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# DIAZENE LIGAND GEOMETRY EFFECTS ON THE FORMATION AND PROPERTIES OF METAL CARBONYL COMPLEXES. GROUP VIB PENTACARBONYL COMPLEXES OF *cis*- AND *trans*-1,2-DIISOPROPYLDIAZENE AND 1,2-DIISOPROPYLHYDRAZINE

MARTIN N. ACKERMANN *, RITA M. WILLETT, MARK H. ENGLERT,
CAROLYN R. BARTON, and DEBORAH B. SHEWITZ

*Oberlin College, Department of Chemistry, Oberlin, Ohio 44074 (U.S.A.)*

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## Summary

The Group VIB complexes $M(CO)_5L$ have been synthesized for the cases L = *cis*-1,2-diisopropyldiazene (*c*-DIPD) with M = Cr, Mo, W, L = *trans*-1,2-diisopropyldiazene (*t*-DIPD) with M = Cr, W, and L = 1,2-diisopropylhydrazine (DIPH) with M = Cr, W. Failure to obtain any bimetallic complexes is discussed in terms of steric interactions of these and related complexes. The significance of diazene ligand geometry is demonstrated by the differences in properties of the *c*-DIPD and *t*-DIPD complexes. The available evidence indicates that *cis* diazenes are better ligands than their *trans* isomers. Complex stability decreases in the order $W > Cr >> Mo$ and *c*-DIPD > *t*-DIPD. Infrared, visible, and NMR spectra are interpreted in terms of bonding in the complexes. A 30—60 $cm^{-1}$ reduction of $\nu(N{=}N)$ of the diazenes upon coordination is attributed to metal-ligand $\pi$-bonding with *c*-DIPD being a better $\pi$-acceptor than *t*-DIPD. The NMR spectra of the *c*-DIPD complexes are temperature dependent and show that the $M(CO)_5$ moiety undergoes coordination site exchange between the two nitrogen atoms. No exchange occurs in the *t*-DIPD complexes. Coalescence temperatures of 10, —48, and 6°C were recorded for the Cr, Mo, and W complexes of *c*-DIPD respectively, with the Gibbs free energy barriers of 15.0, 11.5 and 15.0 kcal/mol. A comparison with exchange in other $M(CO)_5$(*cis*-diazene) complexes is made and the role of the diazene structure on the reaction rate is discussed. The $M(CO)_5$(DIPH) (M = Cr, W) complexes have been oxidized by $H_2O_2/Cu^{2+}$ and by activated $MnO_2$ to DIPD complexes in low yield. The tungsten DIPH complex gives only $W(CO)_5$(*t*-DIPD) but the chromium system gives predominantly $Cr(CO)_5$(*c*-DIPD).

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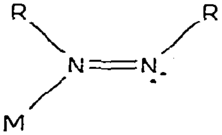
## Introduction

The synthesis and study of transition metal carbonyl complexes containing coordinated diazenes (azo compounds) is an area of active investigation [1]. For the most part these studies have utilized cyclic ligands in which the diazene linkage is in a fixed *cis* configuration. Relatively few acyclic diazenes have received serious attention, with complexes having been reported only for diazene [2], 1,2-diphenyldiazene [3], 1,2-dicyclohexyldiazene [4], phenyldiazene [5], and 1,2-dimethyldiazene [5]. We became interested in acyclic diazenes because they can exist in both *cis* and *trans* isomeric forms. Our goal has been to study the consequences of diazene geometry on the properties of transition metal carbonyl complexes. In addition to our work described here and in a preliminary report [6] only diazene (HN=NH) and 1,2-diphenyldiazene (azobenzene) have been reported in both the *cis* and *trans* forms in metal carbonyl complexes. Direct reaction of free *cis*- or *trans*-1,2-diphenyldiazene with $M(CO)_5THF$ (M = Cr, Mo, W) gave the monometallic *cis* complex I (R = $C_6H_5$) or the bimetallic *trans* complex II (R = $C_6H_5$), where M stands for the metal pentacarbonyl unit [3]. The *cis* complex is more stable than the *trans* complex which decomposes readily in solution even at −40° C. For *cis*- and *trans*-diazene a wider variety of metal systems has been studied but in every case only bimetallic complexes of types II (R = H; M = $Cr(CO)_5$, $C_5H_5Mn(CO)_2$, $C_5H_5Re(CO)_2$) and III (R = H; M = $Cr(CO)_5$, $Mo(CO)_5$, $W(CO)_5$) are known [2]. These complexes were all prepared by oxidation of related hydrazine complexes because of the extreme instability of the free diazene ligands.



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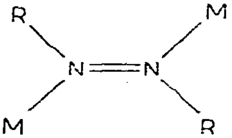

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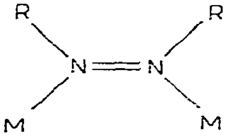

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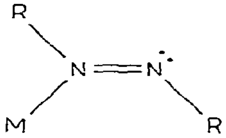

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In this paper we present our results using *cis*- and *trans*-1,2-diisopropyldiazene (DIPD) as ligands with the Group VIB metal carbonyls. This ligand pair imposes fewer experimental constraints because DIPD is more stable than free diazene (HN=NH) and does not undergo thermal or photochemical interconversion of the *cis* and *trans* isomers which can occur with the 1,2-diphenyldiazenes. Indeed, *cis*-DIPD is almost unique among acyclic, non-aromatic diazenes in being stable enough to work with at room temperature [7]. The DIPD ligands are of interest too because the isopropyl group has substantially different electronic and/or steric properties compared with diazene or 1,2-diphenyldiazene. We have also examined the oxidation of some 1,2-diisopropylhydrazine complexes to help to determine what factors may contribute to the in situ formation of a *cis* or *trans* diazene complex. A long term goal is the selective synthesis of metal carbonyl complexes of *cis* diazenes in which the diazene would be unstable without coordination.

