Tungsten and Chromium Pentacarbonyl Complexes of Unsymmetric Dialkylhydrazines (RNHNHR′) and *cis*- and *trans*-Dialkyldiazenes (RN=NR′)

Martin N. Ackermann,* L. Charles Hardy, Yong Zhuang Xiao,[†] David J. Dobmeyer,
Judy A. Dunal, Kenneth Felz, Sylvia A. Sedman, and Kari F. Alperovitz

Department of Chemistry, Oberlin College, Oberlin, Ohio 44074

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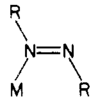
The complexes $M(CO)_5(RNHNHR')$, $M(CO)_5$(*trans*-RN=NR′), and $M(CO)_5$(*cis*-RN=NR′) have been synthesized for M = W [$R = CH_3$, $R' = CH_2CH_3$, $CH(CH_3)_2$; $R = CH_2CH_3$, $R' = CH_2CH_3$, $CH(CH_3)_2$] and for M = Cr [$R = CH_3$, $R' = CH(CH_3)_2$; $R = R' = CH_2CH_3$] from the reaction of the uncoordinated ligand with $M(CO)_5THF$. In most cases oxidation of $M(CO)_5(RNHNHR')$ with activated MnO_2 provides a mixture of $M(CO)_5$(*trans*-RN=NR′) and $M(CO)_5$(*cis*-RN=NR′) and is a viable alternative route to these complexes. The ratio of cis/trans product decreases as the size of the alkyl group increases and parallels results for oxidation of uncoordinated RNHNHR′. The selectivity for cis product is notably higher for M = Cr. NMR data support coordination of the metal to the lone pair at one of the nitrogen atoms. The complexes of RNHNHR′ and *trans*-RN=NR′ (R ≠ R′) consist of a mixture of isomers with the $M(CO)_5$ unit coordinated preferentially at the nitrogen with the smaller alkyl group. The complexes of *cis*-RN=NR′ (R ≠ R′) exist as only one isomer with the metal coordinated only at the nitrogen bearing the smaller alkyl group. This difference is attributed to coordination site exchange in $M(CO)_5$(*cis*-RN=NR′), which has been observed by NMR for $R = CH_3$, $R' = CH_2CH_3$ and for $R = R' = CH_2CH_3$. The reduction of $\nu(N{=}N)$ by 25–50 cm^{-1} upon coordination demonstrates modest π-acceptor ability for the diazenes. Only *cis*-$CH_3N{=}NCH_2CH_3$ shows appreciable tendency to isomerize to the hydrazone; its complex rearranges to $W(CO)_5(CH_2{=}NNHCH_2CH_3)$ which also has been characterized.

Introduction

In previous studies we have reported on the metal carbonyl complexes of acyclic dialkyldiazenes (RN=NR′) with particular emphasis on the extent to which a cis or trans geometry of the diazene influences the type and properties of the complexes which are formed.[1,2] Reaction of the symmetric ligands 1,2-dimethyldiazene (DMD; $R = R' = CH_3$)[1] and 1,2-diisopropyldiazene (DIPD; $R = R' = CH(CH_3)_2$)[2] with group VIB (6[18]) carbonyls have provided examples of complexes I–IV (M = $Cr(CO)_5$, $Mo(CO)_5$, or $W(CO)_5$).[3] A notable difference in the two ligand systems was the absence of bimetallic complexes (III, IV) with DIPD. In the monometallic complexes those of the *cis*-diazene (II) were found to be somewhat more stable than those of the *trans*-diazene (I). However, the most important geometry-dependent difference was the fluxional behavior of the *cis*-diazene complexes associated with the $M(CO)_5$ moiety shuttling between the two nitrogen coordination sites (eq 1). The *trans*-diazene complexes did not exhibit fluxional behavior.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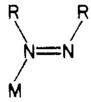
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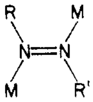
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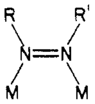
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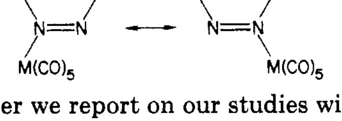
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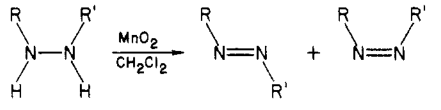
In this paper we report on our studies with a series of unsymmetric dialkyldiazenes (R ≠ R′). These studies were undertaken in order to examine further the effects of alkyl group size on the types of complexes formed and the influence of two different alkyl groups of different sizes on coordination site preference in the monometallic complexes. Also we have examined further the effectiveness of activated manganese dioxide in synthesis of *cis*-diazenes and *cis*-diazene complexes through oxidation of the appropriate free hydrazine (eq 2) or hydrazine complex (eq 3). Most of our work has been done with tungsten complexes, but several studies were also done with chromium. The latter confirm the special selectivity for the formation of *cis*-diazene complexes when M = Cr in the MnO_2 oxidation according to eq 3.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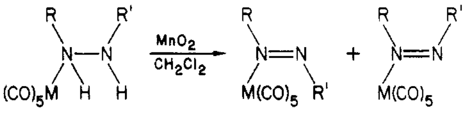
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Experimental Section

All manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques. Solvents were dried and distilled under nitrogen: tetrahydrofuran (THF) from Na/benzophenone, dichloromethane from P_4O_{10}, and hexane from CaH_2. Chromatography was performed on a column of Florisil which was slurry-packed with petroleum ether (bp 30–60 °C). Reduction of solution volumes or stripping to dryness was done at <0.1 mmHg at the temperature specified. Melting points were taken in open capillaries and are uncorrected.

Infrared spectra were recorded on a Perkin-Elmer Model 621 or 580B spectrometer and visible spectra on a Cary 17 spectro-

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[†] Visiting faculty fellow from the Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan, China, 1981–1983.

