and H_C and the mutually trans methyl groups.

An explanation of the lowest energy fluxional process in **1** is a proton 1,2-shift of H_B from one nitrogen atom to the other (eq 4) with $\Delta G^* \approx 11.3$ kcal mol^{-1} at 250 K (11.1 (2) kcal mol^{-1} at 263 K from interconversion of *N*H and *N*H$_2$, 11.3 (3) kcal mol^{-1} at 253 K from interconversion of H_A and H_C, and 11.4 (3) kcal mol^{-1} at 228 K from interconversion of Me and Me′). Note that



(4)

H_B does not change environments. Therefore, if the 1,2-shift were the only fluxional process, the average resonance for H_A/H_C at high temperature would be a doublet and that for H_B a triplet (if spins remained correlated). This limiting spectrum cannot be observed because of the slightly higher energy second process ($\Delta G^* = 12.7$ (4) kcal mol^{-1}) that interconverts all three protons. We propose that this second process involves the dissociation of the $\mathrm{NH_2}$ end of the η^2-$\mathrm{NHNH_2}$ ligand to give an η^1-$\mathrm{NHNH_2}$ ligand followed by inversion of the $\mathrm{NH_2}$ and/or rotation of the η^1-$\mathrm{NHNH_2}$ ligand about the W–N bond and recoordination of $\mathrm{NH_2}$ to the metal (eq 5). This would lead, along with the concomitant



(5)

1,2-shift process, to interconversion of all three $\mathrm{NHNH_2}$ protons. Note that the 18-electron count in **1** is maintained in the process shown in eq 5 because the lone pair on N_α almost certainly is strongly donated to the metal in the η^1-$\mathrm{NHNH_2}$ intermediate. (This type of coordination was the one first proposed in **1**,[3] but actually it is less common than η^2-$\mathrm{NHNH_2}$ bonding, especially when the metal is electron-deficient; see later.) The activation energy for the second fluxional process may be as low as it is because the 18-electron count is maintained in the η^1-$\mathrm{NHNH_2}$ intermediate.

The presence of a basic lone pair on the NH nitrogen in **1** is further supported by the reaction of **1** with acid to give what we propose is a very unstable η^2-hydrazine complex[7] (**3**; eq 6). (An analogous triflate salt also can be prepared.) It is tempting to assume that the proton adds directly to the NH lone pair, but such an assumption is not on firm ground in view of the fact that $\mathrm{WCp^*Me_4}(\eta^1\text{-}\mathrm{NHNH_2})$ is likely to be in ready equilibrium with **1**; i.e., the proton might add most rapidly to the β-nitrogen atom in unobservable $\mathrm{WCp^*Me_4}(\eta^1\text{-}\mathrm{NHNH_2})$ followed by a proton 1,2-shift. Addition of a base such as DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) to **3** converts it quantitatively back into **1** (eq 7), as shown by ^{1}H NMR studies. A weaker base such as triethylamine will also convert **3** into **1**. Because of the result shown in eq 7, and the fact that excess triethylamine will deprotonate **3** on a preparative scale, we conclude that $[\mathrm{WCp^*Me_4(NH_2NH_2)}]^+$ is formed first in the reaction between $[\mathrm{WCp^*Me_4}]^+$ and hydrazine (eq 2) and that it is then deprotonated by hydrazine to give **1**. Unfortunately, even if the structure of $[\mathrm{WCp^*Me_4(NH_2NH_2)}]^+$ is virtually identical with that of $\mathrm{WCp^*Me_4(NHNH_2)}$, we have no guarantee that the proton that is removed from **3** is one that points toward the Cp* ligand. An alternative is that a proton that points *away* from the Cp* ligand is removed by base (eq 8), and hypothetical "$\mathrm{WCp^*Me_4(NH_{up}NH_2)}$" is then converted into the observed isomer by rapid inversion of the NH configuration in "$\mathrm{WCp^*Me_4(NH_{up}NH_2)}$" (eq 9). In this context it is worthwhile noting that it is H(2) in

$$\underset{\mathbf{1}}{\mathrm{WCp^*Me_4(NHNH_2)}} + \mathrm{HBF_4} \rightarrow \underset{\mathbf{3}}{[\mathrm{WCp^*Me_4(NH_2NH_2)}]^+\mathrm{BF_4}^-} \tag{6}$$

$$[\mathrm{WCp^*Me_4(NH_2NH_2)}]^+ + \mathrm{DBU} \rightarrow \mathrm{WCp^*Me_4(NHNH_2)} + \mathrm{DBUH^+} \tag{7}$$

$$[\mathrm{WCp^*Me_4(NH_2NH_2)}]^+ + \text{base} \rightarrow \text{base}\cdot\mathrm{H^+} + \text{“}\mathrm{WCp^*Me_4(NH_{up}NH_2)}\text{”} \tag{8}$$

$$\text{“}\mathrm{WCp^*Me_4(NH_{up}NH_2)}\text{”} \rightarrow \mathrm{WCp^*Me_4(NH_{down}NH_2)}\ \text{(obsd isomer)} \tag{9}$$

---

(7) (a) Complexes of η^2-hydrazine itself are relatively rare.[7b] In $[\mathrm{CpMo(NO)I(NH_2NHPh)}][\mathrm{BF_4}]$ the hydrazine is side-on bonded with Mo–N distances of 2.184 (3) and 2.134 (3) Å and a N–N distance of 1.430 (5) Å.[7c] The conformation about the N–N bond is eclipsed. (b) Bultitude, J.; Larkworthy, L. F.; Povey, D. C.; Smith, G. W.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1748. (c) Bailey, N. A.; Frisch, P. D.; McCleverty, J. A.; Walker, N. W. J.; Williams, J. *J. Chem. Soc., Chem. Commun.* **1975**, 350.

(8) (a) Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Chem. Commun.* **1983**, 1368. (b) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 385. (c) The authors propose that the NR′R″ lone pair interacts with the d_{z^2} orbital but that the NR lone pair is nonbonding. According to the MO diagram, the d_{xy} orbital would seem to be of the correct symmetry to interact with the NR lone pair.

the second molecule of $WCp^*Me_4(NHNH_2)$ in the asymmetric unit (Figure 2), a "down" proton, that hydrogen-bonds to N(21). Therefore one might postulate that H_{down} in $[WCp^*Me_4(NH_2NH_2)]^+$ is sterically more accessible than H_{up}, a priori the most plausible conclusion.

An ^1H NMR spectrum of **3** at 40 °C (Figure 4a) shows two resonances of relative area 2 at 4.97 and 4.62 ppm that can be assigned to two sets of hydrazine protons. If we assume that the structure of **3** is virtually identical with that of **1**, then we can assign one resonance to the two protons that point toward the Cp* ligand and the other resonance to the two protons that point away from the Cp* ligand; we do not know which is which, although since the resonance for H_B in **1** is downfield of that for H_C, the downfield resonance might be assigned to the set that points toward the Cp* ligand. We postulate that both signals are broad in part because the hydrazine protons comprise an AA′BB′ set and because there is quadrupolar broadening by ^{14}N. The widths of these resonances vary with temperature, the lower field resonance being slightly broader than the higher field resonance at −80 °C. There is no qualitative difference in such behavior in samples of either the BF_4^- or OTf^- salt that differ by an 8-fold concentration range (from 9 to 70 mM).