## Experimental

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

A nitrogen atmosphere was routinely used for all operations. Solvents were dried and distilled under nitrogen as follows: tetrahydrofuran (THF) from sodium benzophenone ketyl, dichloromethane from phosphorus pentoxide and pentane and hexane from calcium hydride. Chromatography was performed on a column that was slurry-packed with alumina (Alcoa, F-20, chromatographic grade) or Florisil (Fisher Scientific) using petroleum ether (b.p. 30—60° C). Reduction of solution volume or stripping to dryness was done at <0.1 Torr at the temperature specified.

The metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) were purchased commercially and sublimed before use. The norbornadiene derivatives $(C_7H_8)M(CO)_4$ (M = Cr [8], Mo [8], W [9]) were prepared by published procedures. Activated manganese dioxide was purchased from Ventron Corporation (Alfa Division) and also prepared by the method of Attenburrow [10]. 1,2-Diisopropylhydrazine hydrochloride was prepared by the method of Stowell [11]. The free hydrazine was obtained by treating the powdered hydrochloride in vacuo with a two-fold excess of powdered potassium hydroxide and enough water (~1 ml) to make a slurry. The free hydrazine was distilled off and dried over 4Å molecular sieve. *trans*-1,2-Diisopropyldiazene (*t*-DIPD) was obtained from the hydrazine by mercuric oxide oxidation [12].

*cis*-Diisopropyldiazene (*c*-DIPD) was synthesized by oxidation of diisopropyl sulfamide [13] and by the photosensitized isomerization of *t*-DIPD [14]. In the latter preparation 200 ml of a cyclopentane (spectroscopic grade) solution containing naphthalene ($1.4 \times 10^{-2}$ *M*) and *t*-DIPD (0.35 *M*) were placed in a quartz flask and irradiated with General Electric G15T8 germicidal lamps until photo-equilibrium occured (~35% conversion). Reaction progress was monitored by NMR analysis of samples in $CDCl_3$. In both synthetic procedures the majority of the solvent was removed by normal distillation and the remaining solution submitted to bulb-to-bulb fractionation on a vacuum line. Residual solvent and *t*-DIPD distill from a —40°C bulb leaving *c*-DIPD behind. Pure *c*-DIPD can be separated from naphthalene by several transfers from a —15° C bulb to a —196° C bulb.

*$M(CO)_5L$ syntheses.* All of the organometallic compounds $M(CO)_5L$ (Table 1) reported in this paper were prepared by essentially the same indirect photochemical method. The general procedure is described here with specific conditions, e.g. scale, reaction temperature, yield, for each compound summarized in Table 1.

Solid hexacarbonyl and 180 ml of THF were placed in a pyrex immersion type photolysis apparatus and irradiated at ~20° C with a 450 watt medium pressure mercury lamp until the infrared spectrum showed an absence of the

TABLE 1

PREPARATIVE DETAILS AND ELEMENTAL ANALYSIS OF GROUP VIB PENTACARBONYL COMPLEXES OF *cis*- AND *trans*-1,2-DIISOPROPYLDIAZENE AND 1,2-DIISOPROPYLHYDRAZINE

| Compound $M(CO)_5L$ | $M(CO)_6$ (mmol) | L (mmol) | Reaction and stripping temperature (°C) | Yield (mmol (%)) [a] | Mp. (°C) | Elemental analysis (Found (calcd.) (%)) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N |
| $Cr(CO)_5$(*t*-DIPD) | 14.0 | 20 | ~20 | 7.2 (51) | ~70dec. | 43.15<br>(43.14) | 4.64<br>(4.61) | 9.16<br>(9.15) |
| $W(CO)_5$(*t*-DIPD) | 5.7 | 6.7 | 0 | 0.28 (7.1) | 81–83 | 30.04<br>(30.14) | 3.22<br>(3.20) | 6.45<br>(6.39) |
| $Cr(CO)_5$(*c*-DIPD) | 7.1 | 7.1 | ~20 | 40–50% [b] | <0 | | [c] | |
| $Mo(CO)_5$(*c*-DIPD) | 4.0 | 4.0 | 0 | ~30% [b] | 27–28 | | [c] | |
| $W(CO)_5$(*c*-DIPD) | 6.6 | 9.2 | ~20 | 3.4 (52) | 32–34 | 30.36<br>(30.14) | 3.25<br>(3.20) | 6.43 [d]<br>(6.39) |
| $Cr(CO)_5$(DIPH) | 10.4 | 11.5 | 0 | 7.9 (76) | 27–28 | 42.66<br>(42.86) | 5.22<br>(5.23) | 8.98<br>(9.09) |
| $W(CO)_5$(DIPH) | 8.8 | 10.2 | ~20 | 5.4 (62) | 42–43 | 29.88<br>(30.02) | 3.63<br>(3.66) | 6.28<br>(6.36) |

[a] All compounds are yellow or gold colored. [b] Sample handling difficult, an estimated value. [c] Not available due to sample instability. [d] mol.wt. 447 by osmometry in chloroform; calculated 438. Done by Galbraith Laboratories, Inc., Knoxville, Tenn.

hexacarbonyl. The yellow solution was transferred to a flask, equilibrated at the reaction temperature, and the ligand added by pipet. In most cases the solution color darkened noticeably to an orange-brown at this point. After 1—2 h the solution was stripped to dryness (see Table 1 for temperature) and the solid residue taken up in hexane or pentane and filtered at room temperature. If necessary the filtrate volume was reduced, then the product crystallized at —78° C. The solid was isolated by decantantion or cold filtration; several washings with cold solvent were employed in this step. Finally the solid was pumped dry ($<$0.1 Torr) while still cold and pumping continued while the temperature gradually rose to ambient. The *t*-DIPD and hydrazine complexes were further purified by sublimation ($10^{-2}$ Torr) from ambient to a 0° or a —78° C probe.

