

Conclusion

The empirical generalizations of Table I are based on the existing experimental evidence. This evidence is neither abundant nor entirely compelling; additional facts would certainly be useful in order to substantiate the present proposal. As a matter of fact, Table I might be of some help in carrying out future experiments.

From a more theoretical point of view, the connection between labilization modes and stereochemistry has been shown to be compatible with a detailed ligand field analysis. The formulation of electronic selection rules is an interesting feature apparently underlying the photochemistry of both the d^3 and d^6 complexes.

References and Notes

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Nature of the Lowest Excited States and Dynamic Behavior of Group 6B (Diazeno)pentacarbonylmetal Complexes

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Electronic absorption and emission data are reported for (diazeno) $M(CO)_5$ ($M = Cr, Mo, W$; diazeno = *trans*-dicyclohexyldiazeno, 2,3-diazanorbornene, 4-R-3,3-bis(methoxycarbonyl)-1-pyrazoline ($R = isopropyl, phenyl$), pyridazine, *cis*-azobenzene, benzo[*c*]cinnoline). The lowest absorption band is assigned to a metal \rightarrow diazeno charge-transfer transition (CTML) on the basis of solvent, ligand, and temperature effects and the next higher band is assigned to a metal-centered transition (LF). Dynamic vis-UV spectroscopy at -100 to $-185^\circ C$ gives evidence for small differences in the contribution of π bonding to the M-N bond and for restricted rotation around this bond. In addition to this fast process, a slow 1,2-shift of the $M(CO)_5$ group along the N=N linkage occurs at higher temperatures as demonstrated by dynamic ^{13}C and 1H NMR spectra.

Preparatively and structurally, transition-metal complexes of diazenes have been increasingly investigated during the last decade.¹ The electronic spectroscopy of these compounds has not been explored in a comparable fashion. Recently the lowest absorption band in the spectra of the π complexes bis(triethylphosphine)(*trans*-azobenzene)nickel have been assigned to an $n \rightarrow \pi^*$ transition on the basis of its variation upon introduction of substituents in the para position of azobenzene.² Tentative assignments of the two low-energy bands of the σ complexes $Cr(CO)_5$ (*cis*-azobenzene)³ and $M(CO)_5$ (benzo[*c*]cinnoline)⁴ ($M = Cr, Mo, W$) as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of the coordinated diazeno ligand have appeared while this work was in progress. Comparison with the well-investigated spectra of $W(CO)_5(L)$, where L is an oxygen or nitrogen σ donor like acetone or an amine,⁵ points to the

more likely assignment of these transitions as ligand field (LF) and charge transfer $M \rightarrow$ diazeno (CTML). In this paper this latter assignment is experimentally supported by examining the influence of the metal, the diazeno ligand, the solvent, and the temperature on the low-energy bands of a series of pentacarbonylmetal σ -diazeno complexes. Some of the tungsten compounds exhibit emission at low temperature. With regard to the current interest⁶ in low-lying CTML states of transition-metal compounds we note that these diazeno complexes constitute the fifth class of substituted mononuclear metal carbonyls having CTML lowest excited states. The other examples known are $(L)W(CO)_4$ ($L = 1,10$ -phenanthroline, 2,2'-bipyridine,⁷ 1,4-diazabutadienes⁸), $(L)W(CO)_5$ ($L = 4$ -R-pyridine (R is an electron-withdrawing group like CN, CH_3CO , etc.)^{9a}), $(C_5H_5)Mn(CO)_2(NCAr)$ ($Ar = C_6H_5$

Table I. Physical Data for Some (L)M(CO)₅ Complexes

	$\nu(\text{CO}), \text{cm}^{-1}$ ^a	fp (dec), °C ^b	M ⁺ ^c
1c	2075 m, 1998 m, 1954 vs, 1948 vs, 1932 vs	71-72	392
2e	2076 m, 1947 vs, br, 1919 s	68-69	316
3b	2075 m, 1941 vs, br, 1926 s	69-71	420
3c	2076 m, 1990 m, 1949 vs, 1945 vs, 1931 vs	82-84	(524)
3d	2078 m, 1990 m, 1949 vs, 1943 vs, 1930 vs	82-84	(558)
3e	2074 m, 1938 vs, br, 1918 s	85-86	404
4	2075 m, 1935 vs, br, 1921 vs	73-75	
5	2076 m, 1960 m, sh, 1946 vs, 1932 s	87-88	428

^a At room temperature in *n*-hexane. ^b In closed capillary tubes.
^c Highest peak in the mass spectrum; corresponds to molecular ion except for 3c and 3d (M⁺ - 28); MAT-CH5 instrument, I_v = 70 eV.

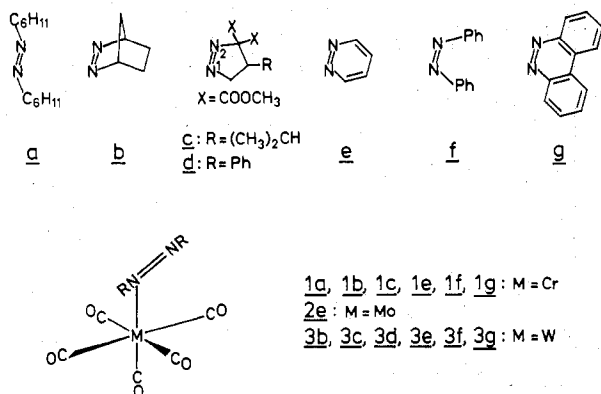
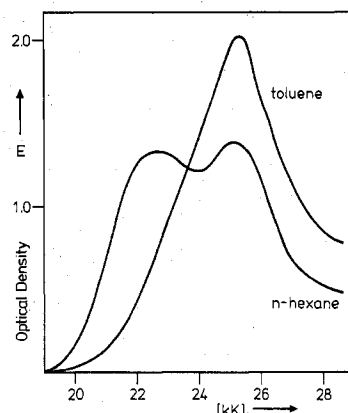
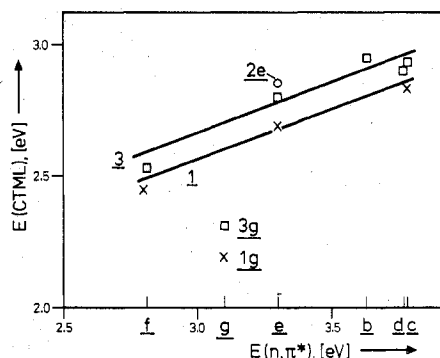


Figure 1.

and para-substituted derivatives^{9b}), and the carbene complexes ArC(OCH₃)Cr(CO)₅.^{9c} The complexes studied in this work show two types of dynamic processes: restricted rotation around the M-N bond and a 1,2-shift of the pentacarbonylmetal fragment along the N=N bond. The occurrence of the latter process is demonstrated by dynamic ¹H and ¹³C NMR spectra, whereas evidence for the former process comes from dynamic electronic absorption spectroscopy.