When 2 equiv of triethylamine is added to a sample of **3**, the two N_2H_4 resonances coalesce to one broad, shifted signal of relative area 4 at 4.55 ppm. Qualitatively the same result is observed for a sample that contains 2% DBU, a base that irreversibly deprotonates **3**, except the average signal is found at ~4.8 ppm (Figure 4b). Since the three hydrazido protons in $WCp^*Me_4(NHNH_2)$, the deprotonation product, are exchanging rapidly on the NMR time scale at 25 °C (see above), the average signal in the spectra of **3** in the presence of base can be ascribed in part to rapid proton scrambling in $WCp^*Me_4(NHNH_2)$, if proton exchange between $[WCp^*Me_4(NH_2NH_2)]^+$ and $WCp^*Me_4(NHNH_2)$ is rapid. Since we cannot observe the $[Et_3N\mathit{H}]^+$ resonance in the sample of **3** that contains Et_3N, we think it likely that the proton is partitioned between $WCp^*Me_4(NHNH_2)$ and triethylamine and that all proton-exchange reactions are rapid; i.e., the broad, shifted proton resonance at 4.55 ppm is an average of all hydrazine protons in $[WCp^*Me_4(NH_2NH_2)]^+$, all hydrazido protons in $WCp^*Me_4(NHNH_2)$ (in which proton scrambling is rapid), and the NH proton in $[Et_3NH]^+$. When the sample of **3** that contains 2% DBU is cooled, the rate of exchange between $[WCp^*Me_4(NH_2NH_2)]^+$ and the 2% $WCp^*Me_4(NHNH_2)$ that is generated by DBU slows to the point where resonances for the two types of hydrazine protons once again are observed (Figure 4b).

In Figure 4c are shown −80 °C spectra of samples of **3** in CD_2Cl_2 that contain 0%, 2%, 5%, and 10% of DBU. Apparently, H_{up} and H_{down} in **3** exchange, and the rate increases as the percentage of DBU (i.e., $WCp^*Me_4(NHNH_2)$) in the sample increases. The latter must be true since proton exchange between $[WCp^*Me_4(NH_2NH_2)]^+$ and $WCp^*Me_4(NHNH_2)$ is overall a degenerate process. But since H_A, H_B, and H_C in $WCp^*Me_4(NHNH_2)$ are exchanging slowly on the NMR time scale at −80 °C (the NH coupling in the 213 K spectrum in Figure 3a has just disappeared), proton averaging between $[WCp^*Me_4(NH_2NH_2)]^+$ and $WCp^*Me_4(NHNH_2)$ at −80 °C must take place via some other mechanism. Unfortunately, so little is known about proton exchange in such species that any proposal is extremely risky. We pointed out some of the unknowns above. We should also point out that very little is known about hydrogen bonding between molecules such as $[WCp^*Me_4(NH_2NH_2)]^+$ and $WCp^*Me_4(NHNH_2)$, so that the details of the exchange mechanism may have little or no precedent. One *possible* explanation of the exchange of H_{up} and H_{down} is the sum total of the reactions shown in eq 8–10 (where base = $WCp^*Me_4(NHNH_2)$).

$$WCp^*Me_4(NH_{down}NH_2) + base{\cdot}H^+ \rightarrow base + [WCp^*Me_4(NH_2NH_2)]^+ \quad (10)$$

We stated above that $WCp^*Me_4(NHNH_2)$ decomposes in solution and in the solid state to give $WCp^*Me_3(NNH_2)$ (**2**; eq 3). $WCp^*Me_3(NNH_2)$ is an ivory-colored, crystalline solid that can be isolated in high yield. It often appears to be orange to red due to a highly colored, and as yet unidentified, product of its decomposition. We believe that the configuration about the metal in **2** is square pyramidal, analogous to the geometry about each metal in $[WCp^*Me_3]_2(\mu\text{-}N_2)$,[4] on the basis of ^{15}N NMR spectra of **2** and $[WCp^*Me_3]_2(\mu\text{-}N_2)$. The ^{15}N NMR spectrum of **2** in CD_2Cl_2 shows a doublet at δ 368.08 (J_{NN} = 11 Hz, J_{NW} = 129

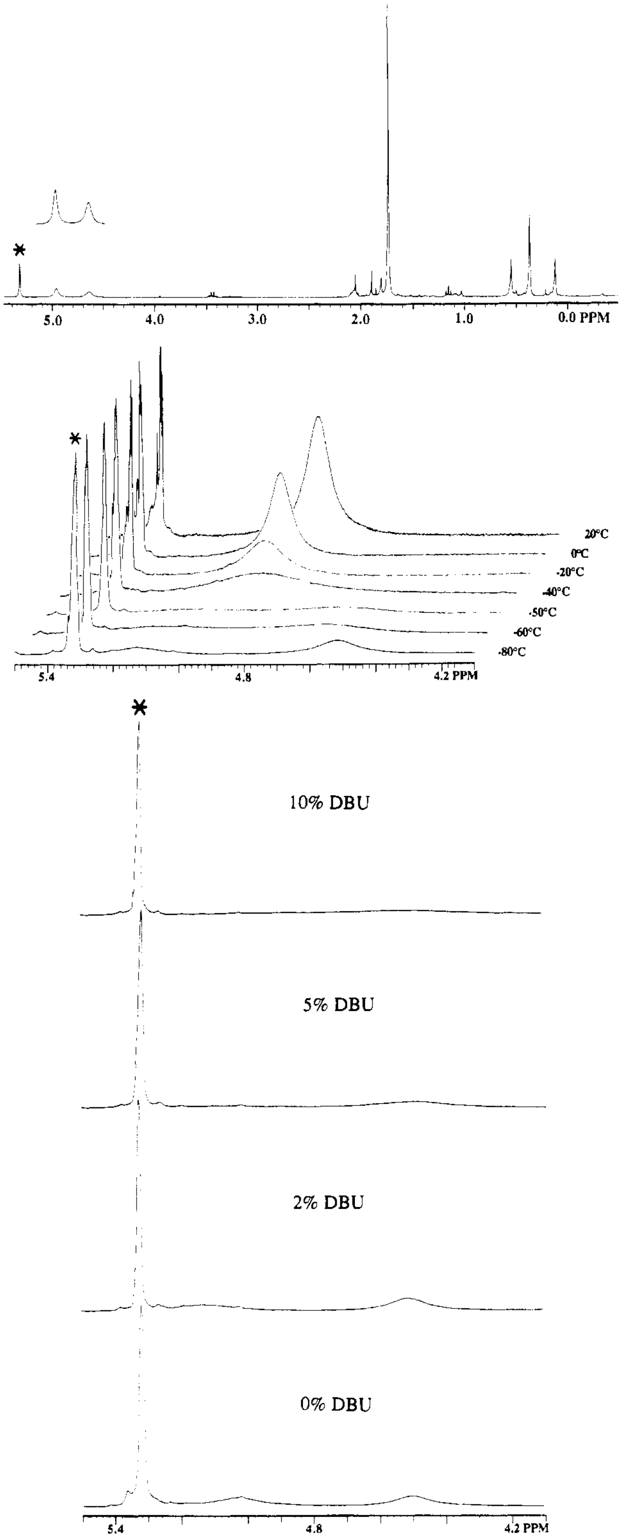


Figure 4. (a, Top) ^1H NMR spectrum of $[WCp^*Me_4(NH_2NH_2)]^+BF_4^-$ (**3**) at 40 °C in CD_2Cl_2 (asterisk indicates $CHDCl_2$). (b, Middle) Variable-temperature ^1H NMR spectra of $[WCp^*Me_4(NH_2NH_2)]^+BF_4^-$ at 25 °C in CD_2Cl_2 in the presence of 2% DBU (asterisk indicates $CHDCl_2$). (c, Bottom) ^1H NMR spectra of samples of $[WCp^*Me_4(NH_2NH_2)]^+BF_4^-$ at −80 °C in CD_2Cl_2 that contains 0–10% DBU (asterisk indicates $CHDCl_2$).

Table III. Kinetics of Decomposition of $\mathrm{WCp^*Me_4(NHNH_2)}$ in Dichloromethane

batch	concn, M	10^4k, s^{-1}	*R* factor
A	0.140	8.27	0.9990
		8.26	0.9989
		8.06	0.9999[a]
B	0.105	6.70	0.9997
		7.07	0.9997
		7.06	0.9998[a]
		7.20	0.9997[a]
C	0.280	7.16	0.9998
		6.97	0.9988
	0.0697	7.31	0.9997
		7.28	0.9980

[a] Trimethylsilylated NMR tubes. The tubes were rinsed with butyllithium in hexane followed by $\mathrm{Me_3SiCl}$, pentane, and toluene.

