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Tungsten Pentacarbonyl Complexes of cis- and trans-1,2-Dimethyldiazene and 1,2-Dimethylhydrazine. Preferential Oxidation of the Coordinated Hydrazine to the cis-Diazene Complex.

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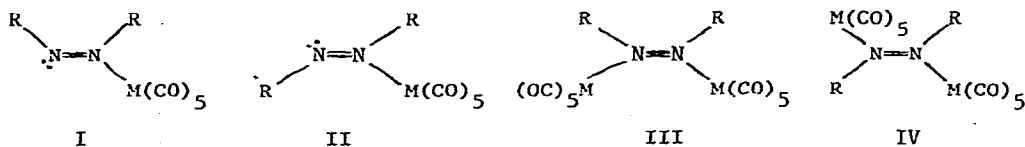
#### Summary

The complexes  $W(CO)_5L$  ( $L=CH_3NHNHCH_3$ ,  $c-CH_3N=NCH_3$ , and  $t-CH_3N=NCH_3$ ) and  $[W(CO)_5]_2(t-CH_3N=NCH_3)$  have been obtained from the reaction of  $W(CO)_5THF$  with the corresponding ligand. Each  $W(CO)_5$  group is coordinated to the lone pair of one of the nitrogen atoms of the ligand.  $W(CO)_5(c-CH_3N=NCH_3)$  undergoes coordination site exchange between the two nitrogen atoms with a coalescence temperature of  $40 \pm 2^\circ C$  and  $\Delta G^\ddagger = 16.0 \pm 0.1$  kcal/mole in the NMR spectrum. Infrared, visible, and NMR spectra are interpreted and comparisons drawn with other Group VIB carbonyl complexes of diazenes. The role of alkyl group size in determining the types of complexes formed by cis and trans acyclic diazenes and the properties of these complexes is discussed. Activated  $MnO_2$  was found to preferentially oxidize  $CH_3NHNHCH_3$  to  $c-CH_3N=NCH_3$  at  $-50^\circ C$ , offering a convenient large scale synthesis of this molecule. The hydrazine complex  $W(CO)_5(CH_3NHNHCH_3)$  is similarly

oxidized in high yield to about a 5:1 mixture of  $W(CO)_5(\underline{c}\text{-CH}_3\text{N=NCH}_3)$  and  $W(CO)_5(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  and is the better synthetic route to these complexes.  $W(CO)_5(\underline{c}\text{-CH}_3\text{N=NCH}_3)$  tautomerizes readily to a complex of formaldehyde methylhydrazone  $W(CO)_5(H_2C=NNHCH_3)$ , which is believed to be coordinated through the imino nitrogen.

### Introduction

Our current research concerns the coordination of acyclic diazenes in transition metal carbonyl complexes with emphasis on exploring the role that a cis or trans geometry of the diazene ligand has in complex formation and stability. Recently we reported results for the Group VIB complexes of cis- and trans-1,2-diisopropyldiazene (DIPD) [1]. This diazene system was selected for initial studies in this area because the uncoordinated diazenes were both conveniently synthesized and stable at room temperature. In this paper we describe our work with tungsten carbonyl complexes of the ligands cis- and trans-1,2-dimethyldiazene. The methyl groups of the dimethyldiazene ligands are intermediate in size between the large isopropyl groups in c- and t-DIPD, which gave only monometallic complexes I and II ( $M=Cr, Mo, W; R=CH(CH_3)_2$ ), and the hydrogen atoms in c- and t-HN=NH, for which only bimetallic complexes III ( $M=Cr, Mo, W; R=H$ ) and IV ( $M=Cr$  or  $C_5H_5Mn(CO)_2$  and  $C_5H_5Re(CO)_2; R=H$ ) are known [2]. Thus the dimethyldiazene ligands offer a chance to probe the role of alkyl group size on complex formation. Only one metal carbonyl complex of a dimethyldiazene,  $C_5H_5Mn(CO)_2(\underline{t}\text{-CH}_3\text{N=NCH}_3)$ , has been reported previously [3].



We have also extended our studies on the direct formation of diazene

complexes by oxidation of the hydrazine complex  $W(CO)_5(CH_3NHNHCH_3)$  with activated manganese dioxide and note strikingly different results from these obtained in the diisopropyl system.

### Experimental

Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer and ultraviolet and visible spectra on a Cary 17 spectrophotometer. Proton NMR spectra were obtained on a Perkin-Elmer R12B spectrometer which was equipped with variable temperature and double resonance capability. Organometallic samples were sealed in vacuum using degassed solvents. Melting points were taken in open capillaries and are uncorrected.

A nitrogen atmosphere was routinely used for all operations. Tetrahydrofuran (THF) was distilled under nitrogen from benzophenone ketyl, dichloromethane from phosphorus pentoxide, and hexane and pentane from calcium hydride. Reduction of solution volumes or stripping to dryness was done at  $<0.1$  Torr at the temperature specified. Chromatography was performed on a 2 x 35-cm column of Florisil (Fisher Scientific) which was slurry-packed in petroleum ether (b.p. 30-60°C).

Commercial tungsten hexacarbonyl was sublimed before use. Solutions of  $W(CO)_5(THF)$  were photochemically generated as previously described [1]. Activated manganese dioxide was purchased from Ventron Corporation (Alfa Division). 1,2-Dimethylhydrazine was obtained by treating the dihydrochloride salt (Aldrich) with powdered potassium hydroxide and a small amount of water in a vacuum system. The free hydrazine was distilled off, dried over 4A molecular sieve, and stored in vacuum. Trans-1,2-dimethyldiazene was obtained by mercuric oxide oxidation of  $CH_3NHNHCH_3$  [4].