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(3) Ligand abbreviations: 1,2-dimethylhydrazine, DMH; 1,2-dimethyldiazene, DMD; 1,2-diethylhydrazine, DEH; 1,2-diethyldiazene, DED; 1,2-diisopropylhydrazine, DIPH; 1,2-diisopropyldiazene, DIPD; 1-methyl-2-ethylhydrazine, MEH; 1-methyl-2-ethyldiazene, MED; 1-methyl-2-isopropylhydrazine, MIPH; 1-methyl-2-isopropyldiazene, MIPD; 1-ethyl-2-isopropylhydrazine, EIPH; 1-ethyl-2-isopropyldiazene, EIPD.

Table I. Synthesis of $M(CO)_5L$ Complexes from $M(CO)_5$ THF and L

compd	$M(CO)_6$, mmol	L, mmol	reactn temp, °C	purificatn[a] method	yield, mmol (%)	mp, °C
$W(CO)_5$(MEH)	5.0	5.0	0	c	1.8 (35)[b]	oil
$W(CO)_5$(DEH)	10.0	13.6	0	c	8.0 (80)[b]	oil
$Cr(CO)_5$(DEH)	10.4	17.2	0	c	6.3 (60)[b]	oil
$W(CO)_5$(MIPH)	10.0	13.2	20	c	6.1 (61)[b]	oil
$Cr(CO)_5$(MIPH)	10.5	10.5	20	c	5.4 (51)[b]	oil
$W(CO)_5$(EIPH)	10.0	11.2	20	c	5.1 (51)[b]	oil
$W(CO)_5$(*trans*-MED)	10.0	10.3[c]	−25	cc	*d*	oil
$W(CO)_5$(*cis*-MED)						
$W(CO)_5$(*trans*-DED)	5.0	5.0	−30	cc	0.061 (12)	~25
$Cr(CO)_5$(*trans*-DED)	5.0	4.0	−25	c	1.8 (45)[b]	oil
$W(CO)_5$(*trans*-MIPD)	8.5	2.5	20	cc	0.89 (36)	65–66
$W(CO)_5$(*cis*-MIPD)	6.1	4.6	−30	cc	0.40 (8.7)	55–56
$Cr(CO)_5$(*trans*-MIPD)	9.4	2.1	20	c	0.61 (29)	53–54
$W(CO)_5$(*trans*-EIPD)	5.6	4.9[e]	20	cc	1.5 (31, 42)[f]	35–37
$W(CO)_5$(*cis*-EIPD)					0.31 (6, 25)[f]	32–34

[a] c indicates crystallization only while cc means chromatography was necessary prior to crystallization. [b] Less accurate due to difficulty of handling an oil. [c] Ligand ratio was 2:1 cis/trans. [d] Not determined. [e] Ligand ratio was 1:3 cis/trans. [f] Second number in parentheses is yield based on the amount of diazene isomer in ligand mixture.

photometer. Proton NMR spectra were obtained on a Perkin-Elmer R12B spectrometer equipped with variable-temperature and double-resonance capability. Raman spectra of *trans*-diazenes were taken at 25 °C in a sealed capillary tube as previously described.[4] Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

Activated MnO_2 was purchased from Alfa Division of Thiokol/Ventron. The metal carbonyls $M(CO)_6$ (M = Cr, W) were sublimed before use.

Synthesis of Ligands. 1,2-Diethylhydrazine (DEH),[5] 1-ethyl-2-isopropylhydrazine (EIPH),[6] and 1-methyl-2-ethylhydrazine dihydrochloride[7] were prepared according to literature methods. Free 1-methyl-2-ethylhydrazine (MEH) was obtained from the dihydrochloride as previously described for 1,2-dimethylhydrazine.[1] 1-Methyl-2-isopropylhydrazine (MIPH) was prepared by $LiAlH_4$ reduction of acetone methylhydrazone[8] according to the method used to make symmetric hydrazines.[5] *trans*-1,2-Diethyldiazene (*trans*-DED) and *trans*-1-methyl-2-ethyldiazene (*trans*-MED) were obtained by HgO oxidation of the corresponding hydrazines.[5] *trans*-1-Methyl-2-isopropyldiazene (*trans*-MIPD) was obtained from the base-catalyzed isomerization of acetone methylhydrazone.[9]

trans-1-Ethyl-2-isopropyldiazene (*trans*-EIPD) was prepared by oxidation of EIPH with excess activated MnO_2 on a vacuum line. The EIPH was distilled onto the MnO_2 at −196 °C, and the system was allowed to warm gradually to ambient. Then the reaction flask was cooled to −45 °C to retain any *cis*-diazene formed and the desired *trans*-EIPD distilled into a −196 °C trap. Finally the product was dried over 4-Å molecular sieve.

The *cis*-diazenes were obtained by oxidation of the appropriate hydrazine with excess activated MnO_2. The procedure is illustrated by the oxidation of MIPH. A solution of 1.8 g (20.5 mmol) of MIPH in 40 mL of CH_2Cl_2 (dried over K_2CO_3) was placed in a Schlenk tube with a stirring bar and cooled to 0 °C. Then, 5.0 g (65.6 mmol) of MnO_2 was added slowly. (Rapid addition can cause local warming.) The mixture was stirred vigorously. Samples were withdrawn periodically with a pipet tightly packed with glass wool and the NMR recorded in $CDCl_3$ to monitor reaction progress. When all of the MIPH had reacted (~2 h), the solution was filtered at −78 °C and the filtrate degassed on a vacuum line by several freeze/evacuate/thaw cycles. The solution was held at −40 °C and exposed to three traps at −55, −78, and −196 °C for fractionation. NMR analysis showed that CH_2Cl_2 and *trans*-MIPD collected in the −78 and −196 °C traps while the *cis*-MIPD remained mostly in the −40 °C flask with some collecting at −55 °C. The *cis*-MIPD was transferred to a storage vessel and kept at −196 °C. Yield was 0.52 g (6.0 mmol, 30%). *cis*-1-Methyl-2-ethyldiazene (*cis*-MED) was obtained by oxidation of MEH (7.5 mmol) at −25 °C overnight. The *cis*-MED remained behind at −68 °C when the CH_2Cl_2 and *trans*-MED were distilled off to −196 °C traps. Oxidation of DEH was carried out at −50 °C to give a mixture of *trans*-DED and *cis*-DED which were used in subsequent reactions without separation. Oxidation of EIPH was done at 25 °C and did not give synthetically useful amounts of *cis*-EIPD.