Hz) downfield of $^{15}\mathrm{NH_3}$ that can be assigned to N_α and a triplet of doublets at δ 127.23 ($J_{\mathrm{NH}} = 77$ Hz, $J_{\mathrm{NN}} = 11$ Hz) that can be assigned to N_β. These values compare favorably with those for several hydrazido(2−) complexes of tungsten in lower oxidation states ($\delta(N_\alpha) \approx 150$, $\delta(N_\beta) \approx 295$, $J_{\mathrm{NN}} \approx 10$ Hz, $J_{N_\alpha W} \approx 120$ Hz).[6b] The much larger difference in chemical shift between the α- and the β-nitrogen atoms in **2** must be a consequence of bonding to the more electropositive high-oxidation-state metal. The ^{15}N NMR spectrum of $[\mathrm{WCp^*Me_3}]_2(\mu\text{-}\mathrm{N_2})$[6c] in $\mathrm{CD_2Cl_2}$ shows a singlet at δ 428.7 ($^1J_{\mathrm{NW}} = 125$ Hz, $^2J_{\mathrm{NW}} = 104$ Hz). The similar values for $^1J_{\mathrm{NW}}$ in **2** and $[\mathrm{WCp^*Me_3}]_2(\mu\text{-}\mathrm{N_2})$ suggest that the bonding between N_α and the metal is similar in each case, i.e., a pseudo triple bond. The difference in N_α chemical shifts in the two compounds might be ascribed to π-electron delocalization throughout the WNNW core in $[\mathrm{WCp^*Me_3}]_2(\mu\text{-}\mathrm{N_2})$. The relatively large value for $^2J_{\mathrm{NW}}$ in $[\mathrm{WCp^*Me_3}]_2(\mu\text{-}\mathrm{N_2})$ relative to a $^2J_{\mathrm{NW}}$ in **2** (too small to observe) is consistent with electron delocalization.

The decomposition of **1** to **2** in dichloromethane appears to be first order over a 4-fold concentration range (Table III). The rates are reproducible for samples prepared from the same batch of **1**, but they vary from batch to batch more than one would expect. We thought the variation might be ascribable to acid or base catalysis. Trimethylsilylation of the NMR tubes produced no marked change in the rate, so acid catalysis can be ruled out. Addition of triethylamine did appear to accelerate the rate somewhat, but the rates were not even as reproducible as those shown in Table III. No intermediate has ever been observed. Although the decomposition of **1** to **2** overall appears to be an intramolecular loss of methane by an "α-hydrogen abstraction" process, we are not convinced that the process is straightforward and, therefore, cannot state any conclusions with confidence at this stage.

Preparation and Characterization of $[\mathrm{WCp^*Me_3(NHNH_2)}]^+\mathrm{OTf}^-$ (4). The addition of triflic acid to **2** yields **4** (eq 11). An

$$\underset{\mathbf{2}}{\mathrm{WCp^*Me_3(NNH_2)}} \underset{\text{base}}{\overset{\mathrm{HOSO_2CF_3}}{\rightleftharpoons}} \underset{\mathbf{4}}{[\mathrm{WCp^*Me_3(NHNH_2)}]^+\mathrm{OTf}^-} \tag{11}$$

analogous reaction involving $\mathrm{HBF_4}$ yields a less thoroughly studied $\mathrm{BF_4}^-$ salt (see Experimental Section). Addition of excess triethylamine (or 1 equiv of DBU) to **4** regenerates **2** in good yield. **4** and the $\mathrm{BF_4}^-$ analogue are significantly more stable than **1**, although **4** and its $\mathrm{BF_4}^-$ analogue decompose slowly to give as yet undefined products. Crystals of **4** were subjected to an X-ray diffraction study. Two views of this molecule are shown in Figure 5. Bond lengths and angles are listed in Table IV. The protons on the $\mathrm{NHNH_2}$ ligand were located and refined.

The geometry of **4** is close to a four-legged piano stool if one considers only the three methyl groups and the NH nitrogen atom (N(1)). The three methyl groups are bent away from the Cp* ring to about the same degree as they are in **1** (107–111°), while the Cp(cent)–W–N(1) angle is slightly larger (116.2°). The two methyl groups cis to N(1) (C(21) and C(41)) are bent away from it (Figure 5b), as are the methyl groups cis to the hydrazido(4−) ligand in $(\mathrm{WCp^*Me_3})_2(\mu\text{-}\mathrm{N_2})$;[4] for example, C(31)–W–C(41) = 74.1 (4)° while N(1)–W–C(41) = 93.5 (4)°. The methyl group trans to the $\mathrm{NHNH_2}$ ligand (C(31)) lies only 0.078 Å out of the plane defined by W, N(1), and N(2).

The W–N(1) distance of 1.86 (1) Å and W–N(2) distance of 2.15 (1) Å, along with the fact that the N(1)–H(1) bond lies only approximately 20° out of the plane defined by W, N(1), and N(2), suggest that N(1) is essentially sp^2 hybridized and that there is

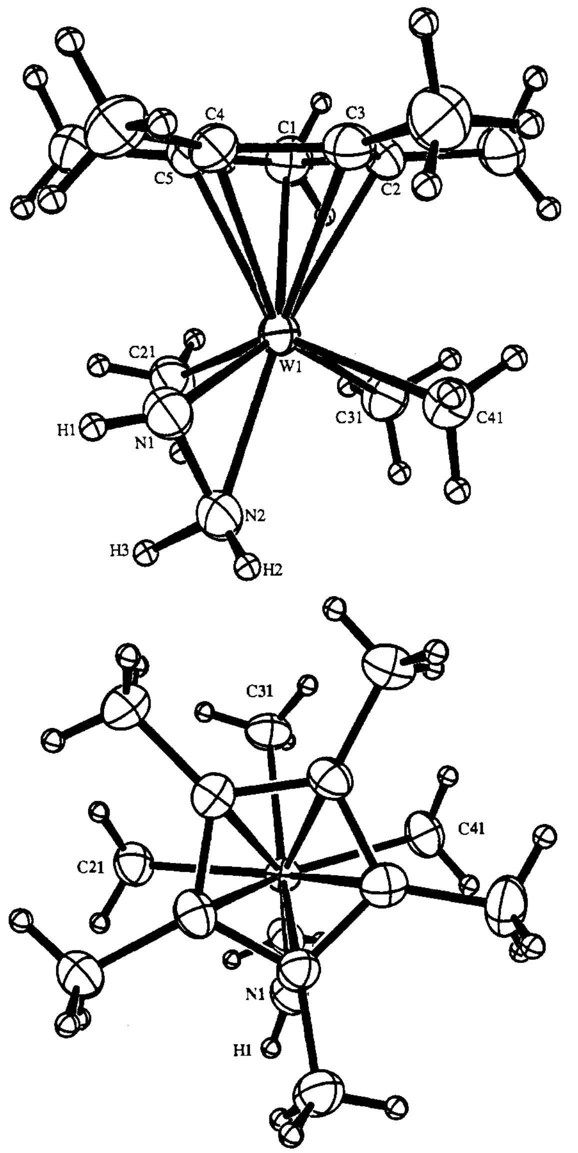


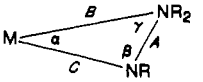
Figure 5. (a, Top) Side-on view of $[\mathrm{WCp^*Me_3(NHNH_2)}]^+$. (b, Bottom) Top view of $[\mathrm{WCp^*Me_3(NHNH_2)}]^+$.