Results and Discussion

Synthesis. The recently published thermal reaction of M(CO)₅(THF) with the appropriate diazene^{3,4,10-12} has been used to prepare several of these complexes. However, we find also⁴ that in most cases the rate of reaction is increased if it is performed photochemically. This method was used to prepare the new complexes 1c, 2e, 3b, 3c, 3d, 3e, (2-Mepy)W(CO)₅ (Mepy = methylpyridine) (4), and (2-CNpy)W(CO)₅ (CNpy = cyanopyridine) (5). Purification was achieved by column chromatography on silica gel. In all compounds the nitrogen ligand is σ bonded to the metal as demonstrated by comparison of IR, UV, and NMR data with those of the published^{3,4,9,10} compounds (Tables I and II). The metal carbonyl IR absorptions of all pyrazoline complexes (1c, 3c, 3d) contain a split "E" band indicating deviations from local C_{4v} symmetry of the M(CO)₅ fragment. By analogy with the known structure of the corresponding tetracarbonyliron complexes¹³ we assume that the pyrazoline ligands are bonded to the metal via the N(1) nitrogen atom (Figure 1). The unsymmetrical coordination of the diazene ligand is most clearly demonstrated by the ¹H and ¹³C NMR data (see also Experimental Section) of, for example, the diazaborbornene complex 3b: the bridgehead protons give rise to two broad apparent singlets at δ 4.1 and 4.3 (relative to Me₄Si), the corresponding carbon atoms appear at δ 78.03 and 87.4, and the values for the free ligand are δ 4.7 and 75.5, respectively. Coordination of the 2-cyanopyridine via the cyano group is

Figure 2. Solvent dependence of low-energy absorption bands of (pyrid)Mo(CO)₅, 2e.Figure 3. Variation of the M \rightarrow diazene charge-transfer energy (CTML) of (diazene)M(CO)₅ complexes as a function of the $n_1 \rightarrow \pi^*$ energy of the free diazene: (1) M = Cr, (2) M = Mo, (3) M = W.

excluded on the basis of the same $\nu(\text{CN})$ frequency of 2230 cm^{-1} , in toluene, for the free and complexed ligand.

Room-Temperature Electronic Spectra. The lowest energy absorption band of the group 6B pentacarbonyl diazenes studied in this work shows a characteristic blue shift as the polarity of the solvent increases (Table II). The band moves within a range of 1900–3200 cm^{-1} on going from *n*-hexane to acetonitrile. In the case of Mo(CO)₅(pyrid) (pyrid = pyridazine), for example, the band apparently moves under the next absorption maximum on exchanging *n*-hexane for toluene as a solvent. This typical solvent effect is shown in Figure 2. The observed solvent dependence is comparable to the shift of 3800–4500 cm^{-1} observed for the CTML state of group 6B M(CO)₄(1,10-phen) (phen = phenanthroline) complexes on substituting cyclohexane for acetonitrile as the solvent.^{7,14} The transition energy of the low-energy band is strongly dependent on the diazene ligand. With tungsten as the metal center, a difference of 5100 cm^{-1} is realized on exchanging 2,3-diazaborbornene (Figure 1, b) for benzo[*b*]cinnoline (Figure 1, g). Thus, the two lowest bands become separated by 5000–7000 cm^{-1} in the case of the azobenzene and benzo[*c*]cinnoline complexes (Table II). The continuous decrease in absorption energy from 3b to 3g parallels the expected lowering of the $\pi^*(\text{N}=\text{N})$ level of the free diazenes on going from b to g.¹⁵ A plot of this energy vs. that of the $n \rightarrow \pi^*$ transition of the free ligand, taken as a rough measure for the energy of the $\pi^*(\text{N}=\text{N})$ level, clearly shows that both chromium and tungsten complexes experience the same influence of the diazene ligand (Figure 3).

Except for the benzo[*c*]cinnoline compounds 1g and 3g, an approximate linear correlation is observed. For the same ligand, e.g., pyridazine (Figure 1, e), the transition energy is

Table II. Solvent^a and Temperature^b Dependence of Electronic Absorption Bands of (diazene)M(CO)₂ Complexes

complex	<i>n</i> -hexane			toluene			chloroform			acetonitrile			22–25 °C			–185 °C			behavior on cooling
	CTML	LF	CTML	CTML	LF	CTML	CTML	LF	CTML	CTML	LF	CTML	CTML	LF	CTML	CTML	LF		
1a	<i>d</i>	25.4 (~5.4)	<i>d</i>	25.7 (~5.6)															<i>f</i>
1b	sh?	25.2 (7.95)			25.6 (7.8)														(Figure 6a) ^g
1c	22.8	25.2 sh	~24.0 sh	~24.9 sh															(Figure 6c) ^g
			(6.8)	(6.8)															(Figure 6b) ^g
1e	21.7 (5.22)	24.3 (4.71)	23.9 (6.31)	24.4 (6.39)	23.8 (6.23)	24.3 (6.4)	24.9 (6.32)	25.3 (6.44)	21.4	23.9	25.0–25.7	19.7	25.0						(Figure 6d) ^g
1f	19.8 ^e	25.6 ^e																	(Figure 6b) ^d
1g	17.7 (3.9)	24.9 (2.0)	19.0 (4.3)	24.5 (3.0)	25.6 (3.6)														Figure 6a
2e	23.1 (5.1)	25.4 (5.4)	<i>d</i>	25.5 (8.7)	26.0 (8.66)	<i>d</i>	<i>d</i>	26.7 (8.22)	23.8 sh	25.6	25.6	<i>d</i>	26.3						Figure 6c
3b	~23.7 sh	25.7 (9.72)	<i>d</i>	25.9 (9.31)	26.0 (8.66)	<i>d</i>	<i>d</i>	26.7 (8.22)	23.8 sh	25.6	25.6	<i>d</i>	25.9						Figure 6c
	(6.3)																		Figure 6c
3c	23.6 (9.35)	25.5 sh	24.1 (8.76)	25.4 (8.5)	24.0 (9.12)	25.4 sh (8.45)													Figure 6c
		(7.73)																	Figure 6c
3d	23.4 (9.18)	25.5 sh	23.9 (8.01)	25.5 (7.28)	23.6 (8.63)	25.5 sh (7.3)													Figure 6c
		(6.92)																	Figure 6b
3e	22.6 ^e	25.0 ^e	<i>d</i>	25.1 (8.57)	~23.0 sh	25.1 (8.88)	<i>d</i>	25.9 br	22.5	25.0	25.0	23.5 sh	25.3						Figure 6d
					(~6.1)			(7.64)											Figure 6d
3f	20.4 (7.7)	25.8 (3.7)																	Figure 6d
3g	18.6 ^e	25.6 ^e	20.0 (6.3)	25.5 (4.2)	20.1 (5.7)	25.4 sh (4.1)													Figure 6d
		26.1		26.5 (4.3)		25.8 (4.3)													Figure 6d
						26.6 (4.4)													Figure 6d

^a At room temperature; band positions are $\times 10^3 \text{ cm}^{-1}$; numbers in parentheses are $\epsilon \times 10^{-3} [\text{L mol}^{-1} \text{ cm}^{-1}]$. CTML and LF designate the M \rightarrow diazene charge transfer and the ligand field absorptions, respectively; br = broad, sh = shoulder. ^b In 2,2-dimethylbutane/*n*-pentane (8:3) by volume. ^c Values from ref. 4. ^d Probably hidden under the LF band. ^e No ϵ values could be obtained because of poor solubility. ^f Shows only the usual sharpening. ^g Similar to spectrum indicated in parentheses.