Deviations from the basic procedure were as follows. $W(CO)_5$(*t*-DIPD) and $W(CO)_5$(*c*-DIPD): the stripped THF residue was extracted with pentane, the solution volume reduced, and chromatographed on a 2.5 × 55 cm alumina column. After elution of $W(CO)_6$ with petroleum ether, the major yellow product band was eluted with 10—25% dichloromethane in petroleum ether solution. The solvent was removed, and the residue crystallized from hexane. This was the only way to obtain significant quantities of $W(CO)_5$(*t*-DIPD) free of $W(CO)_6$.

$Cr(CO)_5$(*c*-DIPD): most of the residual $Cr(CO)_6$ in the stripped THF residue was sublimed ($<$0.05 Torr) from the 0° C flask onto a —78° C probe before $Cr(CO)_5$(*c*-DIPD) was extracted and crystallized.

In general the solid left after extracting and filtering the stripped THF residue was worthless decomposition material. However, in the synthesis of $Cr(CO)_5$(DIPH) a mustard-colored solid soluble only in polar solvents remained which appears to be *cis*-$Cr(CO)_4(DIPH)_2$ based on spectroscopic data. In $CH_2Cl_2$ $\nu$(CO) at 2062w, 1930s, 1870vs, 1842s; NMR in acetone-$d_6$ (ppm, $\tau$ relative to internal TMS) 4.49d (NH), 7.44 m (NH, two CH), 8.54d ($CH_3$), 8.75d ($CH_3$). Yield: 210 mg (0.53 mmoles), 9.2% based on DIPH. Analysis was not possible but the following NMR data support the proposed formula. 32.6 mg of the chromium compound and 34.7 mg of *p*-dibromobenzene dissolved in acetone-$d_6$ were sealed in an NMR tube. The ratio of the relative areas of the DIPH protons in the complex to the *p*-dibromobenzene protons ($\tau$ 2.6) was determined at 25° C. Found: 4.6; calcd. for $Cr(CO)_4(DIPH)_2$: 4.5; calcd. for $[Cr(CO)_5]_2$(DIPH): 1.8.

*Photolysis of a $W(CO)_6$-t-DIPD mixture.* 2.08 g (5.92 mmol) of $W(CO)_6$ and 1.0 ml (6.7 mmol) of *t*-DIPD were photolyzed as described in the general procedure. The resultant solution was chromatographed on a 2.5 × 52-cm alumina column. The yellow bands of $W(CO)_5$(*t*-DIPD) and $W(CO)_5$(*c*-DIPD) were eluted successively with petroleum ether and a 2/3 dichloromethane/petroleum ether solution. Isolated yields were 117 mg (4.5%) and 29 mg (1.1%), respectively.

*$Mo(CO)_5$(c-DIPD) from $Mo(CO)_4$(norbornadiene).* A mixture of 304 mg (1.0 mmol) of $Mo(CO)_4(C_7H_8)$ and 0.2 ml (1.4 mmol) of *c*-DIPD in 35 ml of hexane was stirred for 6 h at —20° C. A gold solid gradually deposited which was isolated by decantation, washing with 10 ml of —78° C hexane, and dried under vacuum at —25° C. Yield: 215 mg (0.61 mmol, 61%).

*Oxidation studies*

*A. With $MnO_2$.* To 5—10 ml of $CH_2Cl_2$ at 0°C were added 100—500 mg of hydrazine complex $M(CO)_5$(DIPH) (M = Cr, W), a ten-fold molar amount of activated $MnO_2$, and 1 g of anhydrous $Na_2SO_4$. The mixture was warmed to room temperature and stirred. Reaction progress was monitored by withdrawing samples, drying under nitrogen purge, and examining the hexane extract by infrared spectrometry. When reaction was complete, the mixture was filtered and the filtrate stripped to dryness at 0° C. Product composition was determined by infrared and NMR spectrometry; with M = W some samples were worked up by chromatography on alumina as described above.

Free DIPH (1 mmol) was oxidized as above at temperatures from ambient to —30° C. The reaction was monitored by filtering a sample into $CDCl_3$ and recording the NMR.

*B. With $H_2O_2/Cu^{2+}$.* The method is similar to that of Sellmann [2]. In a typical reaction 410 mg (1.0 mmol) of $Cr(CO)_5$(DIPH), 5 ml of THF, 4 g of anhydrous $Na_2SO_4$, 2 drops 0.15 *M* $CuSO_4$, 1.7 ml of $H_2O_2$ solution (1.1 ml 30% $H_2O_2$ in 5.0 ml THF), and a stirring bar were placed in a Schlenk tube at —50° C. The temperature was raised to 10° C and the reaction monitored by gas evolution (76 ml). After 2 h the solution was filtered while cold and stripped to dryness at 0° C. Analysis was as described in the $MnO_2$ oxidations.

Free DIPH (0.4 g) was oxidized in a similar manner (1.1 ml $H_2O_2$ solution) at 10° C.