cis-1-Ethyl-2-isopropyldiazene (*cis*-EIPD) was prepared by photoisomerization of *trans*-EIPD by the procedure previously used to prepare *cis*-1,2-dimethyldiazene from the trans isomer.[10] A mixture of 4 mL of cyclopentane, 0.55 g of *trans*-EIPD, and 7 mg of naphthalene was photolyzed at 0 °C for 8 h. The reaction mixture was freed of naphthalene by bulb-to-bulb distillation on a vacuum line. The mixture of *cis*-EIPD and *trans*-EIPD was used for the synthesis of complexes without further separation. However, pure *cis*-EIPD was needed in order to record $\nu(N{=}N)$. It was obtained by fractionation of the photolysis solution using traps at −196, −78, and −65 °C with the solution at −60 °C. Pure *cis*-DED was similarly prepared by photolysis of *trans*-DED followed by the same fractionation procedure.

Synthesis of Complexes. Method A. Reaction of L with $M(CO)_5$THF. A solution of $M(CO)_5$THF (M = Cr, W) in THF was cooled to the reaction temperature and the desired ligand added by pipet or, for the more volatile ligands, as a cooled solution in CH_2Cl_2 which had been prepared on a vacuum line. In some cases a mixture of cis and trans isomers in CH_2Cl_2 was employed. After 1–3 h the mixture was stripped to dryness at or below the reaction temperature. The residue was taken up in hexane or a CH_2Cl_2/hexane mixture, filtered, and crystallized at −78 °C. The solution was decanted from the crystals by using a cannula. The crystals were washed with cold solvent and the residual solvent removed under vacuum as the crystals gradually warmed to ambient. In some instances further purification by chromatography followed by crystallization was needed; chromatography was a necessity when a ligand mixture had been used. $M(CO)_6$ elutes with pure petroleum ether. Because some *trans*-diazene complexes also elute with pure petroleum ether while others need about 5% CH_2Cl_2, separation of $M(CO)_6$ from *trans*-diazene complexes can be difficult. The *cis*-diazene complexes elute with 10–25% CH_2Cl_2. A summary of the reactions run, conditions employed, and yields obtained is given in Table I.

Method B. Oxidation of Hydrazine Complexes. The hydrazine complex $M(CO_5)L$ (M = W, Cr; L = MEH, DEH, MIPH, EIPH) was oxidized with activated MnO_2 in CH_2Cl_2 and monitored by infrared spectral changes in the carbonyl stretching region as previously described.[1,2] Anhydrous Na_2SO_4 was added in early

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Table II. Synthesis of Diazene Complexes by MnO_2 Oxidation of Hydrazine Complexes

compd	amount, mmol	MnO_2, mmol	temp, °C	time, h	isolated yield of complex,[a] mmol (%)	
					trans-diazene	*cis*-diazene
$W(CO)_5$(MEH)	0.45	11.5	10	22	*b*	*b*
$W(CO)_5$(DEH)	3.2	28.5	0	60	1.2 (37)[c]	1.2 (37)[c]
$Cr(CO)_5$(DEH)	0.87	3.7	20	4	0 (0)	0.43 (50)[c]
$W(CO)_5$(MIPH)	2.7	47.5	0	32	1.3 (48)	0.32 (12)
$Cr(CO)_5$(MIPH)	1.0	11.0	20	24	0.10 (10)	0.24 (24)
$W(CO)_5$(EIPH)	1.5	17.3	20	45	0.41 (27)	0.057 (3.8)

[a] All products are oils or have melting points as given in Table I. $Cr(CO)_5$(*cis*-MIPD) decomposes around 60 °C. [b] Not isolated; NMR shows equal amounts of the two diazene complexes. [c] Less certain due to difficulty of handling an oil.

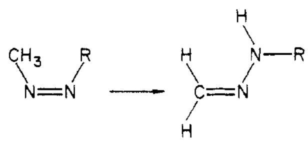
work but not in later oxidations since its presence did not have a noticeable effect. When the reaction appeared to be over, the solution was filtered at or below the reaction temperature, stripped to dryness, chromatographed, and crystallized as in method A. Unreacted hydrazine complex, if present, required at least a 3:1 CH_2Cl_2/petroleum ether mixture for elution, and most underwent extensive decomposition in the process. In studies designed to determine most accurately the oxidation results, an NMR spectrum was run on the product mixture prior to chromatography. Table II summaries the reactions run, conditions employed, and products obtained.

Anal. Calcd for $W(CO)_5$(*cis*- or *trans*-MIPD): C, 26.36; H, 2.46, N, 6.83. Found for *cis*-MIPD: C, 26.56; H, 2.51; N, 6.86. Found for *trans*-MIPD: C, 26.41; H, 2.46; N, 6.84. Anal. Calcd for $W(CO)_5$(*cis*- or *trans*-EIPD): C, 28.31; H, 2.85; N, 6.61. Found for *cis*-EIPD: C, 28.31; H, 2.87; N, 6.50. Found for *trans*-EIPD: C, 28.20; H, 2.85; N, 6.53. All attempted analyses of the oils and the Cr complexes were unsatisfactory because of their instability so their stated identity is based on the method of synthesis and spectroscopic data.

Results and Discussion

The *cis*-diazenes used in these studies are new compounds which can be obtained through the oxidation of the appropriate hydrazine by activated MnO_2 (eq 1) as previously reported for *cis*-$CH_3N{=}NCH_3$.[1] These new syntheses show the generality of the MnO_2 oxidation procedure as a route to *cis*-diazenes and confirm the preliminary observation that the cis to trans ratio in the products (Table I) is strongly dependent on the size of the alkyl groups. For bulky alkyl groups, the yield is low enough that photosensitized isomerization of the *trans*-diazene is a more practical route to appreciable quantities of the cis isomer, even though photosenitized isomerization is more time-consuming and requires prior synthesis of trans isomer from the hydrazine.

