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Supplementary Material Available: Table of data for new compounds[6] and crystallographic data on **3c** including tables of positional parameters, thermal parameters, bond lengths and angles, torsion angles and numbering schemes and packing diagram (17 pages); structure factor tables for **3c** (27 pages). Ordering information is given on any current masthead page.

High-Pressure Studies of Transition-Metal Complexes. 1. Induced Torsional Deformation in $Re_2Cl_8^{2-}$

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In complexes containing a metal-metal quadruple bond, such as $Re_2Cl_8^{2-}$, the ability to vary the rotational conformation, and the metal-metal distances, between the two ML_4 units is vital to understanding the role of δ-orbital interactions in determining structure, electronic state energies, and electronic transition intensities.[1-8] Variations in rotational conformation have been obtained heretofore by incorporating bridging ligands which force the complexes to adopt partially staggered geometries. This synthetic approach has yielded a series of complexes which nearly span the entire range of X-M-M-X torsional angles ($0° \leq \chi \leq 40°$).[5-13] However, no means of *inducing varying degrees of torsion in a specific complex* or of systematically altering M-M distance have been reported.

Recently Carroll et al.[14] reported the pressure dependence of the electronic spectrum of $[(C_4H_9)_4N]_2Re_2X_8$ ($X = Br^-, I^-$). With increasing pressure a new, red-shifted absorption band appears which is attributed to the fully staggered conformer ($\chi = 45°$). The intensity of this band increases relative to that of the eclipsed conformer as pressure is increased, while the transition energies remain essentially unchanged. This result is interpreted as a pressure-dependent shift in a two-state equilibrium between the potential surfaces of the two conformers. The observed red shift of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ absorption for the staggered conformer is in qualitative accord with both theoretical predictions[3,5,6] and experimental observations[5,6] of the behavior of these complexes as $\delta(d_{xy})$ overlap goes to zero at $\chi = 45°$. Quantitatively, the red shift with pressure[14] is much smaller than that which is expected[3] or observed[5] as χ approaches 45°. Concerning the observation[14] of substantial $\delta\delta^*$ absorption intensity at $\chi = 45°$, theoretical considerations[15,16] suggest that the $\delta\delta^*$ intensity should tend toward zero for fully staggered conformers. This view is supported by expermental results which demonstrate that, in $Mo_2Cl_4(PR_3)_4$ complexes, the $\delta\delta^*$ extinction coefficient decreases from 3110 M^{-1} cm^{-1} at $\chi = 0°$ to 210 M^{-1} cm^{-1} at $\chi = 40°$.[5] Clearly, these inconsistencies need to be understood.