Table III. Luminescence Data^a

complex	emission max, ^b $\text{cm}^{-1} \times 10^3$	intens
3c	16.1 (2.3)	weak
3d	~16.0	very weak
3e	17.2 (2.7)	strong
3f	18.0 (2.7)	moderate
3g	18.2 (1.6)	moderate

^a In 2,3-dimethylbutane/*n*-pentane (8:3 by volume) at 77 K; excitation at $23.2 \times 10^3 \text{ cm}^{-1}$. Data known for free ligands (see Figure 1): (e) $23.8 \times 10^3 \text{ cm}^{-1}$; (g) $13.6, 20.4 \times 10^3 \text{ cm}^{-1}$; (s) excitation spectra match absorption spectra at $< 33.3 \times 10^3 \text{ cm}^{-1}$. ^b Un-corrected for change in sensitivity of detector with wavelength; half-bandwidth in parentheses.

Table IV. Temperature-Dependent $\nu(\text{CO})$ Bands of $\text{M}(\text{CO})_2(\text{pyrid})$ Complexes^a

complex	$T, ^\circ\text{C}$	$\nu(\text{CO})$ ("E")	$\nu(\text{CO})$ ("A ₁ ")
1e ^b	25	1944	1919
	-30	1945, 1938	1918
2e ^c	25	1947	1922
	-50	1947, 1941	1919
	-70	1947, 1941	<i>d</i>

^a Band positions in cm^{-1} ; "A₁" is related with the CO group trans to the pyridazine ligand.³⁸ ^b In *n*-hexane. ^c In 2,2-dimethylbutane/*n*-pentane (8:3 by volume). ^d Too weak to be precisely determined, since complex has partially precipitated.

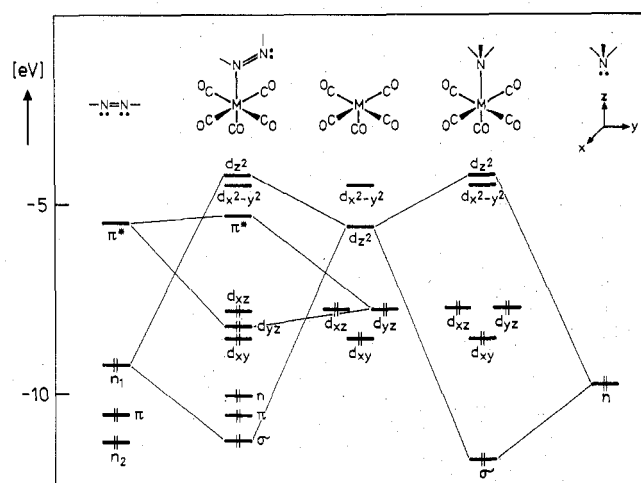


Figure 4. Simplified molecular orbital diagram for (*cis/trans*-diazene)- and (amine) $M(\text{CO})_5$ complexes. See also ref 18.

related to the metal in the order $\text{Mo} > \text{W} > \text{Cr}$ as observed for the CTML transitions in $M(\text{CO})_4(1,10\text{-phen})$ complexes.⁷

On the basis of the above observations, in particular their analogy to $\text{W}(\text{CO})_5(4\text{-R-py})$ ^{9,16} and $M(\text{CO})_4(1,10\text{-phen})$, we assign the lowest energy absorption band in the room-temperature solution spectra of group 6B pentacarbonyl diazenes to an $M \rightarrow$ diazene charge-transfer transition. The next lowest energy absorption band is only slightly influenced by variation of the diazene ligand (Table II); for the tungsten and chromium complexes the largest difference in *n*-hexane is 1100 and 1300 cm^{-1} , respectively. For a given diazene ligand the transition energy varies with the metal in the order $\text{Mo} > \text{W} > \text{Cr}$; the ordering $\text{Mo} > \text{W}$ as observed for the unique pyridazine complexes contradicts simple ligand field predictions but is in line with other (amine) $M(\text{CO})_5$ compounds having LF bands in the order $\text{Mo} \geq \text{W}$.^{5c,16} Solvent dependence is small, with maximal shifts of 1000 cm^{-1} on going from *n*-hexane to acetonitrile. These observations are consistent with the characteristics of ligand field transitions. We therefore assign this absorption band to a metal-centered $d_{yz,xz} \rightarrow d_{x^2-y^2,z^2}$ transition (LF, *vide infra*).

In addition to this experimental evidence, the band assignments are supported by the following qualitative discussion of the electronic structure of these compounds: The essential features of the frontier orbitals of an $M(\text{CO})_5$ (*cis/trans*-diazene) complex are easily deduced by comparison with an $M(\text{CO})_5$ (amine) compound. Figure 4, shows a simplified molecular orbital diagram describing the interaction of an amine or diazene with a square-pyramidal $M(\text{CO})_5$ fragment.^{17,18} The stabilization of the amine lone-pair orbital upon complex formation is approximately 2 eV as was deduced from photoelectron spectra of $\text{W}(\text{CO})_5(\text{NH}_3)$.¹⁸ Due to *ab initio* SCF-MO calculations on $\text{Cr}(\text{CO})_5(\text{NH}_3)$ and $\text{Cr}(\text{CO})_5(\text{PH}_3)$, the highest occupied orbitals have some ($\sim 30\%$) $\text{CO}(2p)$ character but are predominantly localized on the metal ($3d$, $\sim 70\%$).¹⁸ Accordingly, the lowest electronic transitions in $\text{Cr}(\text{CO})_5(\text{L})$ ($\text{L} =$ amine, phosphine) were assigned^{17a} as ligand field (LF) $d_{yz,xz} \rightarrow d_{x^2-y^2,z^2}$. If L is an aromatic amine like a substituted pyridine, the ligand may have a low-lying π^* orbital in the region of the antibonding metal levels giving rise to a low-energy $M \rightarrow$ pyridine charge-transfer absorption (CTML). Very recently it has been shown that the corresponding transition energy decreases as more electron-withdrawing groups are introduced in the 4-position of the pyridine ring.^{9,16}

The relevant frontier orbitals of an $\text{N}=\text{N}$ group are depicted on the left side of Figure 4. For the diazenes in Figure 1, a-g, the nonbonding n_1 orbital lies between 8 and 9 eV and the n_2 level at 10–12 eV.^{19,20} Both orbitals may be thought to arise

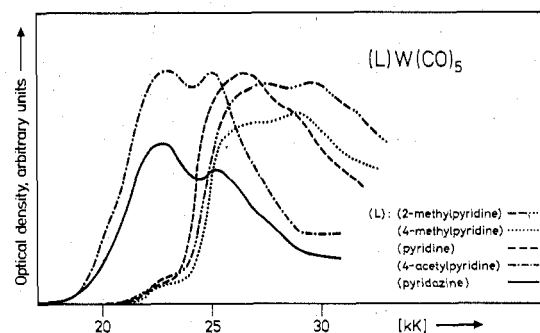


Figure 5. Electronic absorption spectral changes observed on variation of L in $(\text{L})\text{W}(\text{CO})_5$ complexes; in *n*-hexane.