The *cis*-diazenes are yellow liquids that are considerably less volatile than their trans counterparts, consistent with their expected highly polar character.[11] All of the *cis*-diazenes have the potential to tautomerize to a more stable hydrazone form and thus were handled with care and usually at low temperature. However, only *cis*-MED did so to an appreciable extent, although not nearly so readily as does *cis*-DMD.[11] For *cis*-dialkyldiazenes it appears that hydrazone formation is a problem only if at least one of the groups is methyl as represented in eq 4 and hydrazone formation diminishes as the size of the alkyl group R on the other nitrogen increases in the order $CH_3 > CH_2CH_3 > CH(CH_3)_2$.



(4)

Complexes were obtained by using the two synthetic methods previously applied to the dimethyl and diisopropyl systems.[1,2] Reaction of the free ligand with $M(CO)_5THF$ (M = W, Cr) gives reasonable yields in all but a few cases (Table I), while oxidation of the hydrazine complexes to the diazene complexes (eq 3) is effective in providing all but $Cr(CO)_5$(*trans*-DED). The use of these new hydrazine complexes demonstrates the general utility of the MnO_2 method. In certain respects the two synthetic methods are complementary. The MnO_2 method is advantageous because it avoids the necessity of first preparing the diazenes and it can provide complexes of both *cis*- and *trans*-diazene in a single preparation; the disadvantages are that yields are low and the reaction is slow or incomplete for hydrazines with large alkyl groups. Also, the required separation of the mixture of products may be difficult for the less stable complexes. The chief disadvantage of the $M(CO)_5THF$ route is the need to prepare the diazene ligand in a preliminary step. Its advantages are that it is the only way to obtain complexes of some of the diazenes, notably those with large alkyl groups.

For the systems reported in this paper, only monometallic diazene complexes were obtained. Thus *cis*- and *trans*-$CH_3N{=}NCH_3$ have proven to be the only acyclic dialkyldiazenes to form bimetallic complexes in which each nitrogen is coordinated to a $M(CO)_5$ moiety.[1] Even MED, the next "largest" diazene, shows no evidence of a bimetallic product.

All of the monometallic complexes are yellow to golden oils or low melting solids. The *cis*-diazene complexes are the more polar and have only moderate solubility in hydrocarbon solvents. The less polar *trans*-diazene complexes can be sublimed without extensive decomposition. Generally the order of the stability of the complexes is W > Cr and *cis*-diazene > *trans*-diazene. The solids can be handled in air for moderate periods without noticeable decomposition. The Cr complexes of the *trans*-diazenes are the least stable and decompose extensively when chromatographed. Chromatography of $W(CO)_5$(*cis*-MED) causes partial tautomerization to the hydrazone complex $W(CO)_5(H_2C{=}NNHCH_2CH_3)$. This compares with complete tautomerization of $W(CO)_5$(*cis*-DMD) and none for $M(CO)_5$(*cis*-MIPD) (M = W, Cr). Hence, the tendency toward tautomerization of coordinated *cis*-diazenes parallels that of the uncoordinated molecules.

The present study leads to a more complete picture of the ability of activated MnO_2 to oxidize uncoordinated and coordinated hydrazines selectively to *cis*-diazenes. Table III summarizes the percent cis obtained for the full range of hydrazines which we have studied. For the uncoordinated hydrazines the proportion of *cis*-diazene formed decreases as the size of the alkyl groups increases. This is not unexpected since the steric interaction between the alkyl groups in a cis configuration increases with the size of the groups. Elucidation of the mechanism of oxidation by MnO_2 is extremely difficult,[12] and we have not at-

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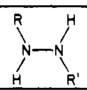
Table III. Percent *cis*-Diazene Formed by Oxidation of Uncoordinated and Coordinated Hydrazines with Activated MnO_2[a]

		uncoord oxid prod	coord oxid prod $M(CO)_5$(*cis*-RN=NR'), %	
R	R'	*cis*-RN=NR', %	M = W	M = Cr
CH_3	CH_3	85[b]	80[b]	
CH_3	CH_2CH_3	67	50[c]	
CH_3	$CH(CH_3)_2$	55	25	60[c]
CH_2CH_3	CH_2CH_3	50	45[c]	100
CH_2CH_3	$CH(CH_3)_2$	10	10	
$CH(CH_3)_2$	$CH(CH_3)_2$	0[d]	0[d]	~50[d]

[a] Uncertainty ±5 unless otherwise noted. [b] Reference 1. [c] Uncertainty ±10. [d] Reference 2; Cr value is an estimate.

tempted to do so. However, at some point prior to formation of the final product, the alkyl groups presumably must adopt a cisoid or eclipsed configuration relative to each other if a *cis*-diazene product is to be formed. This becomes more difficult as the size of the alkyl groups increases and the likelihood of forming a cis product should decrease as is observed.

The proportion of *cis*-diazene product on oxidation of the tungsten hydrazine complexes closely parallels that of the uncoordinated hydrazines. The numbers of the percent of cis product in the chromium oxidations are less certain and must be viewed as upper limits because some of the less stable *trans*-diazene complex decomposes during the course of the reaction. Nonetheless the enhanced selectivity for the cis product first observed with the diisopropyl system[2] is confirmed by the new studies with the diethyl and methylisopropyl systems. The very high selectivity for cis in the diethyl system is striking and has been verified by performing the oxidation of $Cr(CO)_5DEH$ in the presence of added $Cr(CO)_5$(*trans*-DED). Although $Cr(CO)_5$(*trans*-DED) decomposes during the oxidation, it does not do so to the extent that it would be overlooked if it were produced in appreciable quantity during the oxidation.

The reason for this difference between the Cr and W systems is not clear. One possibility is the shorter Cr–N bond length and smaller size of the $Cr(CO)_5$ group[13] compared to W-N and $W(CO)_5$.[14] However, molecular models show that the hydrazine complexes of both metals are very crowded and a clear distinction between the preferred conformations of the two is not obvious.