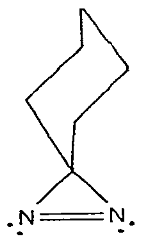
## Results and discussion

*Synthesis and properties.* The compounds described in this study are all of the type $M(CO)_5L$ (M = Cr, Mo, W; L = *c*-DIPD, *t*-DIPD, or DIPH). Analytical (Table 1) and spectroscopic data (vide infra) support their formulations as monometallic complexes. In all cases synthesis was readily accomplished by reaction of the free ligand, L, with photochemically generated $M(CO)_5$THF with generally fair to good yields. Despite several attempts the poor yield of $W(CO)_5$(*t*-DIPD) could not be improved. $Mo(CO)_5$(*c*-DIPD) was also synthesized by the reaction of *c*-DIPD with $Mo(CO)_4$(norbornadiene) in hexane at —25° C. This material was superior in quality to that from the THF method as the product which precipitated during reaction was spectroscopically pure and had the highest melting point. However, neither the chromium nor tungsten *c*-DIPD complexes could be obtained by this alternate route. All attempts to isolate molybdenum complexes of *t*-DIPD and DIPH by either synthetic procedure failed, even when reaction and work up were conducted at —30° C or below.

The stability of complexes was in each case W > Cr >> Mo and for the diazenes *c*-DIPD > *t*-DIPD both for pure materials and in solution. The low-melting solids frequently became oily. The Cr and W solids were stable in air for brief periods. Only the tungsten and DIPH compounds showed no decomposition in solution under nitrogen at room temperature. The tungsten DIPD complexes were stable enough for chromatography on alumina, while $Cr(CO)_5$(*t*-DIPD) and the DIPH complexes decomposed significantly on Florisil. All of the *t*-DIPD and DIPH complexes sublime at moderate temperatures whereas the *c*-DIPD complexes are nonvolatile.

Since synthesis and isolation of *c*-DIPD for use in complex formation is time consuming, in one experiment the more accessible *t*-DIPD was photolyzed along with $W(CO)_6$ in THF. Under these conditions a partial conversion of *t*-DIPD to *c*-DIPD occurs, and it was hoped that the more stable $W(CO)_5$-(*c*-DIPD) could be obtained in good yield. However the ratio of $W(CO)_5$-(*t*-DIPD) to $W(CO)_5$(*c*-DIPD) was 4/1 with a total yield of about 6% which makes this an unattractive synthetic route.

Attempts to synthesize bimetallic complexes of the type $[M(CO)_5]_2L$ by using a four- to six-fold excess of $M(CO)_5THF$ were unsuccessful. This contrasts sharply with the complexes of *cis*- and *trans*-diazene which are all bimetallic [2]. This difference is undoubtedly due to the greater steric bulk of the isopropyl group compared to a hydrogen atom. In the crystal of the THF solvate $[Cr(CO)_5]_2$(*t*-HN=NH) · 2 THF (I,R = H; M = $Cr(CO)_5$) significant interaction between the $Cr(CO)_5$ moiety and the N—H bond *cis* to it is indicated [15]. Space filling models show that replacement of the hydrogen atoms with isopropyl groups would lead to a very crowded bimetallic *t*-DIPD complex. If the C—N=N bond angle is increased to reduce interaction with the *cis*-$M(CO)_5$ group, steric interaction with the *gem*-$M(CO)_5$ group becomes important. Only a monometallic complex of *t*-DIPD can minimize interaction of $M(CO)_5$ with both *cis*- and *gem*-isopropyl groups. Surprisingly *trans*-1,2-diphenyldiazene forms bimetalllic complexes [3]. Based on space filling models it appears highly unlikely that the diazene can retain the planar structure of the free ligand in such a complex and that significant rotation of the phenyl rings out of the C—N=N—C plane probably occurs. The extreme instability of $[M(CO)_5]_2$-(*t*-$C_6H_5N{=}NC_6H_5$) in solution may be indicative of the steric strain that must exist in this complex.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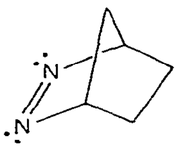
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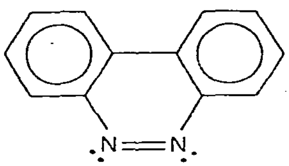
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In bimetallic complexes of type II, $[M(CO)_5]_2L$ in which L is a *cis* diazene, the degree of crowding of the *cis*-$M(CO)_5$ units is influenced by the C—N=N angle of the diazene. The diazirine V has a C—N=N angle around 60° [16] and readily forms type II bimetallic complexes [17]. The rigid bicyclic diazene VI has a C—N=N angle of 116.3° [18]. No complexes of type II have been reported for VI but bridged complexes $(CO)_4ML_2M(CO)_4$ and $(CO)_3ML_3M$-$(CO)_3$ (M = Cr, Mo, W) are easily obtained [19]. For *cis*-1,2-diphenyldiazene and the cyclic analog benzo[*c*]cinnoline (VII) with C—N=N angles of 121.9° [20] and 120—121° [21], respectively, only monometallic complexes $M(CO)_5L$ have been reported [2,22]. In the $[M(CO)_5]_2$(*c*-HN=NH) complexes the H—N=N angle can be reduced to less than the 120° found in the *trans* complex