Synthesis of cis-1,2-dimethyldiazene. Solutions of cis-1,2-dimethyl-diazene were prepared by a variation of the procedure developed by Hyatt [5] to make cis-diphenyldiazenes. In a typical run 20 ml of  $\text{CH}_2\text{Cl}_2$ , which had been dried over potassium carbonate, 7.5g (86.3mmol) of activated  $\text{MnO}_2$ , and a magnetic stirring bar were placed in a three-necked flask on a vacuum line and taken through three freeze/evacuate/thaw cycles. Next 0.51g (8.5mmol) of  $\text{CH}_3\text{NHNHCH}_3$  was distilled onto the  $\text{CH}_2\text{Cl}_2$  solution at  $-196^\circ\text{C}$ . The temperature was raised to  $-50^\circ\text{C}$  and stirring initiated. It is important that the temperature not be permitted to rise much above  $-50^\circ\text{C}$  as c- $\text{CH}_3\text{N}=\text{NCH}_3$  decomposed when in contact with  $\text{MnO}_2$  at higher temperatures [6]. Even filtered solutions of c- $\text{CH}_3\text{N}=\text{NCH}_3$  are best kept cold to inhibit tautomerization to formaldehyde methylhydrazone ( $\text{H}_2\text{C}=\text{NNHCH}_3$ ) [7]. After 1-1.5h of reaction the flask was vented to nitrogen and a sample withdrawn by suction through a small tube of tightly-packed glass wool. The NMR spectrum of this sample in  $\text{CDCl}_3$  showed complete oxidation of  $\text{CH}_3\text{NHNHCH}_3$  to a mixture of c- $\text{CH}_3\text{N}=\text{NCH}_3$  (~85%) and t- $\text{CH}_3\text{N}=\text{NCH}_3$  (~15%). The reaction mixture was filtered at  $-70^\circ\text{C}$  through a medium frit and the filtrate stored at  $-60^\circ\text{C}$  until it was needed.

Synthesis of  $\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$ . A solution of  $\text{W}(\text{CO})_5\text{THF}$ , prepared from 1.56g (4.4mmol) of  $\text{W}(\text{CO})_6$ , was cooled to  $0^\circ\text{C}$  and 0.32ml (4.4mmol) of  $\text{CH}_3\text{NHNHCH}_3$  added. After 1h the solvent was removed at  $0^\circ\text{C}$ , the oily yellow residue taken up in hexane, filtered, and the filtrate cooled to  $-78^\circ\text{C}$ . The supernatant was decanted from the yellow crystals which formed, and the crystals washed with a small amount of cold hexane. The residual solvent was pumped away as the crystals slowly warmed to ambient. Yield: 1.26g (3.3mmol), 75%. The stripped mother liquor provided another 0.14g of solid which was also of adequate purity for use in subsequent oxidation studies. Further purification was effected by chromatography with considerable loss of material. The yellow band of  $\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$  was eluted with a 3:1 mixture of dichloromethane/petroleum ether. Chromatography of 185 mg of crystallized product yielded 89 mg of analytically pure material. Analysis for  $\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$ : Calcd: C, 21.88; H, 2.08; N, 7.29. Fd: C, 21.93; H, 2.09; N, 7.21. Mp.  $47-48^\circ\text{C}$ .

Reaction of  $W(CO)_6$  with  $t\text{-CH}_3\text{N=NCH}_3$ . A solution of  $W(CO)_5\text{THF}$ , prepared from 1.60g (4.6mmol) of  $W(CO)_6$ , was stripped to dryness at  $-25^\circ\text{C}$  and a  $-30^\circ\text{C}$  solution of 6.1 mmol of  $t\text{-CH}_3\text{N=NCH}_3$  in 20 ml of  $\text{CH}_2\text{Cl}_2$  was added to the residue with stirring. After 1h the mixture was filtered cold to provide a reddish filtrate. The solid on the filter was washed with  $-30^\circ\text{C}$   $\text{CH}_2\text{Cl}_2$  until the filtrate was nearly colorless. The solution volume was reduced at  $-30^\circ\text{C}$  from  $\sim 300$  ml to  $\sim 75$  ml, and 50 ml of cold hexane were added. After being cooled to  $-78^\circ\text{C}$  the mixture was filtered at that temperature to collect a brick-red solid which was washed with two 15 ml portions of cold hexane. The solid was pumped dry on the filter as it gradually warmed to ambient for a yield of 344 mg (0.49 mmol, 21.2% based on  $W(CO)_6$ ) of analytically pure  $[W(CO)_5]_2(t\text{-CH}_3\text{N=NCH}_3)$ . The filtrate was stripped to dryness at  $-30^\circ\text{C}$ , warmed to ambient, and subjected to sublimation with a  $-78^\circ\text{C}$  probe where 354 mg of a mixture of  $W(CO)_6$  and  $W(CO)_5(t\text{-CH}_3\text{N=NCH}_3)$  collected. A further portion of 425 mg (0.60 mmol, 26% based on  $W(CO)_6$ ) of nearly pure, nonvolatile  $[W(CO)_5]_2(t\text{-CH}_3\text{N=NCH}_3)$  remained. Chromatography of the sublimate provided a single yellow band which was eluted with petroleum ether. Removal of solvent provided 70 mg (0.18 mmol, 4.0% based on  $W(CO)_6$ ) of  $W(CO)_5(t\text{-CH}_3\text{N=NCH}_3)$ .