Infrared Spectra. The carbonyl stretching patterns of the complexes support a pentacarbonyl structure (Table IV). The number of bands, frequency values, and relative intensities for a given type of ligand are remarkably independent of the identity of the alkyl groups. All of the complexes have a band around 2070 cm^{-1} which in ideal C_{4v} symmetry would be A_1. Only the hydrazine and *cis*-diazene complexes show a weak B_1 band in the 1970–1990 cm^{-1} region which would be forbidden if the geometry were truly C_{4v}. The *trans*-diazene complexes usually have a single strong band around 1940 cm^{-1}. In the hydrazine complexes this band is clearly split by about 20 cm^{-1} into two features, while in the *cis*-diazene complexes the splitting is less pronounced and may consist of only one or two well-defined shoulders. Thus the ν(CO) pattern alone is nearly sufficient to distinguish whether the complex contains a hydrazine, a *cis*-diazene, or a *trans*-diazene ligand.

All of the diazene complexes have an infrared absorption in the 1500–1600 cm^{-1} region which can be assigned to the N=N stretch. This mode is also clearly visible in the infrared spectra of the uncoordinated *cis*-diazenes and in the Raman spectra of the *trans*-diazenes. The reduction in ν(N=N) of 25–50 cm^{-1} is consistent with the now well-established π-acceptor ability of the diazene functional group.[1,2,15] The earlier indication[1] that the magnitude of the reduction of ν(N=N) on coordination and thus π-acceptor ability might be correlated to the size of the alkyl groups in acyclic diazenes is not supported by these new complexes.

Visible Spectra. The visible spectra of the complexes are similar to those for the dimethyl- and diisopropylhydrazine and dimethyl- and diisopropyldiazene complexes.[1,2] The single absorption around 380–410 nm is due to the overlap of the charge-transfer metal-to-ligand and ligand field bands. The hydrazine complexes have a strong ligand field band; sometimes the weak singlet-to-triplet ligand field transition around 450 nm also is observed.

NMR Spectra. The proton NMR spectral features of the ligands and complexes studied are summarized in Table V. In nearly every case, the chemical shift of the alkyl groups in the uncoordinated unsymmetric ligands is within 0.1 ppm of that predicted from the values for the symmetric ligands. This correlation was useful, along with infrared data, in confirming the syntheses of the previously unknown *cis*-diazenes. Because of their broadness, the NH resonances in the hydrazines and their complexes cannot always be found.

Upon coordination, the signal due to the protons on the α-carbon atom on one of the nitrogens on the ligand is significantly downfield shifted, while the other resonances change relatively less. As before, we have assigned this signal to the alkyl group on the coordinated nitrogen.[1,2] In $M(CO)_5$(*trans*-DED) (M = W, Cr) the CH_2 quartets were sufficiently separated to use decoupling to assign the CH_3 signals with certainty. The signals in the DEH complexes were too close for decoupling, and decoupling was not possible in the *cis*-DED complexes at 35 °C because of their fluxional character. Hence the assignments of the CH_3 groups could be reversed in these complexes.

The chemical shifts of the alkyl groups in the complexes of the unsymmetric diazenes also are well correlated with those of the symmetric systems. Thus for the $W(CO)_5$(*trans*-MED) isomer (vide infra), in which W is coordinated at the methyl nitrogen, the CH_3–N resonance is at τ 5.55 and the CH_2 quartet of N–CH_2CH_3 is at τ 6.12 compared with predicted values of τ 5.49 and 6.03, respectively. The poor correlations found for the isopropyl methine proton in the diazene complexes may be due to steric factors.

In some of the unsymmetric diazene ligands there is evidence of coupling between the alkyl groups across the N=N bond. This is most obvious for *cis*- and *trans*-MED where the CH_3–N group is split into a closely spaced triplet by the CH_2 of the N–CH_2CH_3 group with *J* in the range of 1–2 Hz. However, the expected splitting of the CH_2 quartet is difficult to pick out with confidence. This coupling is also seen in the W complexes but could not be resolved with the MIPD and EIPD ligands or their complexes. The only other instance of coupling across the N=N bond is in $M(CO)_5$(*trans*-DED) (M = W, Cr) where coordination makes the ethyl groups inequivalent. In these complexes each component of the CH_2 quartets is clearly split into a triplet. Complexes of *trans*-CH_3N=NCH_3 with

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Table IV. Infrared and Visible Spectral Data

compd	infrared spectra, cm^{-1} ν(CO)[a]	ν(N=N)[b]	visible spectra[a] λ_{max} ($\epsilon \times 10^{-3}$), nm (M^{-1} cm^{-1})
W(CO)$_5$(MEH)	2074 w, 1973 w, 1932 s, 1924 m (sh)		~450 (~0.2), 404 (4.0)
W(CO)$_5$(*trans*-MED)	2074 w, 1941 s	1528	383 (7.9)
W(CO)$_5$(*cis*-MED)	2072 w, 1983 w, 1937 s, 1921 m	1523	385 (>4.0)[d]
W(CO)$_5$(MIPH)	2071 w, 1970 w, 1932 s, 1927 m (sh)		~450 (~0.4), 406 (4.5)
W(CO)$_5$(*trans*-MIPD)	2071 w, 1940 s, 1935 m (sh)	1529[c]	382 (7.3)
W(CO)$_5$(*cis*-MIPD)	2072 w, 1984 w, 1940 s, 1924 m	1523[c]	395 (7.2)
Cr(CO)$_5$(MIPH)	2069 w, 1978 w, 1935 s, 1921 m		401 (>3.5)[d]
Cr(CO)$_5$(*trans*-MIPD)	2066 w, 1943 s, 1934 m	1532[c]	396 (>3.8)[d]
Cr(CO)$_5$(*cis*-MIPD)	2071 w, 1990 w, 1945 s, 1923 m	1531	406 (6.6)
W(CO)$_5$(DEH)	2074 w, 1972 vw, 1937 s (sh), 1929 s, 1921 m (sh)		~448 sh (~0.3), 401 (3.6)
W(CO)$_5$(*trans*-DED)	2074 w, 1939 s	1518	383 (7.1)
W(CO)$_5$(*cis*-DED)	2072 w, 1982 w, 1941 s, 1921 m	1520	392 (6.1)
Cr(CO)$_5$(DEH)	2068 w, 1978 vw, 1940 s, 1933 s, 1920 m		409 (>3.6)[d]
Cr(CO)$_5$(*trans*-DED)	2066 w, 1942 s, 1933 m (sh)	1530	394[d]
Cr(CO)$_5$(*cis*-DED)	2071 w, 1990 w, 1946 s, 1923 m	1523	407 (4.5)
W(CO)$_5$(EIPH)	2072 w, 1972 w, ~1935 s (sh), 1930 s, 1924 s (sh)		~450 (0.2), 405 (3.6)
W(CO)$_5$(*trans*-EIPD)	2072 w, 1939 s	1523	381 (7.3)
W(CO)$_5$(*cis*-EIPD)	2075 w, 1983 w, 1940 s, 1920 m	1519[c]	393 (6.2)
trans-MED		1571[e]	
cis-MED		1552	
trans-MIPD		1565[e,f]	
cis-MIPD		1562	
trans-DED		1567[e]	
cis-DED		1546	
trans-EIPD		1566[e]	
cis-EIPD		1556[g]	