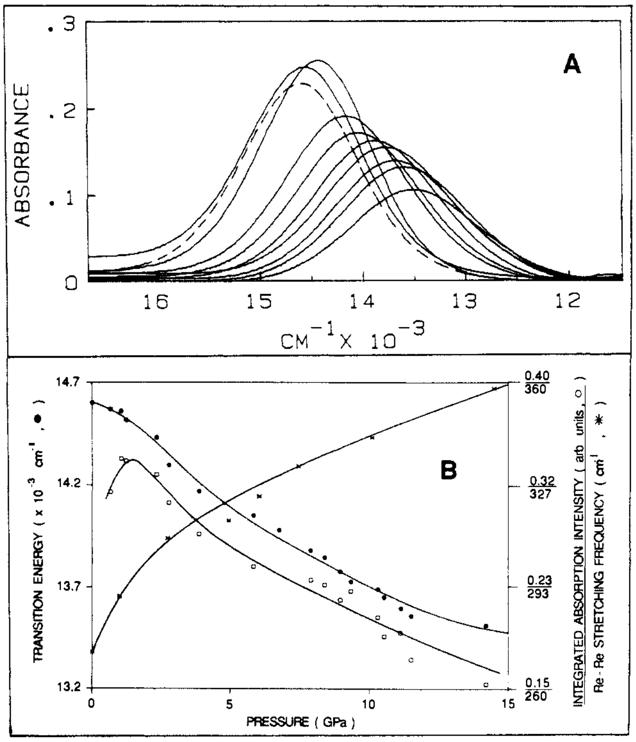

Figure 1. (A) $^1\delta\delta^* \leftarrow {}^1\delta^2$ electronic absorption spectra with increasing pressure for $Re_2Cl_8^{2-}$ in CH_2Cl_2. (---) Ambient pressure spectrum. (Scale is arbitrary for this spectrum, see text.) (—) With increasing shift of the absorption maximum to lower energy, the corresponding pressures are 1.04, 2.33, 3.86, 5.84, 7.90, 8.96, 10.3, 11.1, and 14.2 GPa, respectively. (B) Pressure dependence of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition energy maximum (●) integrated absorption intensity (○), and the Re-Re vibrational mode frequency (*). Integrated intensities were obtained from (maximum absorbance × fwhm) and are corrected for sample volume and concentration changes.

We now report the results of a pressure-dependent study of the electronic absorption and Raman spectroscopy of $Re_2Cl_8^{2-}$ in CH_2Cl_2 solution. The behavior observed is in marked contrast to that reported[14] for the Br^- and I^- complexes. Our results are best interpreted as arising from a gradual change in the torsional coordinate, accompanied by decreasing Re-Re distance, with increasing pressure due to pressure dependence of the shape of the ground-state potential surface.

The present studies were carried out on ~5 mM solutions of $[(C_4H_9)_4N]_2Re_2Cl_8$ in CH_2Cl_2 utilizing diamond anvil cells[17] to attain the static high pressures. Methylene chloride freezes at ~2.2 GPa (1 GPa = 10^4 atm) at room temperatures, and no discontinuities in the spectroscopic data for $Re_2Cl_8^{2-}$ were detected on passing through this phase transition. Absorption energy maxima and resonance Raman frequencies for the metal-metal stretching mode are reversible on cycling of the pressure, indicating negligible sample decomposition at high pressures. These data

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(16) It is possible that new states arising from δ-bonding interactions between d_{xy} and $d_{x^2-y^2}$ orbitals on adjacent metal centers[3] could give rise to new transitions having some intensity. However, such transitions have not been detected for rotamers with torsional angles as great as 40°.[5]

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are quantitatively reproducible independent of sample and regardless of the direction of pressure change. However, while all samples behave qualitatively the same with regard to absorption *intensity*, for experimental reasons related to diamond cell techniques, the intensity data presented in Figure 1 are from a single sample with points obtained only for *increasing* pressure.

The absorption spectra in the region of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition of $Re_2Cl_8^{2-}$ and the pressure dependence of the transition energy, integrated absorption intensity, and the metal–metal stretching frequency are illustrated in Figure 1. Unlike the abrupt two-state result reported for $Re_2I_8^{2-}$,[14] the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition undergoes a monotonic shift to lower energy with increasing pressure. The integrated absorption intensity increases slightly at low pressures (below ~2 GPa), then decreases monotonically with further increases in pressure.

Two factors affect δ overlap in $Re_2X_8^{2-}$ complexes, namely the torsional angle χ and the Re–Re distance. The observation of an initial increase in the intensity of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition suggests that at low pressures the δ overlap increases. This likely arises from shortening of the metal–metal distance prior to any significant torsional deformation. Resonance Raman measurements show that the ambient pressure Re–Re stretching frequency for the Cl^- complex is 272 cm^{-1}.[18,19] This vibration increases in frequency (to 357 cm^{-1} at ca. 15 GPa) over the entire pressure range (Figure 1). A continuous decrease in the metal–metal bond distance is probably the dominant factor in accounting for the frequency increase.

At pressures above ~2 GPa, the repulsive interactions of the halides begin to dominate the torsional potential, resulting in an increase in torsional angle and a net decrease in the amount of δ overlap.[1,11] Decreasing δ overlap should be manifested in two ways. First, the largely covalent $^1\delta^2$ ground state will be destabilized relative to the more ionic $^1\delta\delta^*$ excited state.[5] Second, the oscillator strength for the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition should decrease.[5,15]

Given the above theoretical considerations and spectroscopic results, our observations on $Re_2Cl_8^{2-}$ are consistent with an initial shortening of the Re–Re bond followed by a gradual change in the torsional angle and further shortening of the Re–Re bond with increasing pressure.