A reaction employing 0.50 mmol of  $W(CO)_6$  and 5.0 mmol of  $t\text{-CH}_3\text{N=NCH}_3$  was also carried out. After removing solvent from the original reaction mixture, the residue was sublimed as above. Only 35 mg of impure  $W(CO)_5(t\text{-CH}_3\text{N=NCH}_3)$  was collected on the probe, leaving a red-brown nonvolatile residue.

Analysis for  $W(CO)_5(t\text{-CH}_3\text{N=NCH}_3)$ : Calcd: C, 22.01; H, 1.57; N, 7.33.  
 Fd: C, 21.78; H, 1.63; N, 7.26. Mp.  $68\text{--}69^\circ\text{C}$ . Analysis for  $[W(CO)_5]_2(t\text{-CH}_3\text{N=NCH}_3)$ :  
 Calcd: C, 20.41; H, 3.97; N, 0.85. Fd: C, 20.33; H, 3.93; N, 0.88. Mp.  $97\text{--}98^\circ\text{C}$   
 (dec.).

Reaction of  $W(CO)_6$  with  $c\text{-CH}_3\text{N=NCH}_3$ . A solution of  $W(CO)_5\text{THF}$ , prepared from 2.40g (6.8mmol) of  $W(CO)_6$ , was cooled to  $-20^\circ\text{C}$  and a solution of  $c\text{-CH}_3\text{N=NCH}_3$ , prepared by oxidation of 0.51g of  $\text{CH}_3\text{NHNCH}_3\text{H}$  as described

above, was added giving a red solution. After stirring for 2h at  $-20^{\circ}\text{C}$  the solution volume was brought to  $\sim 150\text{ml}$  by addition of more  $\text{CH}_2\text{Cl}_2$ , cooled to  $-78^{\circ}\text{C}$ , and filtered. About 200ml of hexane was added to the cold filtrate and the volume reduced to half at  $-30^{\circ}\text{C}$ . Filtration gave a solid which was sometimes just gray decomposition material and sometimes brick red suggesting  $[\text{W}(\text{CO})_5]_2(\underline{\text{c}}-\text{CH}_3\text{N}=\text{NCH}_3)$ . The stripped filtrate yielded a mixture of red solid and fluffy gold needles. The latter were removed to give 114 mg (0.30mmol, 4.4%) of  $\text{W}(\text{CO})_5(\underline{\text{c}}-\text{CH}_3\text{N}=\text{NCH}_3)$  as shown by NMR and infrared spectra. The red solid comprised 230 mg which could not be satisfactorily purified or spectroscopically characterized because of instability in solution and low solubility. A 0.44g portion of this material was allowed to decompose fully in  $\text{CH}_2\text{Cl}_2$  to a yellow solution which was stripped and then chromatographed. Elution with petroleum ether gave 30 mg of  $\text{W}(\text{CO})_5(\underline{\text{t}}-\text{CH}_3\text{N}=\text{NCH}_3)$  while 3:7  $\text{CH}_2\text{Cl}_2$ /petroleum ether gave a small second yellow band providing  $\sim 3$  mg of  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$ . Analysis for  $\text{W}(\text{CO})_5(\underline{\text{c}}-\text{CH}_3\text{N}=\text{NCH}_3)$ : Calcd: C, 22.01; H, 1.57; N, 7.33. Fd: C, 21.84; H, 1.56; N, 7.16. Mp.  $50-51^{\circ}\text{C}$ . Analysis for  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$ : Calcd: C, 22.01; H, 1.57; N, 7.33. Fd: C, 22.05; H, 1.59; N, 7.32. Mp.  $54-55^{\circ}\text{C}$ .

Oxidation of  $\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$ .

A. With activated  $\text{MnO}_2$ . Oxidations were conducted at temperatures from  $25^{\circ}$  to  $-78^{\circ}\text{C}$  on samples of  $\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$  ranging from 100-500 mg. In each case the complex and 1.0g of anhydrous  $\text{Na}_2\text{SO}_4$  were placed in 10-45 ml of  $\text{CH}_2\text{Cl}_2$ . After equilibration at the reaction temperature a ten-fold molar excess of activated  $\text{MnO}_2$  was added. The reaction was monitored by withdrawing samples through a plug of glass wool, drying with a nitrogen purge, and examining the hexane extract by infrared spectrometry in the carbonyl stretching region. The spectral changes were not marked so there was some uncertainty when the reaction was complete. In exploratory runs the reaction mixture was filtered at  $-78^{\circ}\text{C}$ , the filtrate stripped, and the residue examined by NMR for product distribution of  $\text{W}(\text{CO})_5\text{L}$  where  $\text{L} = \underline{\text{t}}-\text{CH}_3\text{N}=\text{NCH}_3$ ,  $\underline{\text{c}}-\text{CH}_3\text{N}=\text{NCH}_3$ , and  $\text{H}_2\text{C}=\text{NNHCH}_3$ . Two full work-up procedures were also employed:

(1) A room temperature reaction of 466 mg (1.21 mmol) of  $W(CO)_5(CH_3NHNHCH_3)$  was filtered after 1.5h. The stripped filtrate was chromatographed to give two yellow bands. The first emerged with petroleum ether as eluant and gave 75 mg (0.20 mmol, 16%) of  $W(CO)_5(\underline{t}-CH_3N=NCH_3)$ . The second was eluted with 15%  $CH_2Cl_2$  in petroleum ether to provide 189 mg (0.50 mmol, 41%) of  $W(CO)_5(H_2C=NNHCH_3)$ .