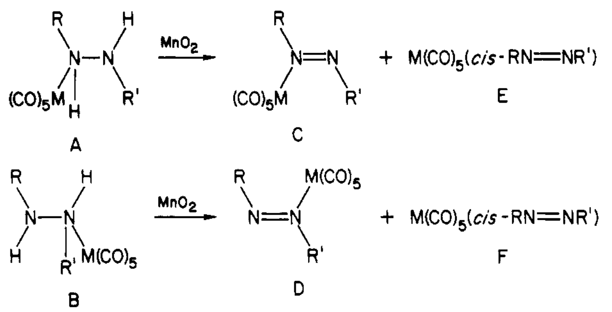
[a] In hexane. Abbreviations: v, very, s, strong; m, medium; w, weak; sh, shoulder. [b] Liquid thin film. [c] KBr pellet. [d] Decomposes too rapidly to obtain reliable ϵ value. [e] Raman value. [f] LeFevre, R. J.; O'Dwyer, M. F.; Werner, R. L. *Aust. J. Chem.* **1961**, *14*, 315. [g] Average of two peaks at 1545 and 1568 cm^{-1}, possibly arising from Fermi resonance.

Table V. Proton NMR Spectral Data of Hydrazines (RNHNHR′), Diazenes (RN=NR′), and Their Complexes (M(CO)$_5$L)[a]

				coordinated end				uncoordinated end			
ligand	metal	solv[a]	*T*, °C	CH$_3$[b]	CH$_2$CH$_3$[c]	HC(CH$_3$)$_2$[d]	NH[e]	CH$_3$[b]	CH$_2$CH$_3$[c]	HC(CH$_3$)$_2$[d]	NH[e]
MEH		C	35					7.46	7.23, 8.92		6.7
MEH	W	A	35	7.05[f]			3.6		7.40, 8.86		*g*
cis-MED		C	35					6.45[h]	6.68, 8.35		
cis-MED	W	C	−30	5.81[h]					6.43, 8.81		
trans-MED		A	35					6.35[h]	6.2, 8.80		
trans-MED	W	A	0	5.55[h]					6.12,[i] 8.42		
	W	A	0		5.39,[i] 8.73			5.96 t[h]			
DEH		A	35						7.27, 9.00		6.7
DEH	W	A	35		6.84, 8.89		4.0		6.95, 8.77		6.4
DEH	Cr	A	35		7.08, 8.95		4.7		7.20, 8.76		6.7
cis-DED		C	35						6.61, 8.33		
cis-DED	W	A	−40		5.42, 8.63				6.22, 8.34		
cis-DED	Cr	A	−44		5.64, 8.68				6.27, 8.42		
trans-DED		A	35						6.20, 8.79		
trans-DED	W	A	35		5.34,[i] 8.71				6.03,[i] 8.40		
trans-DED	Cr	A	−3		5.56,[i] 8.78				5.98,[i] 8.43		
MIPH		C	35					7.44		6.91, 8.97	6.9
MIPH	W	A	35			~6.7, 8.95	4.1	6.9			6.2
	W	A	35	6.89			4.1			6.7, 8.89	6.2
MIPH	Cr	A	15			6.7, 9.00	4.7	7.34			6.6
	Cr	A	15	7.24			4.7			6.79, 8.92	6.6
cis-MIPD		A	35					6.34		5.82, 8.78	
cis-MIPD	W	A	35	5.74						5.75, 8.68	
cis-MIPD	Cr	A	0	6.00						5.80, 8.74	
trans-MIPD		A	35					6.36		6.40, 8.82	
trans-MIPD	W	A	35	5.52						5.90, 8.63	
	W	A	35			*g*, 8.75		5.87			
trans-MIPD	Cr	A	−13	5.73						5.85, 8.64	
EIPH		A	35						7.27, 9.00	7.12, 9.04	6.7
EIPH	W	A	−30		(6.5–7.2 m, 8.6–9.1 m)[j]		4.1		(6.5–7.2 m, 8.6–9.1 m)[j]		6.3
cis-EIPD		C	35						6.42, 8.41	5.93, 8.70	
cis-EIPD	W	A	35		5.55, 8.62					5.72, 8.65	
trans-EIPD		C	35						6.22, 8.73	6.38, 8.77	
trans-EIPD	W	A	0		5.44, 8.73					6.10, 8.64	
	W	A	0			4.66, 8.8			5.87, 8.8		

[a] Chemical shifts in τ units relative to internal tetramethylsilane; solvent CD$_3$COCD$_3$ (A) or CDCl$_3$ (C). [b] Singlet unless otherwise noted. [c] First number is the CH$_2$ quartet and the second the CH$_3$ triplet. $J \approx$ 6–8 Hz. [d] First number is the CH septet and the second the CH$_3$ doublet. $J \approx$ 6–8 Hz. [e] Broad singlet. [f] Doublet. [g] Lost under other signals. [h] Triplet with J in range 1–2 Hz. [i] Each member of quartet shows evidence of further splitting. [j] Signals too overlapped to separate.