TABLE 2

INFRARED AND VISIBLE SPECTRAL DATA

| Compound | Infrared spectra | | Visible spectra | |
|---|---|---|---|---|
| | $\nu$(CO) (cm$^{-1}$) [a,b] | $\nu$(N=N) (cm$^{-1}$) [c] | $\lambda_{max}$ (nm) ($\epsilon \times 10^{-3}$ ($M^{-1}$ cm$^{-1}$)) | Solvent |
| $Cr(CO)_5$(*t*-DIPD) | 2070w, 1944vs, 1933s | 1535 | 392 | hexane |
| $W(CO)_5$(*t*-DIPD) | 2072w, 1940vs, 1933s | 1529 | 378 (6.6) | hexane |
| | | | 368 (>5.6) | $CH_3CN$ |
| $Cr(CO)_5$(*c*-DIPD) | 2068w, 1987w, 1942vs, 1940vs, 1913s | 1504 | 404 | hexane |
| $Mo(CO)_5$(*c*-DIPD) | 2074w, 1990w, 1947vs, 1940vs, 1918s | 1517 | | |
| $W(CO)_5$(*c*-DIPD) | 2072w, 1982w, 1938vs, 1933vs, 1915s | 1500 | ~425 (~3), 391 (6.4) | hexane |
| | | | 383 (6.1) | $CH_2Cl_2$ |
| | | | 376 (5.5) | $CH_3CN$ |
| $Cr(CO)_5$(DIPH) | 2065w, 1978w, 1943s, 1931vs, 1920ms | | 418 (>2.9) | hexane |
| $W(CO)_5$(DIPH) | 2069w, 1970w, 1937s, 1927vs, ~1920(sh) ms | | ~440 (~0.3), 402 (3.5) | hexane |
| | | | ~440 (~0.3), 390 (2.8) | $CH_3CN$ |
| *t*-DIPD | | 1565 [d] | | |
| *c*-DIPD | | 1560 [e] | | |

[a] In *n*-hexane. [b] Abbreviations: v, very; s, strong; m, medium; w, weak; (sh), shoulder. [c] From KBr pellet. [d] Raman value [33]. [e] From liquid thin film.

[15] without crowding the hydrogen atoms. The C—N=N bond angle in *c*-DIPD is estimated to be 130—140° [23]. Steric interaction between the isopropyl groups prevents reducing the C—N=N angle in the complex which would make a bimetallic complex prohibitively crowded.

*Infrared spectra.* The major infrared spectral features of the complexes are summarized in Table 2. The patterns in the carbonyl region are typical of $M(CO)_5L$ structures. The five frequencies for the *c*-DIPD and DIPH complexes indicate significant deviation from ideal $C_{4v}$ symmetry. The weak feature in the 1970—1990 $cm^{-1}$ region in these complexes was reproducible in intensity in separate syntheses and after purification. Hence we confidently assign it to the $B_1$ mode which is formally infrared forbidden in $C_{4v}$ symmetry rather than to $M(CO)_6$ impurity.

For all the diazene complexes there is a 30 to 60 $cm^{-1}$ reduction in $\nu(N=N)$ in the complex relative to the free ligand. We attribute the decrease in $\nu(N=N)$ to $\pi$-acceptor capability of the diazene ligands. Qualitative molecular orbital considerations show that $\pi$-bonding can occur between the metal $d_{yz}$ or $d_{xz}$ orbital of the $M(CO)_5$ unit and the diazene $\pi^*$ molecular orbital [24]. $\pi$-Acceptor ability for the cyclic *cis* diazene VI has been reported previously based on carbonyl frequencies [25] and force constant calculations [19b]. Since the decrease of $\nu(N=N)$ for the *c*-DIPD complexes is nearly twice that for the *t*-DIPD complex of the same metal, it appears that *c*-DIPD is a better $\pi$-acceptor than *t*-DIPD. Interestingly the magnitude of the reduction of $\nu(N=N)$ follows the same order as the stabilities of the complexes for a given ligand, i.e. $Mo < Cr < W$. Work with other *cis,trans* diazene pairs is required to test the generality and significance of this observation.

*Visible spectra.* The absorption spectra of all but the very unstable molybdenum *c*-DIPD complex were recorded and are also summarized in Table 2. A detailed study of the Group VIB $M(CO)_5$(diazene) compounds concerned with a variety of *cis* diazene ligands has recently appeared [24]. The spectral features have been interpreted in terms of the molecular orbital scheme shown in Fig. 1. The two lowest energy transitions expected are a charge transfer M-diazene (CTML) type due to $d_{xz} \rightarrow \pi^*$ (predominantly $\pi^*(N=N)$) and a ligand field (LF) type due to $d_{yz} \rightarrow d_{x^2-y^2}$. The energy of the $\pi^*$ orbital in the complex depends on the energy of $\pi^*(N=N)$ in the free ligand and the extent of metal—ligand $\pi$-bonding. Generally, in spectra of the *t*-DIPD and *c*-DIPD complexes only a single well-defined absorption peak is observed, and we conclude that the CTML and LF bands overlap. Only $W(CO)_5$(*c*-DIPD) shows a shoulder to the low energy side at about 425 nm in hexane which is probably the CTML absorption. In an effort to resolve the two band spectra of the more stable tungsten compounds were recorded in solvents of varying polarity. Both the CTML and LF bands should shift to the blue in more polar medium with the former experiencing the greater effect [24]. Only one major peak was observed in all cases, and the blue shift of ~1000 $cm^{-1}$ is consistent with a LF band. However, there was in each case a broadening of the peak to the high energy side suggesting a somewhat greater movement of the underlying CTML transition.

