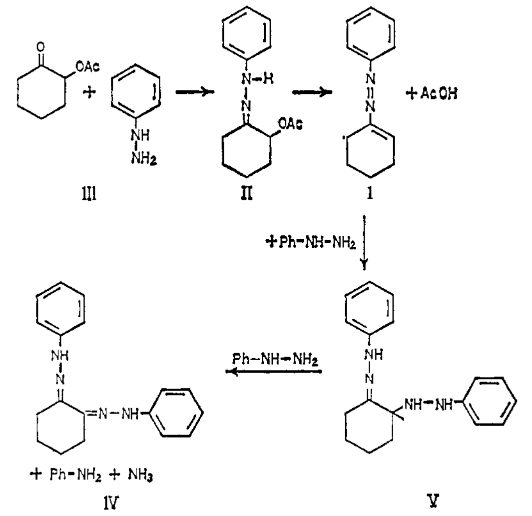

Figure 2.

stable when phenylhydrazine is added and does not seem to be affected by the presence of air. If AcOH is added to a solution of V in methanol or in benzene, IV is formed rapidly. This does not depend upon the presence of an oxygen atmosphere.[9]

This reaction was followed carefully by thin-layer chromatography. It was observed that immediately after the addition of AcOH the 1-(phenylazo)cyclohexene (I) was formed, together with increasing amounts of IV. The yield of IV was 40–42%. The azoalkene I was slowly transformed into other compounds.

If AcOH is added to a mixture of V and excess phenylhydrazine in benzene, IV is formed rapidly. No formation of I is observed.

In this case the yield is over 80%. Ammonium acetate and aniline are also obtained in significant amounts. Oxygen does not take part in this reaction also.[9]

The experiments reported above can be explained if it is assumed that in the presence of AcOH V reacts with phenylhydrazine, leading to aniline, NH_3, and IV. In the absence of phenylhydrazine, a part of V decomposes to phenylhydrazine and I (this reaction can be explained as the reverse of a 1, 4 addition of phenylhydrazine to the phenylazoalkene). The phenylhydrazine thus formed reacts with V leading to the formation of the osazone.

The presence of acetic acid seems to be a critical factor in the formation of this osazone. The reaction of I with excess phenylhydrazine leads to the formation of V, which on standing is not transformed into IV. If AcOH is added to the reaction mixture, however, the osazone is promptly formed. If II or III is used as the starting material for the reaction, the osazone is formed; it should be noted that in both cases 1 mole of AcOH is formed during the conversion of II into I.

The isolation of I, II, IV, and V from the reaction between α-acetoxycyclohexanone and phenylhydrazine, the thin-layer chromatographic examination of the variation with time of the relative amounts of these compounds in the reaction mixture, the significant yields obtained in the conversion of II into I, of I into V, and of V into IV, the thin-layer chromatographic examination of the relative rates of the conversions of I into V and then into IV, and of V into IV under equivalent conditions, allow us to conclude that the formation of osazones from α-acetoxy ketones and phenylhydrazine takes place according to the sequence presented in Figure 2.

Work is in progress to elucidate the mechanism of the conversion of V into IV.

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[9] During the transformation of V into IV oxygen is not absorbed from the atmosphere. A certain quantity of oxygen is absorbed if IV is present in the solution; at the same time, IV is transformed into its degradation products.

A Rhenium-to-Rhenium Triple Bond

Sir:

Recent studies of polynuclear (metal atom cluster type) complexes of rhenium(III) have led to the discovery and description of a Re(III)–Re(III) quadruple bond.[1–3] This bond, which occurs in the $Re_2X_8^{2-}$ (X = Cl, Br, SCN) species and also in the $XRe(O_2CR)_4ReX$ molecules,[4,5] is composed of a σ bond, two orthogonal π bonds, and a δ bond.[3,7] It is the latter, whose strength in $Re_2Cl_8^{2-}$ is estimated at ≤ 50 kcal/mole (about $\leq 14\%$ of the total Re–Re bond energy), which restricts the $Re_2X_8^{2-}$ species to their remarkable eclipsed rotomeric configuration.[8] The Re–Re quadruple bond has a length of 2.25 ± 0.01 A.[2,8–10] This may be compared to the lengths of the Re–Re bonds in various Re_3X_9 species, where the bond order[13,14] is 2, which are, on the average, 2.48 A.[15–20]

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[1] F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *Inorg. Chem.*, 4, 326 (1965).