Scheme I



W[1] and Pd[16] show similar coupling between the CH_3 groups. Although $W(CO)_5(cis\text{-}CH_3N{=}NCH_3)$ also exhibits methyl group coupling,[1] we have been unable to observe this in the *cis*-DED complexes, even at low temperature.

Steric and Geometric Effects. The unsymmetrical ligands used in this study have the potential of forming two isomeric monometallic complexes depending on which nitrogen is the coordination site. This expectation is fulfilled in most of the hydrazine and *trans*-diazene complexes as revealed in the NMR spectra, but the isomers are not separable by crystallization or chromatography. In each case, NMR shows the predominant isomer to be the one in which the metal is coordinated to the nitrogen bearing the smaller alkyl group. $W(CO)_5$(MEH) and $Cr(CO)_5$(*trans*-MIPD) are extreme cases in which only the $N\text{-}CH_3$ coordinated isomer is observed. Once formed, the hydrazine and *trans*-diazene complexes show no evidence of exchange with uncoordinated ligand nor does the $M(CO)_5$ moiety change nitrogen coordination sites intramolecularly. Attempts to detect either intramolecular or intermolecular exchange with variable-temperature NMR only produced decomposition. Thus the relative amount of each coordination isomer present is kinetically and not thermodynamically controlled. For complexes made by the $M(CO)_5THF$ method, the implication is that the nitrogen bearing the smaller alkyl group is more accessible for coordination.

Interpretation of the isomer ratio for the *trans*-diazene complexes made by MnO_2 oxidation is complicated by the fact that the precursor hydrazine complex is itself a mixture of isomers, each of which is oxidized to a different *trans*-diazene complex (Scheme I). Generally the *trans*-diazene product is richer in the isomer in which the metal is coordinated to the nitrogen bearing the smaller alkyl group than was the hydrazine precursor; i.e., if R is larger than R′, then $D/C > B/A$. Or stated differently, the *cis*-diazene product is preferentially obtained from the isomer of the hydrazine complex in which the metal is coordinated at the nitrogen bonded to the larger alkyl group; i.e., $E/C > F/D$. Thus it appears that the preference for formation of a *cis*- or *trans*-diazene complex depends on the coordination site in the precursor hydrazine complex. However, the less abundant *trans*-diazene complex is also the less stable one so its lower yield may be at least partly the result of decomposition and not entirely to a reduced tendency for formation.

The W and Cr complexes of *cis*-DED show fluxional behavior (eq 1) as anticipated based on the dimethyl[1] and diisopropyl[2] analogues. The coalescence temperature and $\Delta G^{\ddagger}$ at coalescence are 28 °C and 14.8 kcal/mol and 46 °C and 16.0 kcal/mol for Cr and W, respectively. The $\Delta G^{\ddagger}$ values are comparable to these other systems and indicate no unusual effects.

It was anticipated that the unsymmetric *cis*-diazene complexes would also show coordination site exchange, but only $W(CO)_5$(*cis*-MED) has been found to do so. At −30 °C the NMR spectrum of this complex is sharp and indicates only one coordination isomer is present. As the temperature is raised, the spectral features broaden and then begin to sharpen again until at 50 °C a sharp spectrum is obtained; significant decomposition occurs above 50 °C. The W and Cr complexes of *cis*-MIPD and *cis*-EIPD do not show similar behavior. Their spectra are sharp throughout the temperature range accessible prior to the onset of decomposition and correspond to only a single coordination isomer. In each case, including *cis*-MED, the chemical shift data indicate that coordination is at the nitrogen bearing the smaller alkyl group. Models support this as the preferred isomer on steric grounds. The absence of fluxionality in the *cis*-MIPD and *cis*-EIPD cases must be due to the large difference in steric effects between an isopropyl group and a methyl or ethyl group. In *cis*-MED the difference between the two alkyl groups is less severe and exchange occurs. A conservative estimate is that we should be able to detect the less favored isomer of the *cis*-diazene complex if it were present in at least 3% abundance in the low-temperature spectra. This establishes a lower limit of 30 for the equilibrium constant in favor of coordination at the nitrogen bearing the smaller alkyl group.

The failure to observe complexes of unsymmetric *cis*-diazene in which the metal is coordinated at the nitrogen bonded to the larger alkyl group does not mean that such complexes are not formed by either of our synthetic methods. They probably are formed but then quickly convert to the more thermodynamically stable form. Because the *trans*-diazene complexes have no ready mechanism for isomer interconversion, both isomers are obtained as "stable" products.

Hydrazone Complexes. $W(CO)_5(H_2C{=}NNHCH_2CH_3)$ was the only hydrazone complex obtained in sufficient quantity to characterize by NMR. Its spectrum in acetone at 35 °C includes an AB quartet ($J = 8.5$ Hz, $\Delta\nu = 12.5$ Hz) at τ 3.00 due to the imino CH_2 group, a broad NH peak at τ 3.43, and an ethyl group with a triplet at τ 8.79 and a doublet of quartets at τ 6.83, the latter arising from coupling between the ethyl CH_2 and the NH groups. These features are similar to those of the analogous complex of $H_2C{=}NNHCH_3$[1] with the differences expected from changing the alkyl group. In this instance uncoordinated $H_2C{=}NNHCH_2CH_3$ is unknown and comparison of chemical shifts with the complex is not possible. However, because the imino group is unsubstituted and the ethyl is even larger than methyl, we again believe that coordination at the imino nitrogen seems more likely.[1,17]