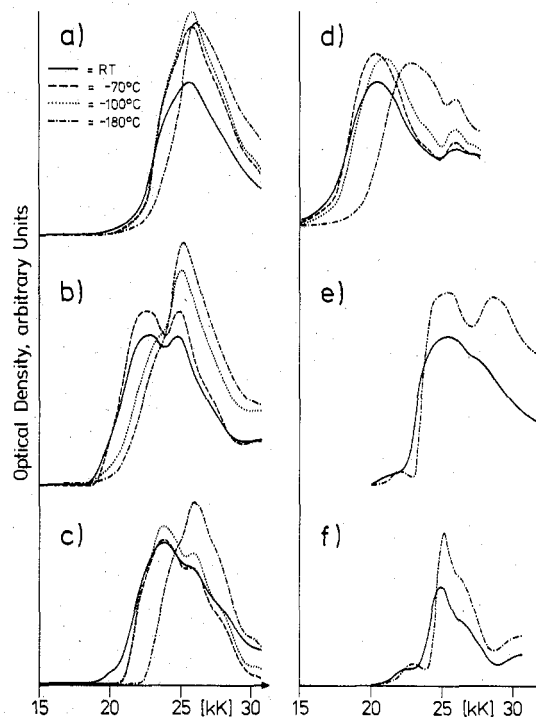


Figure 6. Temperature dependence of low-energy absorption bands of $(\text{L})\text{W}(\text{CO})_5$ in 2,2-dimethylbutane/*n*-pentane (8:3 by volume): (a) $\text{L} = 2,3$ -diazanorbornene (b), (b) $\text{L} =$ pyridazine (e), (c) $\text{L} = 4$ -isopropyl-3,3-bis(methoxycarbonyl)-1-pyrazoline (c), (d) $\text{L} =$ *cis*-azobenzene (f), (e) $\text{L} =$ pyridine,⁹ (f) $\text{L} =$ piperidine.⁹

from interaction between the two "lone pairs" localized on each nitrogen atom. Complex formation via n_1 should be analogous to the amine case and is expected to decrease the n_1 - n_2 interaction. As a consequence thereof, the n_2 orbital should be raised in energy and the corresponding n level of the complex is most likely above the $\pi(\text{N}=\text{N})$ orbital. The availability of a low-lying $\pi^*(\text{N}=\text{N})$ orbital distinguishes the diazene complex from the related amine complex: it allows the formation of a weak π back-bond²¹ via the d_{xz} (or d_{yz}) orbital²⁵ and is responsible for the occurrence of a low-energy $M \rightarrow$ diazene charge-transfer transition. However, in the case of an appropriately substituted aromatic amine, a low-lying π^* level may be also available and the main features of the electronic structure should be the same as for the diazene complex. Accordingly, it seems not surprising that shape and position of the low-energy absorption bands are nearly identical for $\text{W}(\text{CO})_5(4\text{-Acpy})$ ($\text{Acpy} =$ acetylpyridine) and $\text{W}(\text{CO})_5(\text{pyrid})$. Figure 5 shows the corresponding spectral changes obtained by exchange of the piperidine ligand by pyridine, 4-acetylpyridine, and pyridazine. Included are the spectra of (2-methylpyridine)- and (4-methylpyridine)-pentacarbonyltungsten which will be discussed later.

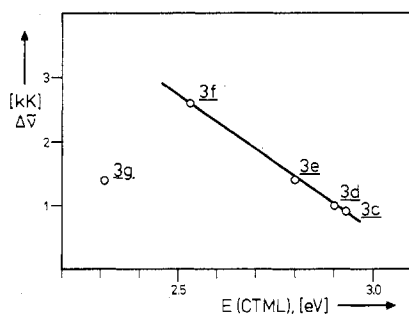


Figure 7. Hypsochromic shift of the CTML band of (L)W(CO)₅ upon cooling to $-185\text{ }^{\circ}\text{C}$ as a function of the CTML energy at room temperature.

Temperature Dependence of Electronic Absorption Spectra.

All the *cis*-diazene complexes studied in this work exhibit a characteristic temperature dependence of the low-energy absorption bands. The CTML band is shifted by $1\text{--}2.6 \times 10^3\text{ cm}^{-1}$ and the LF band only by $0.2\text{--}0.7 \times 10^3\text{ cm}^{-1}$ to higher energy upon cooling from room temperature to $-185\text{ }^{\circ}\text{C}$ in 2,2-dimethylbutane/*n*-pentane (8:3) as a solvent. Depending on the diazene ligand involved, three types of spectral changes are observed (Figure 6; Table II) upon cooling.

The broad band (CTML + LF) of the diazanorbornene complexes **1b** and **3b** sharpens up and decreases in its oscillator strength by approximately 20% (after correction for solvent contraction) (Figure 6a). This decrease most likely originates from a diminished intensity of the CTML absorption since the LF bands in no case show a decrease upon cooling (Figure 6d,f). The pyrazoline and pyridazine complexes **1c**, **1e**, **3c**, **3d**, and **3e** exhibit the second type of behavior (Figure 6b,c). Since for both series of compounds the CTML absorption is clearly separated from the LF band, the hypsochromic shift of the former produces a one-band spectrum similar to that of the diazanorbornene complex **3b** at room temperature. The oscillator strength of the CTML band (LF assumed to be constant) is not changed for the pyridazine complex but decreases by approximately 20% for the pyrazoline complexes. The third type of behavior is shown by the *cis*-azobenzene and benzo[*c*]cinnoline complexes **1g**, **3f**, and **3g** (Figure 6d). In this case the separation of the CTML and LF bands is large enough to prevent their overlap despite the large shifts of $1.4\text{--}2.6 \times 10^3\text{ cm}^{-1}$. The oscillator strength of the CTML band does not change for **3f** and **3g** but decreases by about 20% for **1g**.

The observed changes in the intensity of the CTML band seem to be determined by the energy of the $\pi^*(\text{N}=\text{N})$ orbital of the free ligand. Diazenes with high-lying π^* levels (Figure 1, **b-d**) give rise to a CTML band of decreasing intensity upon cooling solutions of the corresponding complex. No changes or only weak changes are found for complexes containing diazenes with low-lying π^* orbitals (Figure 1, **e-g**). As in the case of the dependence of the CTML energy on the energy of the diazene $n_1 \rightarrow \pi^*$ state (Figure 3), the complex **1g** does not follow this relationship.

Inspection of Table II clearly reveals that the amount of the hypsochromic shift of the CTML band is related to the energy of this transition. A plot of $\Delta\bar{\nu}$, defined as $\bar{\nu}_{\text{max}}(\text{CTML}, -185\text{ }^{\circ}\text{C}) - \bar{\nu}_{\text{max}}(\text{CTML}, \text{room temp})$, vs. the CTML energy value at room temperature gives a linear correlation for the tungsten compounds **3c-3f** (Figure 7).²⁶ The lower this energy, the larger is the measured $\Delta\bar{\nu}$ value. As in the case of the CTML energy dependence on the (n, π^*) energy of the free diazene (Figure 3), the benzo[*c*]cinnoline complex does not follow this linear correlation.

From this experimental evidence it is assumed that the behavior on cooling is largely determined by the energy of the

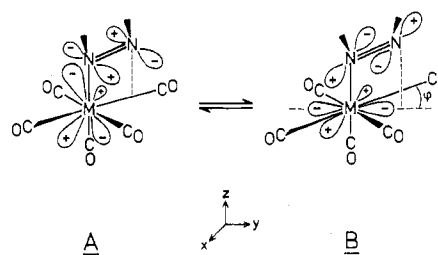


Figure 8. Rotational orientations of the diazene ligand relative to the $\text{M}(\text{CO})_5$ fragment: (A) eclipsed conformation ($\xi = 0^{\circ}$); (B) staggered conformation ($\xi = 45^{\circ}$).

lowest unoccupied molecular orbital (LUMO) of the complex which should have predominantly $\pi^*(\text{N}=\text{N})$ character. If this assumption is valid, other σ complexes of n donors with low-lying π^* levels should have qualitatively the same temperature-dependent electronic absorption spectra. The spectral changes observed for $\text{W}(\text{CO})_5(\text{py})$ (Figure 6e; compare also ref 9) point already to a similar behavior since they differ markedly from the usual sharpening and weak blue shift as found, for example, for $\text{W}(\text{CO})_5(\text{pip})$ (pip = piperidine), a complex without a corresponding low-energy ligand π^* orbital (Figure 6f; compare also ref 9). The compound $\text{W}(\text{CO})_5(4\text{-Acy})$ finally shows exactly the same temperature-dependent spectrum as the pyridazine complex **3e** and thus confirms the necessary presence of a low-lying LUMO to observe this temperature effect.