For the DIPH complexes the bonding can be reasonably described simply by removing the orbitals labelled $\pi$ and $\pi^*$ in the free ligand and the complex in Fig. 1. The lowest energy transition in the complex should be unambiguously

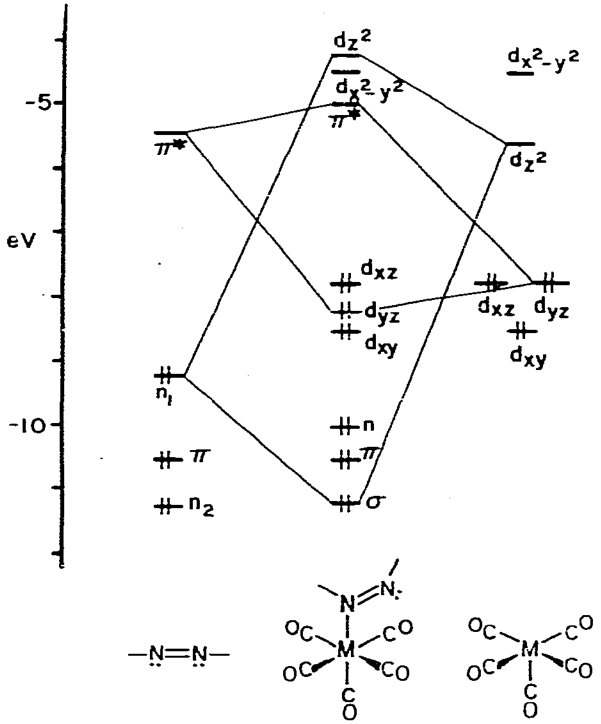


Fig. 1. Simplified molecular orbital energy level diagram for $M(CO)_5$(*cis,trans*-diazene) complexes. See ref. 24.

the LF $d_{xz} \rightarrow d_{x^2-y^2}$. The single band observed in the spectra and the ~700 $cm^{-1}$ blue shift in the more polar solvent is consistent with this assignment. Interestingly the extinction coefficient of the LF band in the DIPH complexes is about half that for the band in the diazene complexes which was assigned to the two overlapped LF and CTML transitions.

With the exception of benzo[*c*]cinnoline (VII) Frazier and Kisch found a good correlation between the energy of the CTML transition in the diazene complex and the energy of the $n \rightarrow \pi^*$ transition of the uncoordinated *cis*-diazene ligand, which was taken as a rough measure of the energy of $\pi^*$(N=N). (The apparent assumption is that the energy of $n_1$ is constant in the sequence of ligands, although there is a variation of nearly 1 eV [1a,23].) For free *c*-DIPD the $n \rightarrow \pi^*$ energy is 3.25 eV [23]. The lowest possible value for CTML in $W(CO)_5$(*c*-DIPD) is 2.92 eV (425 nm) which is well above that predicted by the suggested correlation. Such a deviation is not surprising. The CTML transition energy depends on the energy of both the $\pi^*$ and $d_{xz}$ orbitals in the complex. The change in energy of the $\pi^*$ orbital in the complex relative to the free ligand depends on the effectiveness of metal—ligand $\pi$-bonding, with stronger $\pi$-bonding raising $\pi^*$ and thereby *E*(CTML). While the $d_{xz}$ orbital does not formally bond to the diazene ligand in $C_{4v}$ symmetry, the energy of this orbital is still subject to substantial variation in the complex. Elian and Hoffmann have shown that the energy of the $e(d_{xz}, d_{yz})$ orbitals in the $M(CO)_5$ fragment is sensitive to the angle between the axial and equatorial carbonyls in $C_{4v}$ symmetry [26]. In an $LM(CO)_5$ complex this angle depends on both the $\sigma$-bonding strength of L and its steric requirements. It would seem highly unlikely that the series of *cis* diazene ligands involved [24] would affect the $\pi^*$ and $d_{xz}$ orbitals in the complex in a similar manner.

Only $W(CO)_5$(DIPH) exhibited a weak feature at low energy (~440 nm) that might be the singlet—triplet LF transition which is well-known in analogous systems [27].

*NMR spectra.* The proton NMR spectral features of all compounds studied are summarized in Table 3. The spectra of the *t*-DIPD and DIPH complexes show two inequivalent isopropyl groups as expected for a structure in which only one of the nitrogen atoms is bonded to the $M(CO)_5$ moiety. The $CH_3$ resonances are only slightly affected and in the DIPH complexes only one doublet is discernible. In the *t*-DIPD complexes the more down-field shifted CH resonance is assigned to the isopropyl groups on the coordinated nitrogen. A broad feature due to the NH of the coordinated nitrogen in the DIPH complexes is clearly visible and is well down-field shifted, while the NH signal of the uncoordinated end is buried under the CH resonances. In the tungsten DIPH complex the NH resonances are too broad to see at 35°C and emerge only at lower temperatures. At low temperature the CH and $CH_3$ signals of both $M(CO)_5$DIPH complexes (M = Cr, W) broaden and poorly defined splitting is observed, probably due to slowed conformer interconversion. The chromium complex decomposes slowly to free DIPH and a compound which appears to be $Cr(CO)_4$-$(DIPH)_2$ (see experimental section).

The NMR spectra of the *c*-DIPD complexes are temperature dependent. At 35°C the chromium and tungsten compounds show only one type of isopropyl group; the molybdenum compound decomposes quickly at 35°C but shows a similar spectrum at —20°C. Lowering the temperature causes the signals to broaden and eventually a spectrum indicative of two inequivalent isopropyl groups emerges. A sharp limiting spectrum consistent with a rigid type I structure is reached at —30° for chromium and tungsten and at —85°C for molybdenum. This behavior is indicative of coordination site exchange of the $M(CO)_5$ unit between the lone pairs on the two nitrogen atoms. When the complex and free *c*-DIPD are present together, separate, unbroadened and unshifted signals are observed for each. Addition of *t*-DIPD or triphenylphosphine produces no $M(CO)_5$(*t*-DIPD) or $M(CO)_5PPh_3$. These observations support a non-dissociative site exchange mechanism. Using the $CH_3$ resonances, the coalescence temperatures for the Cr, Mo, and W complexes were determined to be 10, —48, and 6°C respectively from which the corresponding activation free energies, $\Delta G^{\neq}$, were calculated as 15.0, 11.5, and 15.0 kcal/mol [28]. The lower energy barrier for exchange in the case of molybdenum is further support for weaker metal—diazene bonding in this *c*-DIPD complex compared to the other two as deduced above from the change in $\nu(N{=}N)$ and the thermal stability.