A final observation concerns the behavior of the $p\pi$ (Cl) to δ^* (Re) charge-transfer transition of $Re_2Cl_8^{2-}$. This transition remains at constant energy (313 nm) over the entire pressure range examined. The only effect of increasing pressure is to broaden the absorption envelope. If interactions between the medium and the molecular orbitals of the complex[20] were primarily responsible for the observed behavior of the $^1\delta\delta^* \leftarrow {}^1\delta^2$ transition, the energies of *all* electronic transitions would be altered by pressure. Rather, it appears that over the pressure range studied, the main effect of applied pressure is to induce structural changes which in turn alter the intramolecular properties, i.e., those determined by the extent of δ overlap between the two metal atoms.

The evidence developed herein strongly suggests that for $Re_2Cl_8^{2-}$ in CH_2Cl_2, elevated pressure results in an increase in the magnitude of the repulsive steric potential of the halides relative to the δ bonding potential[2] such that the minimum in the *net* torsional potential energy shifts smoothly along the torsional coordinate from the eclipsed to the staggered geometry. This picture is very different from that required to interpret the results of Carroll et al.,[14] which appear to involve a pressure-dependent equilibrium between two *distinct* conformers for $Re_2Br_8^{2-}$ and $Re_8I_8^{2-}$ in poly(methyl methacrylate). The disparity between our results and those of Carroll et al. may be due to the specific complexes examined, the media employed, or other effects. Further study of these systems is indicated and is proceeding in this laboratory.

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Formation of Furans and 1-Rhena-4-oxacyclohexa-2,5-diene Compounds from Reactions of Cp^*ReO_3 ($Cp^* = \eta^5\text{-}C_5Me_5$) with PPh_3 in Alkynes

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Recent literature shows an increasing interest in the chemistry of metal oxide compounds. Several new high-valent organometallic oxides have been reported, e.g., heptavalent Cp^*ReO_3 ($Cp^* = C_5(CH_3)_5$) and pentavalent dimer $(Cp^*ReO_2)_2$.[1] Here we describe (i) the reduction reactions of Cp^*ReO_3 with PPh_3 in alkynes, which may ultimately lead to furans, and (ii) the X-ray structure of an intermediate of this reaction, which features a unique six-membered ring built from two alkynes and one rhenium oxygen fragment.

As a means to create a vacant coordination site an oxo ligand can be removed from Cp^*ReO_3 by phosphines.[1a–c] When Cp^*ReO_3 was allowed to react with PPh_3 in pure alkynes for a short time at room temperature, and the resulting crude reaction mixture chromatographed over silica, rhenium monooxide adducts I were obtained in about 40% yield, eq 1, besides unconverted

$$\begin{gathered} Cp^*ReO_3 + PPh_3 + RCCR' \rightarrow \\ Cp^*(O)Re(RCCR') + OPPh_3 \quad (1) \\ \text{Ia,b: } R = R' = Me, Et \\ \text{Ic: } R = Me, R' = i\text{-}Pr \\ \text{Id: } R = Ph, R' = H \end{gathered}$$

Cp^*ReO_3. Adduct formation occurred with the alkynes mentioned (Ia–d); with sterically more demanding alkynes, e.g., $Me_3SiCCSiMe_3$ and 2,2,7,7-tetramethyloct-4-yne, $(Cp^*ReO_2)_2$ was formed.

Air-sensitive adducts I are oily substances, which are difficult to purify. They were formulated as the monooxide alkyne adducts on the basis of their ^1H NMR, ^{13}C NMR, and IR characteristics[2] and their subsequent reaction with $CpTiCl_3$ ($Cp = C_5H_5$). In the latter reaction complexes II, $Cp^*(Cl)_2Re(RCCR')$, were formed quantitatively, eq 2.

$$\begin{gathered} \text{Ia,b} + CpTiCl_3 \rightarrow Cp^*(Cl)_2Re(RCCR') + {}^1/_4(CpTiClO)_4 \\ \text{IIa,b: } R = R' = Me, Et^2 \end{gathered} \quad (2)$$

Elemental analysis of IIb combined with the stoichiometry of eq 2 suggests the general formula of I to be $Cp^*(O)Re(RCCR')$.[3]

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