The dominating role of this π^* orbital for the behavior upon cooling suggests that the latter is largely determined by the amount of π bonding between the metal and the $\text{N}=\text{N}$ group. This would lead to some double-bond character of the $\text{M}-\text{N}$ bond and therefore to restricted rotation around this bond. As a consequence thereof we assume that this type of complex exists in solution as two conformers. Conformer A represents the higher energy eclipsed conformation in which the $\text{N}=\text{N}$ bond is aligned along one equatorial $\text{M}-\text{CO}$ axis (Figure 8). In this conformation the destabilizing steric interaction between the lone-pair orbital on the noncomplexed nitrogen and the equatorial CO groups may be balanced to some degree by the stabilizing effect of the, however weak, π bond.

The latter should be strongest in this conformer due to maximum interaction of the $\pi^*(\text{N}=\text{N})$ and metal d_{yz} orbitals.²⁵ This electronic stabilization of the eclipsed conformer should be predominantly responsible for the possibility to detect it by UV spectroscopy. Rotation around the $\text{M}-\text{N}$ bond by an angle of 45° is expected to slightly decrease this interaction²⁷ but strongly reduce the steric hindrance. The resulting staggered conformer B should, therefore, have a lower energy content than A. The relative concentrations of both conformers depend on the difference of their free energies.³⁰ A simple estimation³¹ based on the concentration changes observable by UV spectroscopy gives a very rough value of $\Delta G^{\circ} = 0.3\text{--}1\text{ kcal/mol}$. It is therefore assumed that the room-temperature spectrum of a (diazene)pentacarbonylmetal complex arises from a mixture of the two conformers A and B with the latter in excess over A. Upon cooling, the equilibrium is shifted even more in favor of the staggered conformer B and the spectrum at $-185\text{ }^{\circ}\text{C}$ should be that of almost pure B. Due to the overlapping CTML bands and their large bandwidth, e.g., $5 \times 10^3\text{ cm}^{-1}$ for **3f**, it is not possible to determine the ratio of both conformers, however. The hypsochromic shift of the CTML band on going from A to B may be due to the lower ground-state energy of B if the same CTML excited-state energies are assumed for both conformers. From Figure 7 it is evident that a large shift of the CTML band is connected with a low energy of the ligand π^* orbital. The lower this energy, the larger should be the double-bond character of the $\text{M}-\text{N}$ bond and the higher should be the

concentration of the eclipsed conformer A. Introduction of a substituent in the α position of the complexed nitrogen atom should lead to a strong steric repulsion of this group by the equatorial CO groups and therefore shift the conformational equilibrium in favor of the staggered conformer B. This should result in a lower concentration of A and therefore in a smaller shift of the CTML band upon cooling. Thus, the dominating electronic influence of the ligand π^* orbital may be compensated to some degree by the opposite steric effect of a substituent in the α position. These considerations are experimentally supported by the different temperature dependencies of the $W(CO)_5$ complexes of 2-methylpyridine and 4-methylpyridine. Whereas the latter exhibits a shift of $1.4 \times 10^3 \text{ cm}^{-1}$, similar to that of $\sim 1.1 \times 10^3 \text{ cm}^{-1}$, as found for the unsubstituted pyridine complex (Figure 6e), the former gives only a shift of $0.5 \times 10^3 \text{ cm}^{-1}$. Further support comes from comparison of the absorption spectra of (4-CNpy)W(CO)₅ and (2-CNpy)W(CO)₅ in isooctane at room temperature. Due to the strong electron-withdrawing property of the cyano group, the 4-cyano-substituted complex exhibits the CTML band at the relatively low energy of $22.0 \times 10^3 \text{ cm}^{-1}$.⁹ In the 2-cyano isomer this band is shifted by $3.3 \times 10^3 \text{ cm}^{-1}$ to higher energy and appears at $25.3 \times 10^3 \text{ cm}^{-1}$. These data clearly demonstrate the strong steric influence of the α substituent on the CTML energy by locking the conformational equilibrium predominantly into the staggered form B. The (2-Mepy)- and (4-Mepy)W(CO)₅ complexes show the same type of behavior: the former has the CTML band $0.6 \times 10^3 \text{ cm}^{-1}$ at higher energy than the latter ($28.5 \times 10^3 \text{ cm}^{-1}$). This steric effect should be even stronger in the case of a *trans*-diazene complex resulting in a very low concentration of the eclipsed conformer. Accordingly no change, except the usual sharpening, is observed for the lowest absorption band of (*trans*-dicyclohexyldiazene)pentacarbonylchromium (**1a**) upon cooling.

It is interesting to note that the azobenzene and benzo-[c]cinnoline complexes **3f** and **1g** have two bands in the region of the LF transitions (Table I, Figure 6d). Upon cooling, the lowest in energy of these bands gains markedly in intensity while the other almost disappears (Figure 6d). As discussed above, these complexes should have the greatest amount of π bonding in the eclipsed conformation A. As a consequence of the larger energy gap between the d_{yz} and d_{zx} orbitals, two different LF bands may be seen (Figure 4). Upon cooling, the energy gap should be decreased due to the weaker π bonding in the staggered conformer and the intensity of the higher energy LF transition should diminish, as found experimentally.

By analogy with other (L)W(CO)₅ compounds⁹ it is expected that the tungsten diazene complexes should exhibit singlet-triplet LF absorptions slightly red shifted from the singlet-singlet bands.³² The room-temperature solution spectra do not readily allow the S \rightarrow T absorptions to be seen, but on cooling, bands in the appropriate region are seen for the tungsten diazene complexes of *cis*-azobenzene and benzo-[c]cinnoline, **3f** and **3g**, at ~ 24.1 (sh) and ~ 23.2 (sh) $\times 10^3 \text{ cm}^{-1}$, respectively (Figure 6d). The pyrazoline complexes **3c** and **3d** have a shoulder on the lower energy side of the CTML band. This shoulder is difficult to see at room temperature but is easily recognized at $\sim 22.5 \times 10^3 \text{ cm}^{-1}$ in the -100°C spectrum (Figure 6c). Below -100°C the CTML band shifts and diminishes and the shoulder disappears. Due to the location of the band to the lower energy side of the CTML band, due to the relatively low energy position compared to the "singlet-triplet" LF band, and due to the unusual behavior on cooling, these shoulders may be preliminarily assigned as singlet-triplet CTML absorptions.