(2) A  $-60^\circ C$  reaction of 504 mg (1.31 mmol) of  $W(CO)_5(CH_3NHNHCH_3)$  was filtered at  $-78^\circ C$  after 25h. About 175 ml of cold hexane was added to the filtrate ( $\sim 50$  ml  $CH_2Cl_2$ ) and the volume reduced to  $\sim 60$  ml at  $-30^\circ C$ . The solution was cooled to  $-78^\circ C$  and the mother liquor removed by pipet. The crystals were washed once with  $\sim 5$  ml of hexane and then pumped to dryness at  $-25^\circ C$  followed by gradual warming to ambient. Yield: 279 mg (0.78 mmol, 59%) of pure  $W(CO)_5(\underline{c}-CH_3N=NCH_3)$ . A second crop of 50 mg of crystals contained small amounts of  $W(CO)_6$  and  $W(CO)_5(\underline{t}-CH_3N=NCH_3)$ .

B. With  $H_2O_2/Cu^{2+}$ . The procedure was that of Sellmann [2,3] as previously employed for 1,2-diisopropylhydrazine complexes [1]. For reactions run at room temperature gas evolution was complete in  $\sim 1$ h. NMR analysis of the stripped filtrate showed mostly unreacted  $W(CO)_5(CH_3NHNHCH_3)$ . Reactions down to  $0^\circ C$  took longer but did not improve the conversion. Small quantities of  $W(CO)_5(\underline{t}-CH_3N=NCH_3)$  and  $W(CO)_5(H_2C=NNHCH_3)$  could be obtained by chromatography.

## Results and Discussion

Syntheses and Properties. Bright yellow  $W(CO)_5(CH_3NHNHCH_3)$  was readily obtained in high yield from the reaction of the free hydrazine with photochemically generated  $W(CO)_5THF$  in THF. The uncoordinated diazenes  $\underline{t}-$  and  $\underline{c}-CH_3N=NCH_3$  also reacted with  $W(CO)_5THF$  to give mono-metallic and bimetallic complexes. In these syntheses the THF solvent was first removed at low temperature and then a dichloromethane solution of the diazene added in order to minimize competition between the THF and the diazene for the  $W(CO)_5$  moiety. In a 1:1 ligand to metal ratio  $\underline{t}-CH_3N=NCH_3$

gave predominantly brick red  $[\text{W}(\text{CO})_5]_2(\underline{t}\text{-CH}_3\text{N}=\text{NCH}_3)$  and only a small quantity of yellow  $[\text{W}(\text{CO})_5](\underline{t}\text{-CH}_3\text{N}=\text{NCH}_3)$ . Even a ten-fold molar excess of diazene did not favor the monometallic complex. Reaction of  $\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3$  and  $\text{W}(\text{CO})_5\text{THF}$  likewise gave a small yield of gold monometallic  $\text{W}(\text{CO})_5(\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3)$  accompanied by a brick red solid believed to be bimetallic  $[\text{W}(\text{CO})_5]_2(\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3)$ . Instability and low solubility prevented further purification and characterization of this material.

The complex of formaldehyde methylhydrazone,  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$ , was not obtained via the free ligand. It resulted from tautomerization of  $\text{W}(\text{CO})_5(\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3)$  probably through acid or base catalysis. Uncoordinated  $\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3$  shows similar sensitivity to tautomerization [7]. Unless extreme care is exercised some tautomerization accompanies attempted recrystallization of  $\text{W}(\text{CO})_5(\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3)$ . Complete tautomerization occurred when the complex was chromatographed at room temperature on Florisil; this was the most convenient way to obtain substantial samples of the hydrazone complex.  $\text{W}(\text{CO})_5(\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3)$  did survive chromatography at  $-20^\circ\text{C}$  but did not separate from  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$  when present.

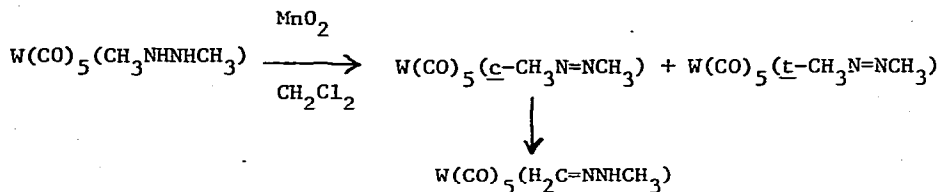
All of the complexes reported here could be handled in air for short periods without notable effect. The monometallic complexes of  $\underline{t}\text{-CH}_3\text{N}=\text{NCH}_3$ ,  $\text{H}_2\text{C}=\text{NNHCH}_3$ , and  $\text{CH}_3\text{NHNHCH}_3$  sublimed readily and only  $\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$  showed appreciable loss on chromatography. Decomposition of the bimetallic diazene complexes in solution provided little in the way of useful products.