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Registry No. *trans*-EIPD, 65586-03-0; EIPH, 3895-31-6; *cis*-MED, 72192-06-4; *cis*-MIPD, 100995-62-8; *cis*-EIPD, 100995-63-9; MEH, 18247-19-3; MIPH, 1615-82-3; $W(CO)_5$(MeH),

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

100995-46-8; W(CO)$_5$(DEH), 101009-61-4; Cr(CO)$_5$(DEH), 100995-47-9; W(CO)$_5$(MIPH) (isomer 1), 100995-48-0; W(CO)$_5$(MIPH) (isomer 2), 100995-58-2; Cr(CO)$_5$(MIPH) (isomer 1), 100995-49-1; Cr(CO)$_5$(MIPH) (isomer 2), 100995-59-3; W(CO)$_5$(EIPH), 100995-50-4; W(CO)$_5$(*trans*-MED) (isomer 1), 100995-51-5; W(CO)$_5$(*trans*-MED) (isomer 2), 100995-57-1; W(CO)$_5$(*cis*-MED), 101141-35-9; W(CO)$_5$(*trans*-DED), 100995-52-6; Cr(CO)$_5$(*trans*-DED), 100995-53-7; W(CO)$_5$(*trans*-MIPD) (isomer 1), 100995-54-8; W(CO)$_5$(*trans*-MIPD) (isomer 2), 100995-60-6; W(CO)$_5$(*cis*-MIPD), 101053-60-5; Cr(CO)$_5$(*trans*-MIPD), 100995-55-9; W(CO)$_5$(*trans*-EIPD), 100995-56-0; W(CO)$_2$(*trans*-EIPD), 100995-61-7; W(CO)$_5$(*cis*-EIPD), 101053-61-6; Cr(CO)$_5$(*cis*-MIPD), 101053-62-7; W(CO)$_5$(*cis*-DED), 101053-63-8; Cr(CO)$_5$(*cis*-DED), 101053-64-9; W(CO)$_5$(H$_2$C=NNHCH$_2$CH$_3$, 100995-64-0; W(CO)$_5$THF, 15038-41-2; Cr(CO)$_5$THF, 36477-75-5; MnO$_2$, 1313-13-9.

Borohydride, Hydride, Halide, and Carbonyl Derivatives of Bis(pentamethylcyclopentadienyl)niobium†

Robert A. Bell, Steven A. Cohen, Nancy M. Doherty, Richard S. Threlkel, and John E. Bercaw*

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology,
Pasadena, California 91125

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A synthetic entry to the chemistry of permethylnicobocene compounds is provided via the borohydride derivative $(\eta^5\text{-}C_5Me_5)_2NbBH_4$, obtained in 30–50% yield from NbCl$_5$, LiC$_5$Me$_5$, and NaBH$_4$ in 1,2-dimethoxyethane. Bridge $\rightleftarrows$ terminal hydride exchange occurs with an exceptionally large barrier ($\Delta G^{\ddagger} = 16.4 \pm 0.4$ kcal·mol^{-1} at 388 ± 8 K). A reinvestigation of the same process for Cp$_2$NbBH$_4$ reveals, contrary to an earlier report, a comparable barrier ($\Delta G^{\ddagger} = 14.6 \pm 0.2$ kcal·mol^{-1} at 346 ± 3 K). Treatment of $Cp^*_2NbBH_4$ with pyridine under 1 atm H$_2$ affords $Cp^*_2NbH_3$. When heated with ethylene or carbon monoxide, $Cp^*_2NbH_3$ yields $Cp^*_2NbH(C_2H_4)$ or $Cp^*_2NbH(CO)$, respectively. Reaction of $Cp^*_2NbH(CO)$ with HCl affords $Cp^*_2NbCl(CO)$, which is cleanly converted to $Cp^*_2Nb(CH_3)(CO)$ with methyllithium. Paramagnetic $Cp^*_2NbCl_2$ is obtained via treatment of $Cp^*_2NbBH_4$ with 3 M hydrochloric acid.

Introduction

Alkyl, hydride, olefin, and carbonyl derivatives of niobocene are among the most extensively investigated organometallic compounds of niobium.[1-7] Following Tebbe and Parshall's report of its synthesis in 1971,[1a] Cp$_2$NbH$_3$ (Cp = η^5-C$_5$H$_5$) has been shown to effect hydrogen–deuterium exchange between H$_2$ and C$_6$D$_6$,[1a,c] to catalyze hydrogenation of ethylene,[1a] and to promote carbon monoxide hydrogenation to methane,[7] albeit in rather low yield. Cp$_2$NbH$_3$ also serves as a convenient synthetic precursor to a number of derivatives which possess important metal–ligand bonding types (e.g., the first isolable cis hydride–olefin complex,[1a,3] some early examples of alkylidenes,[4g] Lewis acid adducts of Nb-H[1b]) or which cleanly undergo some fundamental organometallic transformations (e.g., olefin insertion and β-H elimination[3] and reversible α-H elmination and alkyl migration for zirconoxy carbene derivatives[6]). Cp$_2$NbH$_3$ has also been used in the preparation of some heterobimetallic dimers.[7,8]

A favored decomposition pathway for niobocene derivatives involves activation of a cyclopentadienyl C–H bond, as for example, in the generation of "dimeric niobocene"[9] from Cp$_2$NbH$_3$ (eq 1), a mode of reactivity reminiscent of

$$2(\eta^5\text{-}C_5H_5)_2NbH_3 \rightarrow [(\eta^5\text{-}C_5H_5)(H)Nb(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)]_2 + 3H_2 \tag{1}$$

titanocene, zirconocene, and their hydrides.[10] In view of the greater stabilities exhibited by permethyltitanocene and permethylzirconocene, permethylniobocene derivatives are expected to be thermally more robust. Moreover, due to the increased steric demands of pentamethylcyclopentadienyl ligands, reactions which generate dimeric or polymeric species should be discouraged and a strong steric preference for a single isomeric form of a derivative (e.g., for *endo*-$Cp^*_2NbH(CH_2{=}CHR)$)[11] should be obtained.

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† Contribution No. 7259.

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