This is the first report of this type of dynamic behavior for an acyclic diazene complex. Two cyclic *cis* diazene complexes have been observed to behave similarly. In $ArCr(CO)_2$(2,3-diazabicyclo[2.2.1]hept-2-ene) (VIII, Ar = benzene or substituted benzene) exchange between the two nitrogen sites occurs at elevated temperature [29]. Depending on the substituents on the aromatic ring the coalescence temperature for the bridgehead proton signals

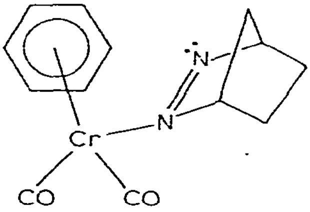
TABLE 3

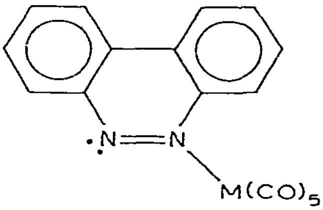
PROTON NMR SPECTRAL DATA [a]

| Compound | $T$ (°C) | $CH$ [c] (uncoord.) | $CH$ [c] (coord.) | $CH_3$ [d] (uncoord.) | $CH_3$ [d] (coord.) | $NH$ (uncoord.) | $NH$ (coord.) |
|---|---|---|---|---|---|---|---|
| $Cr(CO)_5$(*t*-DIPD) | −15 | 5.87 | 4.88 | 8.70 | 8.89 | | |
| $W(CO)_5$(*t*-DIPD) | 35 | 5.91 | 4.71 | 8.63 | 8.78 | | |
| $Cr(CO)_5$(*c*-DIPD) | −40 | 5.37, 5.62 [e] | | 8.59, 8.70 [e] | | | |
| | 35 | 5.74 | | 8.64 | | | |
| $Mo(CO)_5$(*c*-DIPD) | −85 | 5.49, 5.58 [e] | | 8.55, 8.72 [e] | | | |
| | −20 | 5.53 | | 8.63 | | | |
| $W(CO)_5$(c-DIPD) | −30 | 5.38, 5.49 [e] | | 8.58, 8.65 [e] | | | |
| | 35 | 5.49 | | 8.62 | | | |
| $Cr(CO)_5$(DIPH) | 35 | 6.68, 6.74 [e] | | 8.74 | | 4.91(br) | ~7.0(br) |
| $W(CO)_5$(DIPH) | 35 | 6.79, 6.84 [e] | | 8.81 | | 3.9(br) [f] | ~6.5(br) [f] |
| *t*-DIPD | 35 | 6.47 | | 8.86 | | | |
| *c*-DIPD | 35 | 5.86 | | 8.80 | | | |
| DIPH | 35 | 7.20 | | 9.09 | | 7.0(br) | |

[a] Recorded in acetone-$d_6$. [b] In $\tau$ (ppm) units relative to internal tetramethylsilane. The coupling constant for the two types of protons in the isopropyl group is 6.3—6.5 Hz in all cases; (br) broad. [c] Septet. [d] Doublet. [e] Coordinated and uncoordinated resonances too close to distinguish by double resonance. [f] At −30°C.

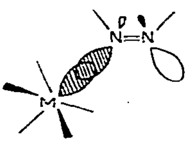
ranged from 50—95°C with $\Delta G^{\neq}$ values from 17.0—19.8 kcal/mol at coalescence. The two complexes $M(CO)_5$(benzo[*c*]cinnoline) (IX, M = Cr, W) are dynamic at room temperature but exchange does not occur at —60°C [22,24]. No coalescence temperature or $\Delta G^{\neq}$ values were given.

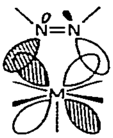

(VIII)


(IX)

Because VIII requires a higher temperature than IX (M = Cr) for site exchange to occur, Frazier and Kisch concluded that the activation energy for this process was higher in complexes with high-lying $\pi^*$(N=N) orbitals [24]. While it is possible that such a correlation may emerge as data on more diazene systems are obtained, it does not appear valid based on the three ligands so far studied. Uncoordinated *c*-DIPD and VI have very close $\pi^*$(N=N) energies [23], and their $LCr(CO)_5$ complexes have comparable electronic spectra [24]. On these grounds $Cr(CO)_5$(*c*-DIPD) would also be classified as a complex with a high-lying $\pi^*$(N=N) orbital. Yet, like IX, which has a low-lying $\pi^*$(N=N) orbital [24], $Cr(CO)_5$(*c*-DIPD) undergoes exchange at a much lower temperature (and with a lower free energy barrier) than VIII. Since VIII has an $ArCr(CO)_2$ rather than a $Cr(CO)_5$-metal carbonyl moiety, this could contribute to the difference in rates. However, $LCr(CO)_5$ (L = VI) is known and does not appear to undergo exchange at NMR probe temperature (~35°) [19a].

We believe that ligand geometry should be an important factor in determining the rate of the nitrogen coordination site exchange process in diazene complexes and might be the dominant influence in the complexes so far studied. In the ground state (static complex of type IV) simple molecular orbital considerations [24] show that the metal—diazene $\sigma$-bonding in $M(CO)_5L$ complexes occurs between the metal $d_{z^2}$ orbital and the $n_1$ orbital of the *cis* diazene as in X. Additionally some $\pi$-bonding between the diazene $\pi^*$(N=N) orbital and the metal $d_{yz}$ orbital also occurs. In the transition state the $M(CO)_5$ fragment spans both lobes of the nitrogen $n_1$ orbital, and bonding must be through the metal $d_{xz}$ (or $d_{yz}$) orbital as in XI.