The role of alkyl group size in the types of pentacarbonyl complexes formed by diazenes is clearly indicated by comparing the current results for the dimethyldiazene ligands with our earlier work on cis- and trans-1,2-diisopropyldiazene [1]. For the latter only monometallic complexes of types I and II ( $\text{R} = \text{CH}(\text{CH}_3)_2$ ) were obtained by the  $\text{W}(\text{CO})_5\text{THF}$  route even when a large excess of metal carbonyl was employed. With the dimethyldiazenes both monometallic and bimetallic complexes form I-IV ( $\text{R}=\text{CH}_3$ ;  $\text{M}=\text{W}$ ) with the bimetallic predominant. The low stability of  $[\text{W}(\text{CO})_5]_2(\underline{c}\text{-CH}_3\text{N}=\text{NCH}_3)$



(type IV) is probably due to interaction between the two cis  $W(CO)_5$  units; the methyl groups are already bumping in the free ligand [8] and cannot be forced together to provide more room for the metal groups.

The monometallic complexes of c- and t- $CH_3N=NCH_3$  could also be synthesized by the oxidation of  $W(CO)_5(CH_3NHNHCH_3)$  with activated manganese dioxide according to the equation



The reaction time varied from a few minutes at 25°C to 3 days at -78°C. The tautomerization reaction occurred only at the higher temperatures. The ratio of cis to trans product (or cis plus hydrazone to trans) was in the 4-5 range and virtually independent of temperature. Thus, NMR analysis of an unseparated reaction mixture gave the ratio (cis + hydrazone)/trans of (1.8 + 2.7)/1 at 25°C and (4.0 + 0)/1 at -60°C. Oxidation at -60°C offered a convenient rate (vld) with excellent product purity.

The manganese dioxide oxidation method offers yields of crystallized, pure  $W(CO)_5(\underline{c}-CH_3N=NCH_3)$  of 50-60% and is clearly preferred over the  $W(CO)_5$ -THF route. Even the yields for  $W(CO)_5(\underline{t}-CH_3N=NCH_3)$  exceed those from the  $W(CO)_5$ -THF procedure since the bimetallic product is not formed.

We have also tried oxidizing  $W(CO)_5(CH_3NHNHCH_3)$  using unactivated  $MnO_2$ ,  $HgO$ , and  $H_2O_2$  catalyzed by  $Cu^{2+}$ . In each case little or no reaction occurred. The failure of the  $H_2O_2/Cu^{2+}$  was particularly puzzling since Sellmann has obtained  $(C_5H_5)Mn(CO)_2(\underline{t}-CH_3N=NCH_3)$  from  $(C_5H_5)Mn(CO)_2(CH_3NHNHCH_3)$  in 10% yield with this reagent [3].

The ability of activated  $\text{MnO}_2$  to oxidize hydrazines preferentially to cis-diazenes was first demonstrated by Hyatt with a series of arylhydrazines [5]. Our work shows that preferential formation of cis isomers extends as well to coordinated dimethylhydrazine. If generalizable, this discovery should be of considerable synthetic utility as the uncoordinated cis-diazenes are usually unstable and not easily made in quantity to use as reactants with  $\text{W}(\text{CO})_5\text{THF}$  to make the  $\text{W}(\text{CO})_5(\underline{\text{c}}\text{-RN=NR})$  complexes. In contrast most hydrazines are readily available and their metal carbonyl complexes appear to form in high yield [1-3]. The success of the  $\text{MnO}_2$  method is apparently strongly dependent on the size of the alkyl groups on the hydrazine. Little oxidation occurred with  $\text{M}(\text{CO})_5(1,2\text{-diisopropylhydrazine})$  ( $\text{M}=\text{Cr},\text{W}$ ) even at room temperature [1]. Further studies are in progress to explore this size effect.

Activated  $\text{MnO}_2$  is also useful in oxidizing uncoordinated hydrazines to diazenes but the proportion of cis and trans diazene product is again strongly dependent on the hydrazine. Thus 1,2-diisopropylhydrazine gave only the trans-diazene [1], while  $\text{CH}_3\text{NHNHCH}_3$  provided about an 85:15 cis to trans mixture. Previously c- $\text{CH}_3\text{N=NCH}_3$  was obtainable only in small quantities either through photochemical isomerization of the trans isomer, or by thermolysis of a bicyclic hydrazine [7,9]. The  $\text{MnO}_2$  method provides a route to large quantities in a relatively short time from readily available starting materials. Separation of the cis/trans mixture can be accomplished by fractional distillation on a vacuum line as previously accomplished for the diisopropyldiazenes [1,6].

The mechanism of the  $\text{MnO}_2$  oxidation of hydrazines and their complexes is not known; in other systems a free radical process has been proposed [10]. Whatever the mechanism, the formation of a cis-diazene requires that the two alkyl groups be on the same side of the nitrogen-nitrogen bond when the diazene forms. As the alkyl groups get larger this would be less favorable sterically, and therefore the proportion of trans-diazene in the product would be expected to increase. The dimethyl and diisopropyl cases are consistent with this prediction.