Table IV. Bond Distances (Å) and Angles (deg) in $[\mathrm{WCp^*Me_3(NHNH_2)}]^+$ Labeled As Shown in Figure 5a[a]

W–N(1)	1.86 (1)	N(1)–W–N(2)	39.7 (4)
W–N(2)	2.15 (1)	N(1)–W–C(21)	89.2 (4)
N(1)–N(2)	1.39 (1)	N(1)–W–C(31)	132.5 (4)
N(1)–H(1)	0.8 (1)	N(1)–W–C(41)	93.5 (4)
N(1)–H(2)	0.71 (9)	N(2)–W–C(31)	92.8 (4)
N(1)–H(3)	1.0 (1)	C(21)–W–C(41)	139.8 (4)
W–C(21)	2.21 (1)	C(21)–W–C(31)	74.7 (4)
W–C(31)	2.22 (1)	C(31)–W–C(41)	74.1 (4)
W–C(41)	2.19 (1)	W–N(1)–N(2)	81.5 (6)
W–C(1)	2.41 (1)	W–N(2)–N(1)	58.7 (5)
W–C(2)	2.42 (1)	Cp(cent)–W–C(21)	107.4
W–C(3)	2.39 (1)	Cp(cent)–W–C(31)	111.2
W–C(4)	2.35 (1)	Cp(cent)–W–C(41)	107.2
W–C(5)	2.37 (1)	Cp(cent)–W–N(1)	116.2
W–Cp(cen)	2.06	Cp(cent)–W–N(2)	156.0

[a] Cent = centroid.

Table V. Comparison of Structural Features and ^{1}H Chemical Shifts of the MNRNR$_2$ Fragments of **1**, **4**, and Some Substituted Hydrazido(1−) Complexes[14]



complex	*A*, Å	*B*, Å	*C*, Å	α, deg	β, deg	γ, deg	δ(HN$_\alpha$)	δ(HN$_\beta$)
		η^2-NRNR$_2$						
CpTiCl$_2$(NPhNH$_2$)[8a,b]	1.411 (16)	2.144 (11)	1.877 (9)	40.4 (4)	80.0 (6)	59.6 (5)		5.17
CpTiCl$_2$(NHNMe$_2$)[8a,b]	1.41 (2)	2.22 (1)	1.83 (1)	39.1 (5)	85.7 (8)	55.3 (7)	8.20	
[Mo(NHNMePh)(NNMePh)(S$_2$CNMe$_2$)$_2$$^+$[9a]	1.388 (12)	2.175 (9)	2.069 (8)	38.1 (3)	75	67		
Mo(NHNHCO$_2$Me)(N$_2$CO$_2$Me)(S$_2$CNMe$_2$)$_2$[9b]	1.40 (2)	2.11 (1)	2.13 (1)	38.4 (5)	69	71		
[Cp$_2$W(NPhNH$_2$)]$^+$[10]	1.43 (1)	2.161 (9)	2.037 (9)	40.0 (3)	74.8 (6)	65.6 (5)		3.92
Cp*WMe$_4$(NHNH$_2$) (**1**)	1.35 (3)	2.105 (16)	2.16 (2)	36.8 (9)	69.3 (12)	73.8 (11)	3.53 (d)	2.44 (d), 2.07 (t)
	1.39 (3)	2.12 (2)	2.17 (2)	37.9 (9)	69.2 (15)	72.9 (14)	*J* = 8.3, 6.7, 2.0 Hz	
[Cp*WMe$_3$(NHNH$_2$)]$^+$OTf$^-$ (**4**)	1.39 (1)	2.15 (1)	1.86 (1)	39.7 (4)	81.5 (6)	58.7 (5)	11.82	5.21
		η^1-NRNR$_2$						
Mo[HB(Me$_2$pz)$_3$](NO)I(NHNMePh)[2]	1.37 (4)		1.88 (3)		144 (2)		12.53	
Mo[HB(Me$_2$pz)$_3$](NO)I(NHNMe$_2$)[2]	1.34 (3)		1.980 (17)		140.3 (15)		12.00	
Mo[N$_2$C(O)Ph][NHNHC(O)Ph]-[PhC(S)N(Me)O]$_2$[11]	1.361 (7)		1.938 (4)		131.9 (3)		15.85	12.51
							J = 10.2 Hz	
{CpRe(CO)$_2$[NHNMe(p-C$_6$H$_4$Me)]}$^+$[12]	1.32 (1)		1.949 (9)		139.1 (7)		16.5	
ReCl$_2$(PPh$_3$)$_2$(NNHCOPh)(NHNHCOPh)[13]	1.44 (1)		2.212 (8)		119.5 (4)			9.8, 6.2
ReCl$_2$(PPh$_3$)$_2$(NNHCOPh)(NHNHCO$_2$Me)[13]	1.44 (1)		2.206 (8)		121.3 (5)			

a significant degree of π bonding between a p orbital on N(1) and a predominantly d orbital on W that lies in a plane parallel to the plane of the Cp* ring. One can argue that this d orbital on W is the only one that is available for forming a W–N π bond. The bonding scheme in both **1** and **4** will be discussed more fully in the discussion section.

^{15}N and ^{1}H NMR studies show that the NHNH$_2$ protons in [WCp*Me$_3$(NHNH$_2$)]$^+$ are not exchanging intramolecularly or intermolecularly at a significant rate in the absence of added base. The ^{15}N NMR spectrum of **4** shows a doublet of doublets at δ 241.26 (J_{NH} = 93 Hz, J_{NN} = 10 Hz) assigned to *N*H and a triplet of doublets at δ 30.97 (J_{NH} = 89 Hz, J_{NN} = 10 Hz) assigned to *N*H$_2$. The fact that the chemical shift of the *N*H signal in **4** is close to the average (228.13 ppm) of the chemical shifts of the N$_\alpha$ signal in WCp*Me$_3$(NNH$_2$) (**2**; W–N bond order of ~3) and the *N*H signal in WCp*Me$_4$(NHNH$_2$) (**1**; W–N bond order of 1) is consistent with the sp^2 hybridization of the NH nitrogen in **4** (W–N bond order of ~2). The ^{1}H NMR spectrum of **4** in CDCl$_3$ at 25 °C shows the expected methyl resonances and two relatively *sharp* singlets at 11.82 ppm (area 1) and 5.21 ppm (area 2) that can be assigned to the H(1) and the H(2/3) protons, respectively (Figure 6). The spectrum is essentially unchanged at −70 °C. A difference NOE experiment showed that irradiation of the Cp* methyl groups enhances the H(1) signal at 11.82 ppm relative to the H(2/3) signal, as expected. In the ^{1}H NMR spectrum of a sample of [WCp*Me$_3$(^{15}NH^{15}NH$_2$)]$^+$, the two resonances are doublets with J_{HN} = 93 and 89 Hz, respectively. ^{1}H NMR magnetization-transfer experiments show that H$_\alpha$ and H$_\beta$ are not exchanging at a rate greater than T_1 for N*H* (0.64 s) or N*H*$_2$ (0.78 s). We conclude that N*H* and N*H*$_2$ simply are not coupled to any significant extent ($J_{HH} \leq 2$ Hz) and also are not broadened significantly by quadrupolar coupling to ^{14}N.

Proton-exchange studies in the presence of added base are not yet conclusive. What we can say at this stage is when a sample of **2** in CD$_2$Cl$_2$ is treated with 1 equiv of CF$_3$SO$_3$D at −78 °C, the resulting [WCp*Me$_3$(N$_2$H$_2$D)]$^+$ contains deuterium that is statistically distributed between the two nitrogen atoms. On the basis of the ^{1}H and ^{15}N NMR data described above, the lifetime of an NH or NH$_2$ proton in **4** at 25 °C before any form of exchange scrambles them is of the order of 1 s. At −80 °C the lifetime would be increased by 3 or more orders of magnitude, assuming an approximate halving of any exchange rate for every 10 °C. Therefore *if* a W(NDNH$_2$)$^+$ complex is formed at −80 °C by addition of deuterium to the α-nitrogen atom, H/D scrambling must occur by another mechanism.

Discussion

We can compare the structural details of **1** and **4** with those of complexes having alkyl and/or aryl substituents on the hydrazido(1−) ligand listed in Table V.