(X)


(XI)

Poor overlap between the $n_1$ and $d_{xz}$ orbitals will raise the energy of the transition state leading to a slower exchange rate. Overlap is expected to decrease as the distance between the lobes of the $n_1$ orbital becomes too large for the $d_{xz}$ metal orbital to span. Since the N=N bond length varies little among diazenes, the distance between the $n_1$ lobes depends primarily upon the C—N=N angle. A large angle brings the lobes together for more effective bonding to the metal. This simple picture ignores the possible effects on the $n_1$ orbital due to mixing with the carbon framework orbitals of the diazene, which can be substantial in small rings [30]. As noted earlier the C—N=N bond angles follow the trend *c*-DIPD >> VII > VI which is consistent with the site exchange rates for their $LCr(CO)_5$ complexes. Unfortunately our attempts to prepare an $ArCr(CO)_2$(*c*-DIPD) complex failed so that a comparison with $ArCr(CO)_2$(2,3-diazabicyclo[2.2.1]hept-2-ene) (VIII) is not possible.

An alternative transition state to that discussed above is one in which the ligand $\pi$(N=N) orbital bonds to the metal $d_{z^2}$ orbital. $\pi$-Bonded complexes of this type are known [1]. This would require rotation of the ligand about the N=N axis, and should be a transition state accessible to both *cis* and *trans* diazene complexes. Since the *t*-DIPD complexes do not show nitrogen coordination site exchange, this mechanism must involve a substantial activation barrier, and we favor the one described earlier.

*Oxidation studies.* Sellmann has synthesized Group VIB metal carbonyl complexes of diazene (HN=NH) by oxidation of the hydrazine complexes $M(CO)_5N_2H_4$ or $[M(CO)_5]_2N_2H_4$ (M = Cr, Mo, W) with hydrogen peroxide and catalytic amounts of cupric ion in THF [2]. While yields were small, this strategy was necessary because the free diazene ligands are too unstable to isolate and use directly in an alternative synthetic route. Both *cis*- and *trans*-diazene complexes were obtained but it was not possible to control by design which was formed. Recently he has extended this approach to the synthesis of complexes $C_5H_5Mn(CO)_2L$ where L is *trans*-phenyldiazene or *trans*-1,2-dimethyldiazene [5]. We have also attempted to oxidize the DIPH complexes directly to DIPD complexes. Our interest here was two-fold: (1) to test the feasibility of such an approach with a rather bulky hydrazine and (2) to determine whether a *c*-DIPD or *t*-DIPD complex was preferentially formed.

Two oxidizing systems were employed: the $H_2O_2/Cu^{2+}$ system of Sellmann and activated manganese dioxide. The latter was selected because Hyatt has reported that activated $MnO_2$, either commercially purchased or specially synthesized, selectively oxidizes a variety of 1,2-diphenylhydrazines to *cis*-1,2-diphenyldiazenes in excellent yields [31*]. We hoped it might lead to a selective *c*-DIPD product on oxidizing the DIPH complexes as well.

Oxidations of $M(CO)_5$(DIPH) (M = Cr, W) were carried out with $H_2O_2/Cu^{2+}$ in THF at 10°C where reactions were over in ~1 h. At lower temperatures the reaction was too slow and above 10°C the DIPD complexes which were formed decomposed extensively. Under these conditions yields of isolatable DIPD complexes were small. Activated $MnO_2$ was a more sluggish oxidizing agent with one or more days required for complete oxidation of the DIPH complexes at 25°C in $CH_2Cl_2$. Yields were only slightly better than those with $H_2O_2$. We conclude that for this crowded hydrazine these oxidation methods are not syn-

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* In our hands two different samples of Alfa activated $MnO_2$ gave no *cis*-1,2-diphenyldiazene when used in the oxidation of 1,2-diphenylhydrazine. With Attenburrow [10] $MnO_2$ only 10—20% cis was produced. The variabilities of activated $MnO_2$ synthesis and usage are well-known [32].

thetically useful compared with the reaction of the uncoordinated DIPD molecules with $M(CO)_5THF$ as described above. Nonetheless, the DIPD complexes formed in these oxidations are of interest. NMR analysis of the products formed with either oxidizing system showed that for tungsten only $W(CO)_5$-(*t*-DIPD) was present while with chromium predominantly $Cr(CO)_5$(*c*-DIPD) occurred. Since $W(CO)_5$(*c*-DIPD) is more stable than its chromium counterpart, we conclude that none of it was formed. When uncomplexed DIPH was oxidized under identical conditions only *t*-DIPD was formed. This rules out a mechanism by which the DIPH dissociates from the chromium complex but not the tungsten complex, is oxidized to *c*-DIPD, and then forms $Cr(CO)_5$-(*c*-DIPD). The origin of the *c*-DIPD complex with chromium thus appears to be dependent on the metal but not the oxidant. Sellmann found that $H_2O_2$ oxidation of $Cr(CO)_5N_2H_4$ gave a mixture of both (*t*-HN=NH)$[Cr(CO)_5]_2$ and (*c*-HN=NH)$[Cr(CO)_5]_2$ but reported only (*c*-HN=NH)$[W(CO)_5]_2$ from $W(CO)_5$-$N_2H_4$ [2a]. Since these are bimetallic diazene complexes and those of DIPD are monometallic a direct comparison of the two studies may not be appropriate. Oxidation studies on other hydrazine complexes of chromium and tungsten are needed before the significance of the current observations can be understood.

## Acknowledgements

Mr. David J. Dobmeyer performed some of the experiments with manganese dioxide and 1,2-diphenylhydrazine. We thank Dr. Thomas Albright, University of Houston, for his interest and helpful comments. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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