Table 1.  
Infrared and Visible Spectral Data

Compound	Infrared Spectra (cm <sup>-1</sup> )		Visible Spectra <sup>a</sup>	
	$\nu(\text{CO})$ <sup>a, b</sup>	$\nu(\text{N}=\text{N})$ <sup>c</sup>	$\lambda_{\text{max}}$ (nm)	$(\epsilon \times 10^{-3} \text{ M}^{-1} \text{ cm}^{-1})$
$\text{W}(\text{CO})_5(\text{CH}_3\text{NHNHCH}_3)$	2080w, 1974vw, 1932s, 1923(sh)m			$\sim 450(\sim 0.3), \sim 400(\sim 0.2)$ <sup>g</sup>
$\text{W}(\text{CO})_5(\underline{\text{t}}\text{-CH}_3\text{N}=\text{NCH}_3)$	2080w, 1944s	1531	384 (7.6)	
$\text{W}(\text{CO})_5(\underline{\text{c}}\text{-CH}_3\text{N}=\text{NCH}_3)$	2080w, 1940s, 1925m	1522	$\sim 435(\sim 1.5), 394(6.9)$	
$[\text{W}(\text{CO})_5]_2(\underline{\text{t}}\text{-CH}_3\text{N}=\text{NCH}_3)$	2074w, 1934s, 1910s <sup>d</sup>			<sup>h</sup>
$\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$	2080w, 1937vs, 1925s		$\sim 440(\sim 0.2), 440(3.8)$	
$\underline{\text{t}}\text{-CH}_3\text{N}=\text{NCH}_3$		1583 <sup>e</sup>	352 <sup>f</sup>	
$\underline{\text{c}}\text{-CH}_3\text{N}=\text{NCH}_3$		1561 <sup>f</sup>	368 <sup>f</sup>	

<sup>a</sup> In  $\eta$ -hexane.

<sup>b</sup> Abbreviations: v, very; s, strong; m, medium; w, weak; (sh) shoulder.

<sup>c</sup> From KBr pellet

<sup>d</sup> Infrared inactive, decomposes in laser beam in Raman at  $-100^\circ\text{C}$ .

<sup>e</sup> Gas phase value [26]

<sup>f</sup> Gas phase value [7a]

<sup>g</sup> Oxidation to  $\text{W}(\text{CO})_5(\underline{\text{t}}\text{-CH}_3\text{N}=\text{NCH}_3)$  prevents accurate determinations.

<sup>h</sup> Decomposes in solution

<sup>i</sup> Reference 7b.

Infrared Spectra. The carbonyl stretching patterns of the complexes synthesized support a pentacarbonyl formulation. For each complex there are fewer carbonyl bands than in the corresponding diisopropyl complex [1], indicating a smaller distortion from an ideal  $C_{4v}$  geometry. This is to be expected based on the relative steric requirements of the methyl and isopropyl groups.

In  $W(CO)_5(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  and  $W(CO)_5(\underline{c}\text{-CH}_3\text{N=NCH}_3)$   $\nu(N=N)$  is reduced by 40-50  $\text{cm}^{-1}$  compared to the free ligands. This reduction is comparable to that in  $C_5H_5Mn(CO)_2(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  [3]. Thus these diazenes show the same ability to act as  $\pi$ -acceptors as previously found for other acyclic [1] and cyclic [11,12] diazenes. The comparable reduction of  $\nu(N=N)$  in both cis- and trans-dimethyldiazene upon coordination suggests no major difference in  $\pi$ -acceptor ability. This contrasts with the corresponding diisopropyl-diazene complexes where the cis ligand gave a much greater effect than the trans ligand [1], suggesting that the size of the alkyl group may be important in metal-nitrogen bond formation in these complexes.

$[W(CO)_5]_2(\underline{t}\text{-CH}_3\text{N=NCH}_3)$ , with both nitrogen atoms coordinated to  $W(CO)_5$  units, would be expected to show an even larger reduction in  $\nu(N=N)$  than the monometallic diazene complexes. As expected for this centrosymmetric complex, no feature for  $\nu(N=N)$  was detected in the infrared. Attempts at recording the Raman spectrum using a 5145 Å laser line were unsuccessful due to sample decomposition in the beam even at  $-100^\circ\text{C}$ .

Visible Spectra. The visible spectra (Table 1) of the monometallic diazene complexes  $W(CO)_5(\underline{c}\text{-CH}_3\text{N=NCH}_3)$  and  $W(CO)_5(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  and the hydrazine complex  $W(CO)_5(\text{CH}_3\text{NHNHCH}_3)$  are very similar to those of the diisopropyl analogs [1]. Again the charge transfer M-diazene (CTML)  $d_{xz} \rightarrow \pi^*$  and ligand field (LF)  $d_{yz} \rightarrow d_{x^2-y^2}$  bands are essentially coincident. Only the shoulder at  $\sim 435\text{nm}$  (2.84 eV) in the spectrum of  $W(CO)_5(\underline{c}\text{-CH}_3\text{N=NCH}_3)$  may reveal the CTML band. The hydrazine complex cannot have a CTML transition so the 400nm peak represents only the LF

transition; the feature at  $\sim 450\text{nm}$  is probably the singlet-triplet LF transition [13].

The visible spectrum of the hydrazone complex  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$  is nearly identical to that of the hydrazine complex and is similarly assigned. Since the hydrazone contains a carbon-nitrogen  $\pi$  bond, a CTML transition is also possible. (NMR data (vide infra) favors metal coordination at the imino nitrogen of the hydrazone, but the CTML should be possible for either nitrogen being the coordination site.) However, photoelectron spectra of a number of hydrazones [14] in conjunction with the observed  $n \rightarrow \pi^*$  transition for free  $\text{H}_2\text{C}=\text{NNHCH}_3$  [15] indicate that the  $\pi^*$  molecular orbital of this hydrazone is at a substantially higher energy than the  $\pi^*$  orbital in the diazenes. Assuming the  $d_{xz}$  orbital energy does not change drastically for these complexes of similar-sized ligands, the CTML transition for  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$  must appear at a much higher energy than in the diazene complexes. A search in the ultraviolet revealed a band at  $291\text{nm}$  ( $\epsilon \sim 2500$ ), but since an identical feature also appears in the spectrum of  $\text{W}(\text{CO})_5(\text{t-CH}_3\text{N}=\text{NCH}_3)$  its assignment to the CTML transition is unlikely.