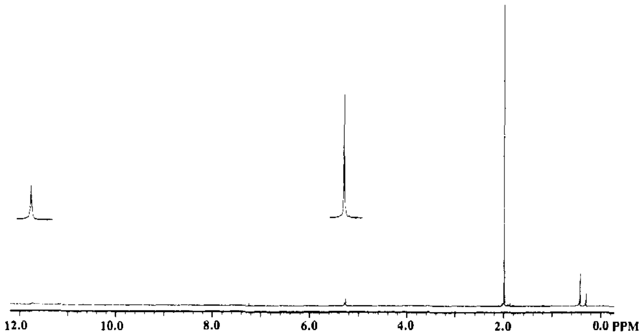
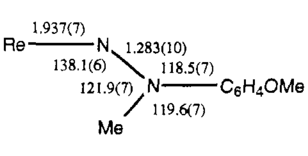
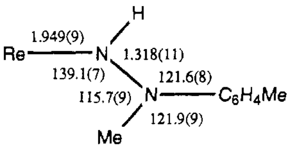


Figure 6. ^{1}H NMR spectrum of [WCp*Me$_3$(NHNH$_2$)]$^+$OTf$^-$ (**4**) at 25 °C in CDCl$_3$.

There are two previously published structure studies of η^2-NRNR$_2$ complexes in which the hybridization at the α-nitrogen atom can be deduced. In CpTiCl$_2$(NPhNH$_2$) the phenyl ring lies in the plane of the metal and the two nitrogen atoms, a fact that suggests the NPh nitrogen atom is sp^2 hybridized and the nitrogen lone pair is being donated to the metal; the metal electron count thereby increases from 14 to 16. The difference in the *B* and *C* bond lengths is similar to what it is in **4**. In [Cp$_2$W(NPhNH$_2$)]$^+$, the ipso carbon atom of the phenyl ring does not lie in the plane of the metal and the nitrogen atoms, since the electron count is 18 without counting the π-electron pair on the NPh nitrogen atom. The *B* and *C* bond lengths differ by ~0.12 Å, however, while the W–N bond lengths in **1** are virtually identical. Nevertheless, it would appear that differences in metal to nitrogen distances can be used as an indicator of the extent of the degree of π bonding in the M–N bond and sp^2 hybridization at the nitrogen in η^2-NRNR$_2$ complexes.

End-bound hydrazido(1−) complexes are listed in Table V for the sake of completion but also for the sake of trying to rationalize when end-bound hydrazido(1−) complexes are formed. {CpRe(CO)$_2$[NHNMe(p-C$_6$H$_4$Me)]}$^+$ is of particular interest because it is structurally similar to the "bent" hydrazido(2−) complex, CpRe(CO)$_2$[NNMe(p-C$_6$H$_4$OMe)], viz.





The η^1-hydrazido(2−) ligand in $CpRe(CO)_2[NNMe(p\text{-}C_6H_4OMe)]$ is bent because if the lone pair on N_α were donated to Re, the electron count would be 20. Therefore, what are presumed to be the same basic structural features in $CpRe(CO)_2[NHNMe(p\text{-}C_6H_4Me)]$ are preserved when a proton adds to the α-nitrogen atom to give an η^1-hydrazido(1−) or "protonated hydrazido(2−) complex", $\{CpRe(CO)_2[NHNMe(p\text{-}C_6H_4Me)]\}^+$, that presumably contains an sp² hybridized α-nitrogen atom. It is worth noting that the chemical shifts of "NH_α" in both **4** and $\{CpRe(CO)_2[NHNMe(p\text{-}C_6H_4Me)]\}^+$ are well downfield. A low-field "NH_α" chemical shift therefore cannot be characteristic of either η^1 or η^2 bonding, although it is consistent with sp² hybridization about N_α in cationic hydrazido(1−) complexes; i.e., one could say that the positive charge is located on N_α and a covalent $M{=}N_\alpha$ double bond is present. Steric arguments would have to be invoked to explain why the hydrazido(1−) ligands are side-bound in $[Mo(NHNMePh)(NNMePh)(S_2CNMe_2)_2]^+$[9a] and $Mo(NHNHCO_2Me)(N_2CO_2Me)(S_2CNMe_2)_2$[9b] but end-bound in $Mo[N_2C(O)Ph][NHNHC(O)Ph][PhC(S)N(Me)O]_2$.[11] $ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCOPh)$ and $ReCl_2(PPh_3)_2(NNHCOPh)(NHNHCO_2Me)$ are 18-electron species since the NNHCOPh ligand is a linear, four-electron ligand.

We now can discuss in more detail the mode of bonding of the hydrazido(1−) ligand in **1** and **4**. If a hydrazido(1−) fragment is to be bound in an η^1 fashion to a WCp^*Me_4 fragment[15] of the geometry found in **1** (the *z* axis is coincident with the W-Cp*(cent) bond and the methyl groups lie along the *x* and *y* axes), the WNN plane should be perpendicular to the Cp* ring in order to allow the $W{-}N_\alpha$ π bond to be formed by using what is essentially a d_{xy} orbital. But such an orientation in **1** would force N_β too close to the "axial" methyl group trans to Cp*; the three other "equatorial" methyl groups and N_α already are being forced to bend toward the axial methyl group by the Cp* ligand. The plausible alternative is to sacrifice the $W{-}N_\alpha$ π bond in favor of another σ bond between N_β and tungsten employing a similar, essentially d_{xy}, orbital. In this "parallel" orientation of the hydrazido(1−) ligand in **1**, there is no accessible metal orbital to form a π bond to the α-nitrogen atom, and the metal has an 18-electron count anyway. In contrast, in **4**, where no axial methyl group is present, the hydrazido(1−) ligand *can* bond to tungsten in a plane that is perpendicular to the plane of the Cp* ligand and thereby form a $W{-}N_\alpha$ π bond. Furthermore, the fact that the electron count of the metal in the $[WCp^*Me_3]^+$ fragment in **4** is less (by 2) than it is in the WCp^*Me_4 fragment in **1** allows a $W{-}N_\beta$ σ bond also to form in **4**. Therefore, the N_2H_3 ligand in **4** behaves as a five-electron donor, while the N_2H_3 ligand in **1** behaves as a three-electron donor.

Fluxional processes are often observed in substituted hydrazido(1−) complexes. For example, $\Delta G^\ddagger$ for interconversion of the methyl groups in the side-bound hydrazido(1−) complex $CpMo(\eta^2\text{-}NMeNMe_2)(NO)I$[16] is 14.1 kcal mol⁻¹ (temperature not reported). In the η^1-$NHNMe_2$ complex $Mo[HB(Me_2pz)_3](NO)I(NHNMe_2)$,[2] where dissociation of the NMe_2 end is not a prerequisite for interconversion of the two methyl groups, $\Delta G^\ddagger$ was found to be 9.3 kcal mol⁻¹ (temperature not reported). The unusually high value for $\Delta G^\ddagger$ (17.5 kcal mol⁻¹ at 328 K) for the η^1-hydrazido(1−) ligand in $\{CpRe(CO)_2[NHNMe(p\text{-}C_6H_4Me)]\}^+$ was attributed by the authors to a partial double bond between the two nitrogen atoms.[12] As reported above, $\Delta G^\ddagger$ for a process that interconverts H_B and H_C in the hydrazido(1−) ligand in **1** is 12.7 (4) kcal mol⁻¹ at 268 K. It is interesting to note that the two complexes with side-bound hydrazido(1−) ligands have similar values for $\Delta G^\ddagger$.

Apparently there is only one other hydrazido(1−) complex in the literature for which ^{15}N NMR data are reported;[10a,b] data for several others have been mentioned, but values were not reported.[8a,b] The chemical shift for the NH_2 nitrogen atom in $[Cp_2WNPhNH_2]^+$ was reported as −38 ppm (J_{NH} = 88 Hz) relative to NH_3.[17] The reason for the difference between this NH_2 chemical shift and that in side-bound hydrazido(1−) complexes **1** (39.95 ppm) and **4** (30.97 ppm) is unclear. (It is interesting to note that the chemical shift of *N*H_2 in **2** is 127.23 ppm.) Clearly more data are required before chemical shifts of β-nitrogen atoms can be discussed meaningfully.