Bands attributable to LF or CTML triplets were not found

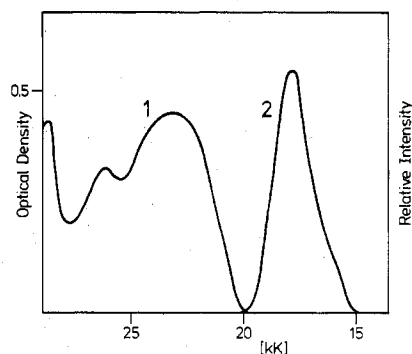


Figure 9. Electronic absorption (curve 1) and emission (curve 2) spectrum of (*cis*-azobenzene)W(CO)₅, **3f**, in 2,3-dimethylbutane/*n*-hexane (8:3 by volume) at 77 K.

for W(CO)₅(diazanorbornene). The shoulder at $\sim 23.5 \times 10^3 \text{ cm}^{-1}$ seen at -185°C in W(CO)₅(pyrid) most probably originates from the CTML state; however, it may be also of LF singlet-triplet character. The spectra of the chromium and molybdenum diazene complexes do not possess features analogous to the triplet absorptions observed for the tungsten compounds.

The above observations may be generalized as follows. If a W(CO)₅(*cis*-diazene) complex has a CTML absorption that is well removed from the lowest LF band, then the singlet-triplet LF transition will be observed and a singlet-triplet CTML band will not be found. If the broad CTML absorption covers the expected position of the LF triplet, then the charge transfer apparently acquires triplet character and the spectrum will exhibit a CTML singlet \rightarrow triplet absorption.

Luminescence Measurements. Since cooling of solutions of M(CO)₅(*cis*-diazene) complexes results in marked changes in the electronic absorption spectra, causing in some instances an apparent change in the nature of the lowest excited state, one is led to speculate on the effect that this has on the emission properties of the complexes. Accordingly we attempted to measure the luminescence of these complexes in solution at 77 K and in a few instances also at room temperature. In EPA the majority of the samples decompose and the characteristic emission maxima^{3c} of W(CO)₅(EtOH) and/or W(CO)₅(Et₂O) at $\sim 18.7 \times 10^3 \text{ cm}^{-1}$ are observed. Only in 2,3-dimethylbutane/*n*-pentane did five of the diazene complexes give rise to emission at 77 K but in no case at room temperature either in solution or in the solid state. The data are summarized in Table III, and Figure 9 shows the absorption and emission spectrum of the *cis*-azobenzene complex **3f**. Due to the fact that some of the emissions occur at too high energy, e.g., **3f**, to arise from the related CTML states and because the relative energetical ordering does not correspond to that expected from the ranking of the CTML absorptions, it can be concluded that emission does not in every case come from a CTML excited state as was found for (4-Y-py)W(CO)₅ for Y = cyano, acetyl, benzoyl, and formyl by Wrighton, Abrahamson and Morse.^{9a} The reported emission maxima for these latter complexes are in the range 17.0 – $15.2 \times 10^3 \text{ cm}^{-1}$.⁹ From the corresponding data of 18.0 and $18.2 \times 10^3 \text{ cm}^{-1}$ for the *cis*-azobenzene and benzo-[c]cinnoline complexes **3f** and **3g** and from the observation of probable singlet-triplet LF absorption bands at -185°C we propose that emission in this case originates from states of increased LF character. The absorption spectra of the pyridazine complex **3e** and of (4-Ac-py)W(CO)₅ show an almost identical temperature dependence, as already mentioned, and have very similar emission energies of 17.2 and $17.0 \times 10^3 \text{ cm}^{-1}$, respectively. From this evidence we assume that the emitting state of **3e** has CTML character. The two pyrazoline

Table V. Temperature Dependence of ^{13}C NMR Spectra^a

species	T, °C	C(1),C(1)'	C(2),C(2)'	C(3),C(3)'	C(4),C(4)'	C(5),C(5)'	C(6),C(6)'
g	room temp	145.8	131.9	131.6	129.4	121.6	121.1
1g	room temp		132.6	130.8	130.1	121.6	
	-60		133.4	130.9	129.4	120.8	
			144.9 ^b	131.7	129.9	121.4	
3g	room temp		133.1	131.8	130.4	121.7	
	-60		132.2	131.1	130.4	121.0	
			133.9	131.9		122.3	

^a In CDCl_3 solution; chemical shifts in δ values relative to Me_4Si as internal standard; see also Figure 11 and ref. 4. ^b Weak signal.

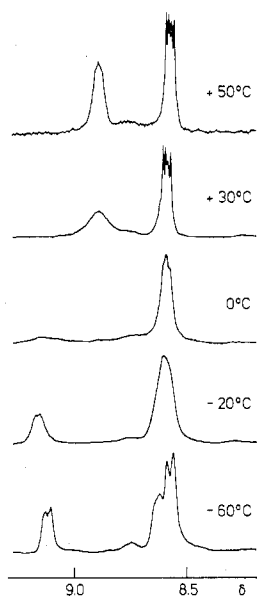


Figure 10. Temperature-dependent 270-MHz ^1H NMR spectra of (benzo[*c*]cinnoline) $\text{Cr}(\text{CO})_5$, **1g**, in CDCl_3 . δ values are relative to CHCl_3 , δ 7.27, as internal standard.

complexes **3c** and **3d** have weak emission bands at energies that seem too low for LF states and which probably arise from the CTML triplets already discussed.

Infrared Spectroscopy. Additional evidence for the existence of a conformational equilibrium (Figure 8) for $\text{M}(\text{CO})_5$ - (diazene) and related complexes should be obtainable also from physical measurements other than electronic. We therefore have examined the temperature dependence of the $\nu(\text{CO})$ IR absorptions. A basic experimental difficulty is the poor solubility of these complexes in hydrocarbon solvents, the medium in which the most significant changes were observed by electronic spectroscopy. It was therefore not possible to measure spectra at temperatures lower than -70°C .

Due to the presence of restricted rotation around the metal–nitrogen bond, the local symmetry at the metal cannot be approximated by C_{4v} which would lead to three $\nu(\text{CO})$ bands ($2A_1 + E$).^{36,37} Most of the diazene complexes at room temperature, therefore, exhibit a weak “ B_1 ” mode and a split “ E ” band,³⁸ whereas the pyridazine and diazanorbornene compounds, e.g., **2e**, **3b**, show an unsplit “ E ” band and no “ B_1 ” mode (Table II). Upon cooling solutions of the chromium or molybdenum pyridazine complex **1e** or **2e**, two changes were observed in the IR spectra. The “ E ” band is split into two absorptions separated by 7 cm^{-1} for **1e** at -30°C and by 6 cm^{-1} for **2e** at -50°C .

The second change consists of a small but significant shift of the lowest frequency band, attributable to the symmetrical stretching mode (“ A_1^{22} ”) of the axial CO group, by 1 and 3 cm^{-1} for **1e** and **2e**, respectively. The splitting of the “ E ” band

indicates an increasing asymmetry of the pentacarbonylmetal fragment upon cooling which most probably arises from the slower rotation of the diazene ligand around the metal–nitrogen bond. The shift of the “ A_1^{22} ” band to lower frequency is in agreement with the increasing concentration of the staggered conformer B upon cooling; this is explained by the decreased metal–diazene π bonding in B as postulated from the electronic spectra. This weak shift is in accordance with the variation of the “ A_1^{22} ” frequencies in substituted $\text{W}(\text{CO})_5(4\text{-py})$: it was found that electron-withdrawing groups ($R = \text{CN}$) shift this band to a higher frequency³⁷ and that the metal–carbonyl absorptions are not very sensitive to slight changes in the amount of tungsten–pyridine π bonding.¹⁶ As was discussed above, small changes of π bonding can be better detected by electronic absorption spectroscopy.