Frazier and Kisch have noted a good correlation between the energy of the CTML transition in a series of diazene complexes and the energy of the  $n \rightarrow \pi^*$  transition of the uncoordinated cis-diazene ligand [16]. We have previously noted that the complex  $\text{W}(\text{CO})_5(\text{cis-1,2-diisopropyldiazene})$  did not obey that correlation and discussed reasons why this was not surprising [1]. However, c- $\text{CH}_3\text{N}=\text{NCH}_3$  with an  $n \rightarrow \pi^*$  transition at  $368\text{nm}$  ( $3.36\text{eV}$ ) [7b] and its complex  $\text{W}(\text{CO})_5(\text{c-CH}_3\text{N}=\text{NCH}_3)$  give a reasonable fit. The reason may be the smaller steric bulk of the methyl group compared to the isopropyl group, resulting in less distortion of the  $\text{W}(\text{CO})_5$  unit from  $C_{4v}$  geometry as noted above in the discussion of the carbonyl infrared spectral patterns. In fact, at  $119.3^\circ$  [8] the CNN angle of c- $\text{CH}_3\text{N}=\text{NCH}_3$  lies near the  $120^\circ$  value of the cis-diazenes which were found to obey the correlation.

Table 2.

Proton NMR Spectral Data <sup>a</sup>

Compound	T(°C)	CH <sub>3</sub> (uncoord.)	CH <sub>3</sub> (coord.)	Other
W(CO) <sub>5</sub> (CH <sub>3</sub> NHNHCH <sub>3</sub> )	35	7.41 <sup>b</sup>	6.92 <sup>b</sup>	5.95(br)s (uncoord.NH); 4.11(br)s (coord.NH)
W(CO) <sub>5</sub> ( <u>c</u> -CH <sub>3</sub> N=NCH <sub>3</sub> )	35	5.49qt <sup>c</sup>	5.99qt <sup>c</sup>	
W(CO) <sub>5</sub> ( <u>c</u> -CH <sub>3</sub> N=NCH <sub>3</sub> )	55			6.03(br)s
	-30	5.88qt <sup>d</sup>	6.29qt <sup>d</sup>	
[W(CO) <sub>5</sub> ] <sub>2</sub> ( <u>c</u> -CH <sub>3</sub> N=NCH <sub>3</sub> )	-30		5.29 <sup>e</sup>	
W(CO) <sub>5</sub> (H <sub>2</sub> C=NNHCH <sub>3</sub> )	35			3.03 AB qt (J=9.1 Hz, Δν = 15.6 Hz, CH <sub>2</sub> ); 7.16 d (CH <sub>3</sub> , J=4.5 Hz); 2.75(br)s(NH) <sup>f</sup>
CH <sub>3</sub> NHNHCH <sub>3</sub>	35	7.56s		<sup>g</sup>
<u>c</u> -CH <sub>3</sub> N=NCH <sub>3</sub>	35	6.37s		
<u>c</u> -CH <sub>3</sub> N=NCH <sub>3</sub>	35	6.49s		
H <sub>2</sub> C=NNHCH <sub>3</sub>	35			3.74 AB qt (J=10.8 Hz, Δν=17.7 Hz, CH <sub>2</sub> ); 7.18s (CH <sub>3</sub> ) <sup>gh</sup>

<sup>a</sup> Recorded in acetone-d<sub>6</sub>. Chemical shifts in τ (ppm) units relative to internal tetramethylsilane.

Abbreviations: s, singlet; d, doublet; qt, quartet; (br) broad.

<sup>b</sup> Nearly broad singlet; some splitting.

<sup>c</sup> J = 1.5 Hz.

<sup>d</sup> J ≈ 0.8 Hz.

<sup>e</sup> Very weak signal due to low solubility. Apparently a singlet.

<sup>f</sup> NH value for -30°; not observable at 35°.

<sup>g</sup> NH signal not observed.

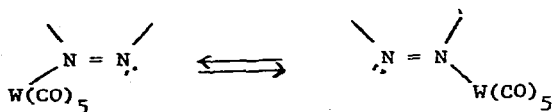
<sup>h</sup> Spectrum in CDCl<sub>3</sub>.

The CNN angle of cis-1,2-diisopropyldiazene is much larger, having been estimated at 130-140° [17].

NMR Spectra. The proton NMR spectra of the complexes and free ligands are summarized in Table 2. The spectra of  $W(CO)_5(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  and  $W(CO)_5(\text{CH}_3\text{NHNHCH}_3)$  show two inequivalent methyl groups and clearly support the coordination of only one of the nitrogen atoms to the  $W(CO)_5$  unit. Two broad but distinct NH resonances are also seen in the spectrum of the hydrazine complex. In each case the more downfield shifted NH or  $\text{CH}_3$  resonance is attributed to the coordinated nitrogen end of the ligand. In  $W(CO)_5(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  each methyl resonance is a closely spaced quartet ( $J=1.5\text{Hz}$ ) due to unexpected long range coupling. No such coupling was reported between the inequivalent methyl groups of  $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  [3]. The magnitude of the coupling is in the range of that typically found in alkenes of the type  $\text{H} - \underset{\text{|}}{\overset{\text{|}}{\text{C}}} - \overset{\text{|}}{\underset{\text{|}}{\text{C}}} = \overset{\text{|}}{\underset{\text{|}}{\text{C}}} - \overset{\text{|}}{\text{C}} - \text{H}$ . [18].