The possibility of forming unusual hydrogen-bonding systems is the main reason that we are reluctant to interpret intermolecular proton-scrambling reactions. For the same reason some of the chemistry of $NHNH_2$ complexes is likely to differ significantly from that for hydrazido(1−) complexes in which one or more of the protons are replaced by (e.g.) alkyl or aryl groups. We will be looking for examples and consequences of hydrogen bonding involving $NHNH_2$ ligands in future studies.

Experimental Section

General Experimental Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres HE43-2 drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. All deuteriated solvents were passed through a column of activated alumina. ^{15}N-labeled hydrazine (95% ^{15}N) was purchased as the dihydrogen sulfate from Cambridge Isotope Laboratories, Inc.

NMR data are listed in parts per million (positive downfield) relative to Me_4Si for ^1H and ^{13}C, $^{15}NH_3$ for ^{15}N,[18] and 85% phosphoric acid for ^{31}P. Coupling constants are quoted in hertz. Obvious multiplicities and aliphatic coupling constants in the range 125–130 Hz are not noted specifically. ^1H NMR spectra were obtained at 250–300 MHz in C_6D_6 at 25 °C unless otherwise noted.

Magnetization-transfer experiments were performed by the method of Dahlquist, Longmuir, and Du Vernet.[19] The assumptions of the absolute and relative magnitudes of T_{1A} and T_{1X} were checked with a separate T_1 determination experiment and found to be valid.

Preparation of Compounds. $WCp^*Me_4(\eta^2\text{-}NHNH_2)$ (1). Hydrazine (7.6 mmol, 242 μL) was added to 20 mL of ether. The suspension was stirred vigorously as 1.0 g (1.9 mmol) of solid $[WCp^*Me_4][PF_6]$[20] was added. The reaction was stirred for 5 min, and a white precipitate was filtered off. The ether was removed from the filtrate to give 0.75 g of $WCp^*Me_4(\eta^2\text{-}NHNH_2)$ (96%). The compound may be crystallized from a 1:3 mixture of THF and pentane or ether at −40 °C, but it is sufficiently pure to be used in crude form: ^1H NMR δ 3.0 (broad lump, 3 H, N*H*), 1.23 (s, 15 H, C_5Me_5), 0.44 (s, 6 H, WMe_{cis}), 0.42 (s, 3 H, WMe_{trans}), 0.34 (s, 3 H, W*Me*); ^1H NMR (CD_2Cl_2) δ 2.68 (broad lump, 3 H, N*H*), 1.51 (s, 15 H, C_5Me_5), 0.01 (s, 6 H, WMe_{cis} (cis to the hydrazido ligand)), −0.1 (s, 3 H, W*Me*), −0.2 (s, 3 H, W*Me*); IR (Nujol mull) 3340 cm⁻¹ (w, N–H). Other low temperature spectra are shown in Figure 3 and discussed in the text.

The white precipitate that was filtered off was identified as $[N_2H_5]^+[PF_6]^-$: ^1H NMR (DMF-d_7) δ 5.78 (broad, s); ^{19}F NMR

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(17) (a) The N_β resonance was observed 68 ppm upfield of external $^{15}NH_4Cl$. $^{15}NH_4Cl$ is assumed to be 30 ppm downfield of $^{15}NH_3$.[17b] (b) Gordon, A. J.; Ford, R. A. *Chemist's Companion, A Handbook of Practical Data, Technique, and References*; Wiley: New York, 1972.

(18) Samples were referenced to external aniline-^{15}*N*, whose ^{15}N NMR signal was assumed to be 56.5 ppm downfield of $^{15}NH_3$.[17b]

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(DMF-d_7, relative to CFCl$_3$) δ 64.1 (d, J_{PF} = 708); ^{31}P NMR (DMF-d_7, relative to 85% phosphoric acid) δ −143.44 (septet, J_{PF} = 711); IR (Nujol mull) 3340 and 3310 (s, N–H), 1620 (m, br), 1100 (s, br), 940 (s, br), 830 cm^{-1} (vs, br, PF$_6^-$).

WCp*Me$_4$(η^2-^{15}NH^{15}NH$_2$). ^{15}N$_2$H$_4$ was prepared by treating 95% ^{15}N-labeled hydrazine (0.5 g) with liquid ammonia in a small glass frit fitted with ground-glass joints at each end, an external side arm that bypasses the frit, and a dry-ice-cooled cold finger. A receiver flask was added, the hydrazine sulfate was placed on the frit, and the assembled apparatus was evacuated for ~1 h and then back-filled with dinitrogen. Liquid ammonia that had been dried over sodium sand was condensed into the apparatus and allowed to reflux gently. It passed through the side arm, condensed on the cold finger, and dipped onto the hydrazine sulfate. The frit was kept cold by swabbing the exterior as needed with a dry ice/2-propanol mixture. After 2–3 h the hydrazine had been extracted into the liquid ammonia, leaving ammonium sulfate behind. The ammonia was allowed to evaporate overnight. The flask containing the hydrazine residue was taken into the drybox, 10 mL of ether was added, and the mixture was stirred overnight in order to allow the last traces of ammonia to evolve. A 95% yield of hydrazine was assumed, and 0.5 equiv of [WCp*Me$_4$]$^+$PF$_6^-$ was added to the stirred solution containing a mixture of hydrazine and ether. After 4 min the mixture was filtered through Celite, and WCp*Me$_4$(^{15}NH^{15}NH$_2$) was recovered as a white solid upon removal of the ether in vacuo: ^{15}N NMR (CD$_2$Cl$_2$, 193 K) δ 88.18 (d, J_{NH} = 58), 39.95 (t, J_{NH} = 84). The ^{1}H NMR spectrum of WCp*Me$_4$(η^2-^{15}NH^{15}NH$_2$) at 25 °C was identical with that observed for WCp*Me$_4$(η^2-NHNH$_2$) except the average hydrazido proton resonance was broader; i.e., coupling to ^{15}N was not resolvable.

Kinetic Studies of the Decomposition of WCp*Me$_4$(η^2-NHNH$_2$). The disappearance of the Cp* signal in the ^{1}H NMR spectrum of WCp*Me$_4$(η^2-NHNH$_2$) at 35 °C in CD$_2$Cl$_2$ was monitored vs toluene as the internal standard.

WCp*Me$_3$(NNH$_2$) (2). WCp*Me$_4$(η^2-NHNH$_2$) (1 g, 2.44 mmol) was dissolved in toluene, and the solution was left at room temperature for ~6 h. The solvent was removed from the slightly red-tinged solution, and the residue was dissolved in a minimum amount of ether. This solution was layered with pentane and cooled to −40 °C to yield WCp*Me$_3$(NNH$_2$) as an off-white precipitate (pure by NMR), which was collected by filtration (603 g, 1.53 mmol, 63% yield). The material recovered from the filtrate was predominantly WCp*Me$_3$(NNH$_2$) (~95% by NMR) and accounts for nearly all of the remaining 37% of the material. However, it was contaminated with a red impurity (believed to be a decomposition product) that we have not been able to separate from the desired product: ^{1}H NMR δ 4.59 (broad singlet, 2 H, N*H*), 1.57 (s, 15 H, C$_2$*Me*$_5$), 0.74 (s, 6 H, W*Me*$_{cis}$), 0.41 (s, 3 H, W*Me*$_{trans}$); ^{1}H NMR (CD$_2$Cl$_2$) δ 5.45 (broad lump, 2 H, N*H*), 1.78 (s, 15 H, C$_5$*Me*$_5$), 0.25 (s, 6 H, W*Me*$_{cis}$), −0.29 (s, 3 H, W*Me*$_{trans}$); IR (CH$_2$Cl$_2$) 3350, 3274, 1603 cm^{-1} (m, N–H). Anal. Calcd for WC$_{13}$H$_{26}$N$_2$: C, 39.61; H, 6.65; N, 7.11. Found: C, 39.60; H, 6.58; N, 7.05. A full study of the decomposition and other reactions of **2** is under way.