Dynamic NMR Spectra. The ^{13}C NMR spectra of (benzo[*c*]cinnoline) $\text{M}(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}, \text{W}$) have been reported very recently.⁴ Four distinct signals were observed for the chromium complex (**1g**) and eight for the tungsten analogue (**3g**) in room-temperature CDCl_3 solutions. On the basis of these observations the authors concluded that in **3g** the $\text{M}(\text{CO})_5$ group is rigidly bonded to one nitrogen of the $\text{N}=\text{N}$ bond, whereas in the case of **1g** it may be “shuttling” back and forth between the two nitrogen atoms.⁴ This type of metal 1,2-shift along the $\text{N}=\text{N}$ bond has been demonstrated to occur in (2,3-diazanorbornene) $\text{Cr}(\text{CO})_2\text{Ar}$ ($\text{Ar} = \text{C}_6\text{H}_6$ etc.) by dynamic ^1H NMR spectroscopy.²²

We have reexamined the spectra of **1g** and **3g** and determined their temperature dependence (Table V).

Contrary to the reported⁴ different ^{13}C NMR data of **1g** and **3g** we observe four signals for both complexes at room temperature. However, eight lines are found for both compounds at -60°C . At this temperature the chemical shifts of **3g** agree well with those reported for room temperature⁴ except one signal at δ 129.4 which we do not observe and which most likely originates from the free ligand formed by partial decomposition of **3g**. This temperature dependence strongly suggests that the complexes **1g** and **3g** at room temperature undergo a 1,2-shift of the $\text{M}(\text{CO})_5$ group which is fast compared to the NMR time scale. The occurrence of this process is unambiguously demonstrated by the dynamic ^1H NMR spectra of **1g** in CDCl_3 (Figure 10).

At -60°C the spectrum contains three groups of signals at δ 9.12, 8.60, and 8.00 of integral ratio 1:3:4, respectively. The signal at δ 8.00, assigned to H^4 , H^5 , H^4 , H^5 , H^5 shows no temperature effect and is therefore omitted in Figure 10; it is only slightly shifted compared to the free ligand value of δ 7.85 (for the atom numbering see Figure 11). The two low-field signals at δ 9.12 and 8.60 are assigned to H^2 , H^2 and H^3 , H^3 , respectively, and clearly demonstrate that the diazene ligand is asymmetrically bonded to the metal; H^2 , H^2 and H^3 , H^3 absorb at δ 8.69 and 8.46 in the free ligand. Thus, at -60°C the metal is rigidly bonded to one nitrogen.

Upon warming up, the signals first broaden (-40 to 0°C), and then become sharp again ($+30$ to $+50^\circ\text{C}$) giving rise to two signals of ratio 1:1 at δ 8.59 and 8.92. The spectral

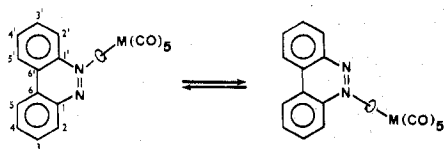


Figure 11. Dynamic behavior of (diazene)pentacarbonylmetal complexes as in, e.g., **1g** and **3g** ($M = \text{Cr}, \text{W}$).

changes observed are best explained by coalescence of the H^2 and H^2 signals due to the facilitated 1,2-shift of $\text{M}(\text{CO})_5$ upon increasing the temperature. At 50°C this "shuttling" is fast enough to give rise to a symmetrical spectrum. The detailed nature of this dynamic behavior is currently under investigation. From the observation that "shuttling" in the diaza-norbornene complex **3b** occurs at much higher temperature, it may be concluded that the activation energy of the process is higher in complexes with high-lying $\pi^*(\text{N}=\text{N})$ orbitals.

Figure 11 summarizes the dynamic behavior of (diazene)pentacarbonylmetal complexes: in addition to restricted rotation around the metal-nitrogen bond as demonstrated by the changes in the electronic absorption spectra at temperatures lower than -100°C , these compounds undergo a 1,2-shift of the $\text{M}(\text{CO})_5$ group at higher temperatures.

Experimental Section

All manipulations with organometallic compounds were carried out in an argon atmosphere. Solvents were distilled under argon from lithium aluminum hydride before use.

Irradiations were performed with a Philips HPK 125-W lamp using a Pyrex filter ($\lambda \geq 290 \text{ nm}$). Florisil was three-times degassed and argonated prior to use. The pyrazolines,^{39,40} benzo[*c*]cinnoline,⁴¹ 2,3-diazanorbornene,⁴¹ *cis*-azobenzene,⁴³ and dicyclohexyldiazene⁴⁴ were prepared according to literature methods. Pyridazine, 2-cyanopyridine, 2-methylpyridine, and the metal hexacarbonyls are commercially available.

IR spectra were obtained with a Perkin-Elmer Model 621 spectrophotometer; a modified Beckman low-temperature cell was used for measuring temperature-dependent spectra.

UV-visible absorption spectra were recorded with a Cary 17 spectrophotometer; temperature-dependent spectra were obtained with a SEM Brückel HRS 4001 C spectrophotometer equipped with cylindrical all-quartz cells surrounded by a cooling and vacuum jacket (Fa. Hellma); cooling was accomplished by nitrogen gas evaporated from liquid nitrogen by electrical heating which was relay controlled via a thermocouple inserted into the sample cell,⁴⁵ in all measurements room-temperature spectra were identical before and after cooling to -185°C demonstrating reversibility and stability of the samples.

NMR spectra were recorded with a Bruker WH-270 and a Varian A 60 A instrument. Variable-temperature samples were freeze-pump-thaw degassed before sealing the NMR tube; all δ values are in ppm relative to Me_4Si as internal standard.

Luminescence data were obtained with a Hitachi MPF-2A spectrophotometer; the photomultiplier was a Hamamazu R 456. Sample solutions were carefully degassed by repeated freeze-pump-thaw cycles in quartz tubes, before insertion into a 77 K all-quartz Dewar. The complexes **3f** and **3g** are particularly sensitive and care must be exercised to prevent decomposition during sample preparation.

Elemental analysis was performed by Mikroanalytisches Laboratorium Dornis & Kolbe, Mülheim/Ruhr.

Synthesis of (L)M(CO)₅. Two millimoles of the appropriate ligand were added to 2 mmol of photogenerated $\text{M}(\text{CO})_5(\text{THF})$ in tetrahydrofuran (THF) and the solution was irradiated. The color generally turned from yellow to red, except for **4** and **5** (yellow to orange); product formation was monitored by TLC and IR spectroscopy. The product was isolated by concentrating the solution at 0.1 Torr to about 10 mL followed by column chromatography on silica gel. In the case of complex **3b** the solution was evaporated to dryness, excess $\text{W}(\text{CO})_6$ was sublimed off at 30°C (0.1 Torr), and the residue was crystallized from *n*-hexane. The concentrated THF solutions of **2e** and **3e** were washed¹⁰ two times with 25 mL of H_2O and dried before chroma-

tography or crystallization. Elution agents, crystallization solvents, yields, and elemental analyses are given below.