In  $[W(CO)_5]_2(\underline{t}\text{-CH}_3\text{N=NCH}_3)$  each nitrogen is coordinated to an  $W(CO)_5$  group, and the equivalent methyl groups give only a single  $\text{CH}_3$  resonance which is more downfield shifted than either  $\text{CH}_3$  signal in the monometallic complex.

The NMR spectrum of  $W(CO)_5(\underline{c}\text{-CH}_3\text{N=NCH}_3)$  is temperature dependent. Two distinct methyl quartets are evident at low temperature, indicative of inequivalent  $\text{CH}_3$  groups. The long range coupling in this cis-diazene is only about half ( $\sim 0.8\text{Hz}$ ) that in the trans counterpart. Upon warming the  $\text{CH}_3$  resonances broaden and eventually coalesce into one peak which sharpens as the temperature is further increased. This behavior is indicative of coordination site exchange as the  $W(CO)_5$  group moves from one nitrogen lone pair to the other. This exchange has previously been observed

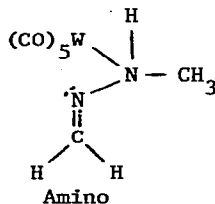
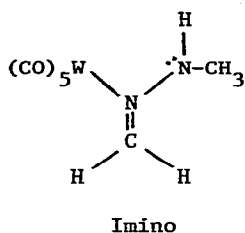


in the Group VIB complexes of cis-1,2-diisopropyldiazene [1] and benzo[*c*]cinnoline [16,19] and in the complexes  $\text{ArCr}(\text{CO})_2(2,3\text{-diazabicyclo[2.2.1]hept-2-ene})$  (Ar = variously substituted benzene rings) [20]. Such fluxional behavior now appears to be a well-established property of complexes of both cyclic and acyclic cis-diazenes. The coalescence temperature for  $\text{W}(\text{CO})_5(\underline{\text{c}}\text{-CH}_3\text{N}=\text{NCH}_3)$  is  $40 \pm 2^\circ\text{C}$  which yields [21]  $\Delta G^\ddagger = 16.0 \pm 0.1$  kcal/mole. This value is higher than that for  $\text{W}(\text{CO})_5(\text{cis-1,2-diisopropyldiazene})$ , supporting our proposal that the angle between the lone pair orbitals of the two nitrogen atoms may be the determining factor for the rate of exchange [1]. The smaller CNN angle of 119.3 in  $\underline{\text{c}}\text{-CH}_3\text{N}=\text{NCH}_3$  [8] means that the lone pair orbitals will be more widely separated and the barrier to exchange larger in its complex. In  $\text{ArCr}(\text{CO})_2(2,3\text{-diazabicyclo[2.2.1]hept-2-ene})$  the different metal carbonyl unit influences the rate but we note that  $\Delta G^\ddagger$  values range from 17.0-19.8 kcal/mole for a variety of Ar groups [20]. These higher values are consistent with the smaller CNN angle of  $109^\circ$  for this diazene ligand [22].

The NMR spectrum of the hydrazone complex  $\text{W}(\text{CO})_5(\text{H}_2\text{C}=\text{NNHCH}_3)$  shows an AB quartet and a broad NH resonance nearly coincident at low field. The NH resonance appears only at low temperature and broadens so as to be unobservable at probe temperature; no NH signal is seen in the free ligand spectrum. The  $\text{CH}_3$  resonance appears as a doublet in the spectrum of the complex, and this pattern is invariant over the temperature range  $-30$  to  $+35^\circ\text{C}$ . This arises from coupling between the NH and  $\text{CH}_3$  protons. (The NH signal is too broad to show the expected quartet structure.) This conclusion is borne out by the collapse of the  $\text{CH}_3$  doublet to a singlet when the spectrum is recorded while irradiating at the NH resonant frequency. This collapse occurs even at  $35^\circ\text{C}$  when the NH proton is not visible. Hence the broadening of the NH resonance in the complex at elevated temperatures must be due to quadrupole effects and not to proton exchange [23]. In uncoordinated  $\text{H}_2\text{C}=\text{NNHCH}_3$  the NH resonance must be exchange broadened since the  $\text{CH}_3$  resonance is only a singlet.



A hydrazone ligand may coordinate to a metal atom through either the imino or the amino nitrogen atom. For  $W(CO)_5(H_2C=NNHCH_3)$  the two possible structures are



Nolte and Reimann have recently reviewed the data on hydrazone complexes and conclude that coordination at the amino nitrogen is favored by " (i) a more sterically crowded octahedral or seven-coordinate metal environment and (ii) the presence of an unsubstituted amino-nitrogen." [24] They demonstrated by an X-ray structure determination that the cations  $[M(C_5H_5)(CO)_2(H_2NN=C(CH_3)_2)]^+$  ( $M=Mo, W$ ) are amino coordinated. In the only other known hydrazone complex of a metal carbonyl,  $Cr(CO)_5(H_2NN=C(CH_3)_2)$ , the NMR was interpreted to indicate a mixture of amino and imino coordinated complexes [25]. Because the amino nitrogen is substituted in  $H_2C=NNHCH_3$  and in addition the  $CH_2$  quartet shifts 0.7ppm upon coordination while the  $CH_3$  chemical shift is nearly unchanged, we favor coordination at the imino nitrogen in the complex.

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