WCp*Me$_3$(^{15}N^{15}NH$_2$). WCp*Me$_3$(^{15}N^{15}NH$_2$) was prepared in a manner identical with that noted above for WCp*Me$_3$(NNH$_2$) employing WCp*Me$_4$(^{15}NH^{15}NH$_2$) (see above): ^{15}N NMR (CD$_2$Cl$_2$) δ 368.1 (d, J_{NN} = 11, J_{NW} = 129, N$_\alpha$), 127.2 (td, J_{NN} = 11, J_{NH} = 77, J_{NW} < 5, N$_\beta$). The ^{1}H NMR spectrum of WCp*Me$_3$(^{15}N^{15}NH$_2$) showed the expected splitting of the hydrazido protons.

[WCp*Me$_4$(NH$_2$NH$_2$)]$^+$[BF$_4$]$^-$ (3). WCp*Me$_4$(η^2-NHNH$_2$) (500 mg, 1.2 mmol) was dissolved in 30 mL of ether, and the solution was cooled to −40 °C. HBF$_4$(OMe$_2$) (155 mg, 0.95 equiv) was added to 5 mL of cold ether, and to this solution was added with vigorous stirring the cold solution of WCp*Me$_4$(η^2-NHNH$_2$). A cream-colored precipitate formed immediately, and the mixture was stored at −40 °C for 5 min. The precipitate was collected by filtration and was washed with cold ether (2 × 10 mL). This cream-white powder was dried in vacuo (yield 486 mg, 80%). This complex is quite unstable even in the solid state at low temperatures (a solid sample decomposed over the period of 1 week at −40 °C to no single product cleanly): ^{1}H NMR (CD$_2$Cl$_2$) δ 4.97 (s, 2 H, N$_2$H$_2$*H*$_2$), 4.62 (s, 2 H, N$_2$*H*$_2$H$_2$), 1.72 (s, 15 H, C$_5$*Me*$_5$), 0.53 (s, 3 H, W*Me*$_{axial}$), 0.34 (s, 6 H, W*Me*$_{cis}$), 0.10 (s, 3 H, W*Me*$_{trans}$).

[WCp*Me$_4$(NH$_2$NH$_2$)]$^+$[OTf]$^-$. WCp*Me$_4$(η^2-NHNH$_2$) (500 mg, 1.2 mmol) was dissolved in 10 mL of ether, and the solution was cooled to −40 °C. HOTf (174 mg, 0.95 equiv) in 5 mL of cold ether was added to the cold solution of WCp*Me$_4$(η^2-NHNH$_2$) with vigorous stirring. A cream-colored precipitate formed immediately, and the mixture was stored at −40 °C for 5 min. The precipitate was collected by filtration and was washed with cold ether (2 × 10 mL). This cream-white powder was dried in vacuo (yield 578 mg, 86%): ^{1}H NMR (CD$_2$Cl$_2$, 293 K) δ 5.25 (s, 2 H, N$_2$H$_2$*H*$_2$), 5.02 (s, 2 H, N$_2$*H*$_2$H$_2$), 1.71 (s, 15 H, C$_5$*Me*$_5$), 0.52 (s, 3 H, W*Me*$_{axial}$), 0.31 (s, 6 H, W*Me*$_{cis}$), 0.06 (s, 3 H, W*Me*$_{trans}$). We have seen no significant difference between the OTf$^-$ and BF$_4^-$ salts except [WCp*Me$_4$(NH$_2$NH$_2$)]$^+$[OTf]$^-$ is less soluble and the hydrazine proton resonances are shifted somewhat from what they are in [WCp*Me$_4$(NH$_2$NH$_2$)]$^+$[BF$_4$]$^-$. We believe that chemical shift differences of this magnitude are not indicative of any significant hydrogen bonding between the cation and counterion.

[WCp*Me$_3$(η^2-NHNH$_2$)]$^+$[OTf]$^-$ (4). A −40 °C solution of triflic acid (26 mg, 0.17 mmol) in 2 mL of diethyl ether was added rapidly to a −40 °C solution of WCp*Me$_3$(NNH$_2$) (65 mg, 0.16 mmol) in 3 mL of diethyl ether. The color of the reaction mixture immediately changed from dark red to yellow, and a yellow precipitate began to form. The reaction mixture was maintained at −40 °C for 0.5 h. The mother liquor was decanted from the yellow product, which was washed with cold (−40 °C) diethyl ether and dried in vacuo to give [WCp*Me$_3$(NHNH$_2$)]$^+$[OTf]$^-$ (55 mg, 0.1 mmol, 62%): ^{1}H NMR (CDCl$_3$) δ 11.82 (s, 1 H, N*H*NH$_2$), 5.21 (s, 2 H, NHN*H*$_2$), 2.01 (s, 15 H, C$_5$*Me*$_5$), 0.44 (s, 6 H, W*Me*), 0.32 (s, 3 H, W*Me*); ^{13}C{^{1}H} NMR (CDCl$_3$, 218 K) δ 115.5 (*C*$_5$Me$_5$), 32.1 (W*Me*), 29.2 (W*Me*), 10.6 (C$_5$*Me*$_5$); ^{19}F NMR (CDCl$_3$) δ −78.94 (C*F*$_3$SO$_3$). An analytically pure sample was prepared by slowly cooling a solution of the product in a 1:1 mixture of tetrahydrofuran and diethyl ether to −40 °C. The yellow crystals thus obtained turned to a yellow powder upon drying in vacuo. Anal. Calcd for WC$_{14}$H$_{27}$N$_2$O$_3$F$_3$S: C, 30.89; H, 5.00; N, 5.15. Found: C, 30.65; H, 5.01; N, 4.99.

[WCp*Me$_3$(η^2-^{15}NH^{15}NH$_2$)]$^+$[OTf]$^-$. WCp*Me$_3$(^{15}N^{15}NH$_2$) was protonated and the product isolated as described above for [WCp*Me$_3$(NHNH$_2$)]$^+$: ^{15}N NMR (CD$_2$Cl$_2$) δ 241.3 (dd, J_{NN} = 10, J_{NH} = 93, N$_\alpha$), 31.09 (td, J_{NN} = 10, J_{NH} = 89, N$_\beta$). The ^{1}H NMR spectrum of [WCp*Me$_3$(^{15}NH^{15}NH$_2$)]$^+$[OTf]$^-$ showed the expected splitting of the hydrazido protons.

[WCp*Me$_3$(η^2-NHNH$_2$)]$^+$[BF$_4$]$^-$. WCp*Me$_3$(NNH$_2$) (400 mg, 1.0 mmol) was dissolved in 60 mL of ether, and the solution was cooled to −15 °C. HBF$_4$(OMe$_2$) (110 mL, 0.95 equiv) was dissolved in 1 mL of THF, and the solution was rapidly added to the vigorously stirred solution of WCp*Me$_3$(NNH$_2$). The color immediately changed from deep red to pale orange, and an orange precipitate formed. The mixture was stirred for 15 min and the precipitate collected by filtration and washed with ether (2 × 30 mL). This yellow-orange powder was dried in vacuo (yield 390 mg, 81%): ^{1}H NMR (CD$_2$Cl$_2$) δ 10.70 (br s, 1 H, N*H*), 4.98 (br s, 2 H, N*H*$_2$), 2.07 (s, 15 H, C$_5$*Me*$_5$), 0.49 (s, 6 H, W*Me*$_{cis}$), 0.37 (s, 3 H, W*Me*$_{trans}$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 116.7 (*C*$_5$Me$_5$), 33.6 (W*Me*$_{cis}$), 30.6 (W*Me*$_{trans}$), 10.7 (C$_5$*Me*$_5$); IR (Nujol mull) 3267 cm^{-1}. We have observed no significant differences between the BF$_4^-$ and triflate salts except for differences in the chemical shifts of the hydrazido protons.