1c: toluene, $\text{Et}_2\text{O}/n$ -hexane, 55%. Anal. Calcd for $\text{C}_{15}\text{CrH}_{16}\text{N}_2\text{O}_9$: C, 42.86; Cr, 12.38; H, 3.81; N, 6.66. Found: C, 42.94; Cr, 11.94; H, 3.86; N, 6.42. ^1H NMR (270 MHz, C_6D_6): 0.3 d ($J = 8 \text{ Hz}$, 3 H); 0.76 d ($J = 8 \text{ Hz}$, 3 H); 1.15 sept (1 H); 2.30 q (1 H); 3.08 s (3 H); 3.27 s (3 H); 3.90, 4.30 (centers of two quartets, CH_2 group).

2e: toluene/ethyl acetate (4:1), THF/*n*-hexane, 3%. Anal. Calcd for $\text{C}_9\text{H}_4\text{MoN}_2\text{O}_5$: C, 34.17; H, 1.26; N, 8.86. Found: C, 34.40; H, 1.33; N, 8.90.

3b: no chromatography, *n*-hexane, 60%. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_5\text{W}$: C, 28.57; H, 1.9; N, 6.67; W, 43.81. Found: C, 28.50; H, 1.65; N, 6.51; W, 43.51. ^1H NMR (60 MHz, C_7D_8): 4.1 s (br, 1 H); 4.3 s (br, 1 H); 1-0 m (6 H). ^{13}C NMR ($\text{CCl}_4/\text{C}_6\text{D}_6$): 87.4, 78.3 (C(1), C(4)); 22.87, 21.59 (C(5), C(6)); 41.54 (C(7)); 202.63 (trans CO); 197.84 (cis CO).

3c: toluene, $\text{Et}_2\text{O}/n$ -hexane, 90%. Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_9\text{W}$: C, 32.60; H, 2.89; N, 5.07; W, 33.33. Found: C, 32.45; H, 2.80; N, 5.08; W, 33.18. ^1H NMR (270 MHz, C_6D_6): 0.35 d ($J = 6 \text{ Hz}$, 3 H); 0.77 d ($J = 6 \text{ Hz}$, 3 H); 1.17 sept (1 H); 2.35 q (1 H); 3.09 s (3 H); 3.27 s (3 H); 3.96, 4.34 (centers of two quartets, CH_2 group).

3d: toluene, toluene/*n*-hexane, 40%. Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{O}_5\text{W}$: C, 36.86; H, 2.39; N, 4.78; W, 31.40. Found: C, 37.63; H, 2.30; N, 4.92; W, 32.06. ^1H NMR (270 MHz, C_6D_6): 2.74 s (3 H); 3.21 s (3 H); 3.79 t (1 H); 4.23, 4.44 (centers of two quartets, CH_2 group); 6.93 m (5 H).

3e: no chromatography (vide supra), *n*-hexane, 50%. Anal. Calcd for $\text{C}_9\text{H}_4\text{N}_2\text{O}_5\text{W}$: C, 26.73; H, 0.99; N, 6.93; W, 45.54. Found: C, 27.44; H, 1.10; N, 6.90; W, 44.92. ^1H NMR (60 MHz, CDCl_3): 9.43 m, 8.95 m (H(3), H(6)); 7.55 m (H(7), H(5)).

4: toluene/ethyl acetate (9:1), $\text{Et}_2\text{O}/n$ -hexane, 20%. Anal. Calcd for $\text{C}_{11}\text{H}_7\text{NO}_5\text{W}$: C, 31.65; H, 1.68; N, 3.36; W, 44.12. Found: C, 31.62; H, 1.93; N, 3.38; W, 43.92.

5: ethyl acetate, toluene/*n*-hexane, 50%. Anal. Calcd for $\text{C}_{11}\text{H}_4\text{N}_2\text{O}_5\text{W}$: C, 30.84; H, 0.93; N, 6.54; W, 42.99. Found: C, 30.60; H, 0.82; N, 6.42; W, 42.66.

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Registry No. **1a**, 56628-81-0; **1b**, 30931-84-1; **1c**, 67049-37-0; **1e**, 54070-89-2; **1f**, 58448-96-7; **1g**, 54218-73-4; **2e**, 67049-36-9; **3b**, 67049-35-8; **3c**, 67049-34-7; **3d**, 67049-33-6; **3e**, 65761-20-8; **3f**, 67049-32-5; **3g**, 54218-80-3; (2-Mepy)W(CO)₅, 39210-59-8; (4-Mepy)W(CO)₅, 17000-14-5; (py)W(CO)₅, 14586-49-3; (4-Acpy)W(CO)₅, 60166-30-5; (2-CNpy)W(CO)₅, 36252-42-3; **g**, 230-17-1.

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Bromyl Fluoride. Vibrational Spectra, Force Field, and Thermodynamic Properties

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Infrared spectra are reported for FBr¹⁸O₂ in the gas phase and for FBr¹⁶O₂ in Ne, N₂, and Ar matrices at 3.6 K. Isotopic shifts were measured for ⁷⁹Br-⁸¹Br and ¹⁶O-¹⁸O and were used for the computation of a valence force field. Thermodynamic properties were computed for FBrO₂ and FClO₂ in the range 0–2000 K.

Introduction

Bromyl fluoride was first synthesized by Schmeisser and Pammer^{1,2} in 1955. Because of its low thermal stability and high reactivity, this compound had been only poorly characterized and was not further studied until 1975. In 1975, Gillespie and Spekkens published³ the Raman spectra of solid and liquid FBrO₂ and proposed a monomeric pyramidal structure, similar to that⁴ of FClO₂. Using Raman frequencies reported³ for liquid FBrO₂, Baran calculated⁵ a modified valence force field and mean amplitudes of vibration for FBrO₂, assuming all bond angles to be 108°. Very recently, Jacob succeeded⁶ in obtaining good gas-phase infrared spectra for FBrO₂ in spite of the fact that gaseous FBrO₂ possesses a half-life of only 30 min at 15 °C. He also prepared a sample of FBr¹⁸O₂ and reported preliminary infrared data for the gas and for the neat and the argon matrix isolated solid. Although the oxygen isotopic shifts were measured, no ⁷⁹Br-⁸¹Br isotopic shifts were given.²⁴

In this paper, we report higher resolution spectra and oxygen and bromine isotopic shifts for gaseous and for Ne, N₂, and Ar matrix isolated FBrO₂. In view of the interest^{3,5} in the nature of bonding in FBrO₂, a new force field computation

appeared warranted, particularly since the previously used⁵ frequencies significantly differ from those of gaseous FBrO₂ and since the previously assumed⁵ geometry of FBrO₂ was only a crude estimate. Furthermore, the availability of both oxygen and bromine isotopic shifts offered a unique opportunity to test the value of such additional data for the refinement of force fields for compounds, such as bromine oxyfluorides.

Experimental Section

The samples of FBrO₂ used for recording the gas-phase spectra were prepared, as previously described,⁶ by low-temperature co-condensation of BrF₃ and H₂O. The infrared spectra of gaseous FBrO₂ were recorded at 15 °C on a Perkin-Elmer Model 325 spectrophotometer in the range 4000–290 cm⁻¹ using a nickel cell with AgBr windows attached to an external mirror system (optical path length 110 cm).

The samples of FBrO₂ used for the matrix isolation study were obtained as a byproduct during a spectroscopic study⁷ of BrF₃O. The spectrometer and handling have been previously described.⁷

Results and Discussion

Infrared Spectra of Gaseous FBrO₂. A survey infrared spectrum of gaseous FBr¹⁸O₂ is shown in Figure 1. The corresponding spectrum of FBr¹⁶O₂ has previously been re-

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