[2] F. A. Cotton and C. B. Harris, *ibid.*, 4, 330 (1965).

[3] F. A. Cotton, *ibid.*, 4, 334 (1965).

[4] F. Taha and G. Wilkinson, *J. Chem. Soc.*, 5406 (1963).

[5] W. R. Robinson, unpublished studies in which a structure identical with that[6] of $Mo_2(O_2CCH_3)_4$, except for the addition of coordinated chloride ions at each end along the fourfold molecular axis, has been proved for $Re_2(O_2CC_6H_5)_4Cl_2$. The Re–Re distance is ~2.21 A, but this is subject to slight change upon further refinement.

[6] D. Lawton and R. Mason, *J. Am. Chem. Soc.*, 87, 921 (1965).

[7] C. B. Harris, Ph.D. Thesis, Massachusetts Institute of Technology, 1966, has carried out a semiquantitative extended Hückel calculation from which the numerical estimate of bond strength is derived.

[8] This configuration has been found for the $Re_2Cl_8^{2-}$ ion also in the pyridinium[9] and collidinium[10] (2,4,6-trimethylpyridinium) salts, in the $Re_2Br_8^{2-}$ ion,[11] and in the $Tc_2Cl_8^{3-}$ ion.[12]

[9] V. G. Kuznetzov and P. A. Koz'min, *Zh. Strukt. Khim.*, 4, 55 (1963). However, further refinement[10] of the structure using the published F_{obsd} values leads to slight changes in bond distances, bringing Re–Re to 2.25 ± 0.01 A.

[10] Unpublished work of W. R. Robinson.

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We wish to report the preparation, characterization, and structure determination of a compound with the formula $Re_2Cl_5(DTH)_2$ (DTH = 2,5-dithiahexane), in which the δ bond has been broken, while the σ and π bonds are retained, giving, therefore, a net bond order of 3.

The compound can be prepared by dissolving 150 mg of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$[1] in 15 ml of acetonitrile containing ~2 ml of 2,2′-dimethoxypropane (to assure anhydrous conditions) and ~1 ml of DTH, with warming. The resulting green solution was refluxed under nitrogen for ~70 hr during which time it turned brown and ~60 mg of red-black, dichroic crystals were deposited.[21] The product was isolated by filtration, washed with acetonitrile, acetone, and ether, and then dried under vacuum at 80°. Composition was first indicated by elemental analyses. *Anal.* Calcd for $C_8H_{20}S_4Re_2Cl_5$: C, 12.1; H, 2.54; S, 16.1. Found: C, 12.2; H, 2.50; S, 16.5. The compound is insoluble in common organic media and apparently unaffected by warming with 12 *M* HCl. The infrared spectrum shows no absorption attributable to Re=O groups. The mean oxidation state of the rhenium atoms is 2.5; presumably the excess DTH serves as the reducing agent.

$Re_2Cl_5(DTH)_2$ crystallizes in the monoclinic system, space group $P2_1/m$ with dimensions $a = 8.023 \pm 0.008$, $b = 14.355 \pm 0.005$, $c = 8.423 \pm 0.006$ A, $\beta = 105.5 \pm 0.10$; $z = 2$; $d = 2.81 \pm 0.01$ g/cc (calculated 2.80 g/cc). Intensities were recorded using a counter diffractometer and Mo $K\alpha$ radiation (Zr filtered) within a sphere limited by $\theta = 21°$. The structure was solved by Patterson and Fourier syntheses and has been refined to an R value[22] of 0.08 using unit weighting and neglecting statistically unreliable reflections. Additional refinement is in progress.