Crystal Structure of WCp*Me$_4$(η^2-NHNH$_2$) (1). Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 κ-geometry diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation (λ = 0.71073 Å). Data collection, reduction, and refinement procedures have been detailed elsewhere.[21] A total of 9092 reflections ($\pm h, \pm k, +l$) were collected in the range $3° \le 2\theta \le 55°$ with the 6185 having $F_o > 4\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (352 variables) using SHELX-76. Final R_1 = 0.0973 and R_2 = 0.1153. C(21) and C(29) behaved poorly in the refinement so they were refined isotropically. Two crystallographically independent molecules of **1** were found in the asymmetric unit along with two molecules of THF. The highest density peaks in the THF molecules were assigned as O(1) and O(2). This assignment was supported by the short N(22)–O distances (2.991 and 3.007 Å), the result of N–H···O hydrogen bonding between the NH$_2$ protons and THF. The final difference-Fourier map showed no chemically significant features. Crystal data: a = 15.100 (7) Å, b = 16.551 (6) Å, c = 8.860 (8) Å, α = 97.26 (6)°, β = 100.92 (5)°, γ = 66.08 (4)°, V = 1984.4 Å^3, space group $P\bar{1}$, Z = 4, M_r = 410.31, ρ(calcd) = 1.564 g cm^{-3}, μ = 55.4 cm^{-1}. A semiempirical absorption correction was applied.

Crystal Structure of [WCp*Me$_3$(η^2-NHNH$_2$)]$^+$[OTf]$^-$ (4). Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 κ-geometry diffractometer equipped with a liquid-nitrogen low-temperature device and using Mo Kα radiation (γ = 0.71073 Å). Data collection, reduction, and refinement procedures have been detailed elsewhere.[21] A total of 5414 reflections ($\pm h, +k, +l$) were collected in the range $3° \le 2\theta \le 55°$ with the 3658 having $F_o > 4\sigma(F_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (248 variables) using the TEXAN crystallographic software package from Molecular Structure Corp. Final R_1 = 0.049 and R_2 = 0.059. The final difference-Fourier map showed no chemically significant features. Crystal data: a = 23.619 (4) Å, b = 8.486 (2) Å, c = 21.921 (6) Å, β = 100.40 (2)°, V = 4321 (3) Å^3, space group $C2/c$, Z = 8, M_r = 544.28, ρ(calcd) = 1.67 g cm^{-3}, μ = 57.9 cm^{-1}. An empirical absorption correction was applied. The entirely normal triflate ion was well separated from the cation.

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Inorg. Chem. **1988**, *27*, 3583-3587 **3583**

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Registry No. **1**, 116263-30-0; **2**, 96999-47-2; **3**, 116263-32-2; **4**, 116263-34-4; $WCp^*Me_4(\eta^2\text{-}{}^{15}NH^{15}NH_2)$, 116278-36-5; $WCp^*Me_3({}^{15}N^{15}NH_2)$, 116263-35-5; $[WCp^*Me_4(NH_2NH_2)]^+[OTf]^-$, 116263-36-6; $[WCp^*Me_3(\eta^2\text{-}{}^{15}NH^{15}NH_2)]^+[OTf]^-$, 116278-38-7; $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+[BF_4]^-$, 116263-37-7; $[WCp^*Me_4]^+[PF_6]^-$, 96999-45-0; $[N_2H_5]^+[PF_6]^-$, 88186-61-2; $HBF_4(OMe_2)$, 67969-83-9; ${}^{15}N_2H_4$, 64066-18-8; hydrazine dihydrogensulfate (${}^{15}N$-labeled), 116416-71-8; ${}^{15}N$, 14390-96-6; hydrazine, 302-01-2.

Supplementary Material Available: Listings of final positional and anisotropic thermal parameters for $W(\eta^5\text{-}C_5Me_5)Me_4(\eta^2\text{-}NHNH_2)$ (Table S1), final positional and *B*(eq) parameters for $[W(\eta^5\text{-}C_5Me_5)Me_3(\eta^2\text{-}NHNH_2)]^+[SO_3CF_3]^-$ (Table S2), and anisotropic thermal parameters for $[W(\eta^5\text{-}C_5Me_5)Me_3(\eta^2\text{-}NHNH_2)]^+[SO_3CF_3]^-$ (Table S3) (5 pages); listings of final observed and calculated structure factors for $W(\eta^5\text{-}C_5Me_5)Me_4(\eta^2\text{-}NHNH_2)$ (Table S4) and $[W(\eta^5\text{-}C_5Me_5)Me_3(\eta^2\text{-}NHNH_2)]^+[SO_3CF_3]^-$ (Table S5) (52 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Birkbeck College, University of London, Gordon House, 29 Gordon Square, London WC1H 0PP, U.K.

${}^{14}N$ NMR Studies of Amine Release from Platinum Anticancer Drugs: Models and Human Blood Plasma[1]

Richard E. Norman[2] and Peter J. Sadler*

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The feasibility of using ${}^{14}N\{{}^1H\}$ NMR spectroscopy to follow reactions of Pt(II) antitumor drugs under biologically relevant conditions has been investigated. Amine release from *cis*-$PtCl_2(NH_3)_2$ upon reaction with both L-methionine and *N*-acetyl-L-methionine and from $PtCl_2$(1,2-diaminoethane) on reaction with L-methionine in aqueous solution can be readily detected. Upon incubation (37 °C for 24 h) of *cis*-$PtCl_2(NH_3)_2$ with human blood plasma supplemented with L-methionine, at least one NH_3 ligand appears to be lost. Ammonia release is also detected upon addition of excess sodium diethyldithiocarbamate (an agent used clinically to reverse cisplatin toxicity) to plasma incubated with *cis*-$PtCl_2(NH_3)_2$ (37 °C for 2 h). Other ${}^{14}N$ peaks assigned in plasma spectra include those for amides, phosphatidylcholines, and N_2. We conclude that ${}^{14}N$ NMR spectroscopy provides a useful probe for studying these drugs at millimolar concentrations under conditions that approach physiological relevance.

Introduction

There is current interest in understanding the chemical basis for the mechanism of action of the antitumor drug cisplatin,[3] *cis*-$PtCl_2(NH_3)_2$, and its toxic side effects. Although current evidence suggests that the important cytotoxic lesion is an intrastrand cross-link arising from *cis*-$Pt(NH_3)_2^{2+}$ binding to DNA,[4] ammonia can be liberated from cisplatin under mild conditions.[5] Naturally occurring sulfur-containing ligands such as methionine and cysteine are particular candidates for study because, on substitution for Cl^- in cisplatin, their high kinetic trans effects[6] may induce rapid NH_3 release.[7] Methionine-containing Pt(II) metabolites have apparently been isolated from the urine of patients receiving cisplatin,[8] and numerous studies have been conducted on blood plasma.[9] However, previous attempts to identify metabolites formed from cisplatin in biological materials have involved chemical separation and isolation procedures[8,9] during which further transformation could occur. We are therefore exploring methods for the speciation of Pt (and other biologically relevant metals) in *intact* biological materials.

The detection limit for many small molecules in ${}^1H$ NMR spectra is now as low as 100 μM, and the background of interfering resonances can often be filtered out via suitable pulse sequences. We have recently shown[10] by ${}^1H$ NMR spectroscopy that cisplatin, $PtCl_2(en)$, and K_2PtCl_4 react with L-Met in cell culture media at 37 °C to produce new species, one of which appears to be Pt(L-Met-*N*,*S*)$_2$. In this paper we explore the use of ${}^{14}N$ NMR spectroscopy for the direct detection of amine release in human

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(2) Current address: Department of Chemistry, University of Minnesota, 207 Pleasant Street, S.E., Minneapolis, MN 55455.

(3) The following abbrevations are used throughout the text: cisplatin, *cis*-$Pt(NH_3)_2Cl_2$; NaDEDTC, sodium diethyldithiocarbamate; en, 1,2-diaminoethane; L-Met, L-methionine; *N*-Ac-L-Met, *N*-acetyl-L-methionine; NMR, nuclear magnetic resonance.

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