The structure is shown in Figure 1. In addition to the bond lengths, given in the caption, other important structural features are: the $Re^b\text{-}Re^a\text{-}Cl$ angles are ~102°; the $Re^a\text{-}Re^b\text{-}S$ angles are ~94°; the $S\text{-}Re^b\text{-}S$ (ring) angles are ~83°; the Re^aCl_4 group is staggered with respect to the Re^bS_4 group. This staggered arrangement is quite unequivocal because it is a requirement of crystallographic symmetry.[23]

The interpretation of this structure in terms of the electronic configuration (or, from another viewpoint, the deduction of the latter from the former) constitutes the chief point of interest. While collateral information, such as visible and esr spectra, will be helpful in settling details, we believe the structure itself clearly suggests the following allocation of electrons. As before[3] we allot four orbitals (d, s, p_x, p_y) on each Re atom to bind the four ligands in a quasi-square array. Two additional p–d hybrid orbitals are formed on each Re atom, one in each set being directed toward the other Re atom. These form a Re–Re σ bond. The other members of the set, (σ_a, σ_b), point outward along the Re–Re direction. The Re atoms now use their d_{xz} and d_{yz} orbitals to form a pair of Re–Re π bonds. At this point there are three valence shell electrons remaining for both Re atoms, and each one has its σ orbital (σ_a or σ_b) and a δ-type d orbital (δ_a, δ_b) still empty. The additional Cl atom is bonded axially to Re^b using its σ orbital (σ_b). Moreover, this Cl atom is weakly bonded to Re^a of the next molecule, thus raising the energy of σ_a. Consequently, the three electrons must occupy the two $d\delta$ orbitals, δ_a and δ_b.

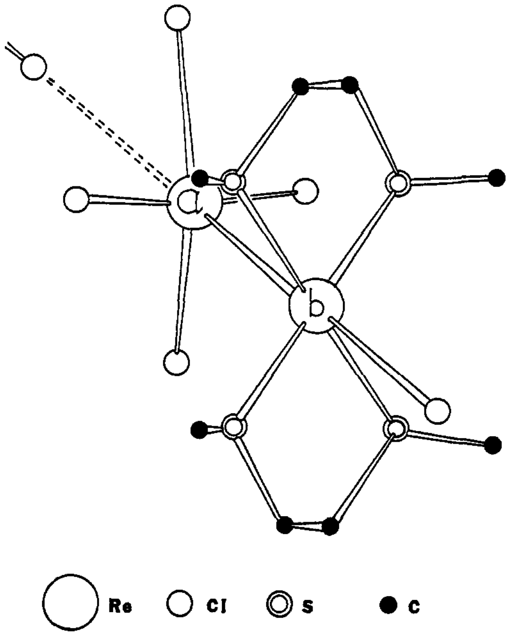

Figure 1. The structure of $Re_2Cl_5(DTH)_2$. The principal dimensions are: Re–Re, 2.29 ± 0.01 A; $Re^a\text{-}Cl$ (av), 2.33 ± 0.03 A; $Re^b\text{-}Cl$, 2.51 ± 0.03 A; $Re^b\text{-}S$ (av), 2.44 ± 0.02 A; $Cl' \cdots Re^a$, 3.22 ± 0.03 A.

If now these two were of equal energy and the configuration were eclipsed, there would result a bonding δMO ($\sim\delta_a + \delta_b$), doubly occupied, and an antibonding δMO ($\sim\delta_a - \delta_b$), singly occupied. Evidently the half-filling of the antibonding δMO, coupled with the inequality in the $d\delta$-orbital energies (the environments of the two Re atoms are *very* different) and abetted by the nonbonded repulsions, destabilizes this configuration, and the staggered one is preferred. Now the δ_a-to-δ_b interaction vanishes by symmetry. Two electrons become localized on one of the Re atoms, giving it a formal oxidation state of II, and one electron occupies the δ orbital of the other Re atom making it, formally, Re(III). The staggered configuration found here thus provides, in itself, clear evidence for the absence of a δ bond.

The δ bond being lost, there is then a Re–Re bond of order 3. Its bond length, 2.29 A, is intermediate between those for bond orders 2 and 4 as expected. Moreover, it is much closer to the distance for bond order 4 since the bond lost on going from bond order 4 to 3 is the relatively weak δ bond.[24]

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(21) Other, more convenient, procedures for preparing the compound do not yield good crystals.

(22) Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(23) A crystallographic mirror plane which includes two *trans* Cl atoms on Re^a must bisect the pair of opposite, nonring $S\text{-}Re^b\text{-}S$ angles.

(24) We are grateful to the U. S. Atomic Energy Commission and the National Science Foundation for financial support.