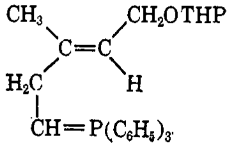
THP, Z = mesitoyloxy, with the central (5,6) double bond *cis*.[15] The mesitoyl and tetrahydropyranyl protecting groups were removed by sequential treatment with lithium aluminum hydride in ether (25°, 1 hr) and slightly acidic methanol at 25° to give the diol **5**, Y = Z = OH, which was converted by phosphorus tribromide[11] to the dibromide **5**, Y = Z = Br.



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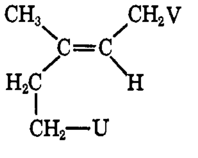

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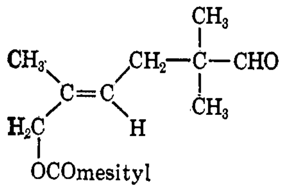

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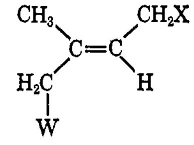

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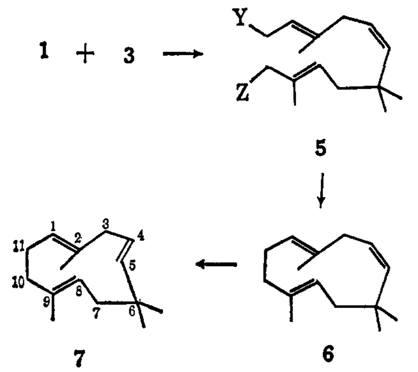

The 4,5-*cis* isomer of humulene (**6**) was formed as the major product when a solution of the dibromide **5**, Y = Z = Br, in N-methylpyrrolidone was added slowly (automatic syringe drive) to 4 mole equiv of nickel carbonyl in the same solvent at 50° under argon together with three other volatile products (0.7, 0.5, and 0.4 parts per part of **6**). Irradiation of the crude cyclization product (>350 mμ) and diphenyl disulfide[16] in cyclohexane at 25° for 2.5 hr caused isomerization of **6** to humulene (**7**) which was obtained from the mixture using extraction with 50% aqueous silver nitrate.[18] Separation of pure humulene from the only contaminant **6** was readily accomplished by preparative vapor phase chromatography (fluorosilicone column, 150°). The synthetic product behaved exactly as did natural humulene[19] upon vpc analysis with fluorosilicone, diethylene glycol succinate, and Carbowax 20M columns (which cleanly resolve a large number of sesquiterpenes). Identity was further established by the correspondence of infrared, nuclear magnetic resonance, and mass spectra.[20]

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[15] The *cis* geometry for the 5,6-double bond in **5** is indicated by the absence of the absorption characteristic of *trans* –CH=CH– at 10.3–10.4 μ, by the ready photoisomerization using diphenyl disulfide[16] to an isomer which *did* exhibit infrared absorption at 10.3 μ, and finally from the observation that the model reaction of pivalaldehyde with *n*-octylidene- and β-phenylethylidenetriphenylphosphorane in dimethyl sulfoxide afforded olefinic product of >98% *cis* content.[17] The subsequent synthetic transformations also allow the *cis* assignment.

[16] C. Moussebois and J. Dale, *J. Chem. Soc.*, 260 (1966).

[17] E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.*, **88**, 5653 (1966).

[18] R. P. Hildebrand and M. D. Sutherland, *Australian J. Chem.*, **14**, 272 (1961), have described an efficient purification of naturally occurring humulene by this technique. In the present case the extraction removes only humulene and any unisomerized 4,5-*cis*-humulene (**6**) from the mixture.

[19] We are indebted to Drs. F. Sorm, S. Dev, and M. D. Sutherland for samples of natural humulene for comparison.

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Structures of Two Compounds Containing Strong Metal-to-Metal Bonds

Sir:

It has been established that the $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ ions have an eclipsed structure[1] with a quadruple bond between the metal atoms.[2] It has been shown that ligand substitution reactions of various kinds proceed readily with these ions.[3] In particular, a compound of empirical formula $ReCl_3P(C_6H_5)_3$ was obtained[3a] by treating $Re_2Cl_8^{2-}$ with $P(C_6H_5)_3$. Unfortunately this compound, which was shown[3a] not to be of the $Re_3Cl_9L_3$ type obtained[4] from Re_3Cl_9, was too insoluble to permit positive structural characterization. It was postulated, however, that it is the dinuclear, 1,2-disubstituted derivative, $(C_6H_5)_3PReCl_3$-$ReCl_3P(C_6H_5)_3$. In order to obtain direct evidence on this, and particularly to see if such a compound retains the short Re–Re bond and the eclipsed configuration which is a consequence[2] of the δ component of the quadruple bond, a soluble, crystallizable analog was sought. The $P(C_2H_5)_3$ analog proved satisfactory; its structure has been determined by single-crystal X-ray methods and is described here.

$Re_2Cl_6[P(C_2H_5)_3]_2$ crystallizes in the space group $P2_1/n$ with unit cell dimensions $a = 7.644 \pm 0.003$, $b = 10.985 \pm 0.005$, $c = 14.206 \pm 0.006$ A; $\beta = 96.5 \pm 0.1°$; $Z = 2$. Intensities were recorded using a counter diffractometer and Cu Kα radiation (Ni filtered) within a sphere limited by $\theta = 55°$. The structure was solved by conventional Patterson and Fourier syntheses and has been refined to an R value[5] of 0.066 neglecting statistically unreliable reflections.

The molecule, shown in Figure 1, lies on a crystallographic inversion center and possesses the expected eclipsed configuration. Important bond lengths and angles are: Re–Re, 2.222 ± 0.003 A; Re–Cl$_1$, 2.35 ± 0.01 A; Re–Cl$_2$ and Re–Cl$_3$, 2.30 ± 0.01 A; Re–P, 2.46 ± 0.01 A; Re–Re–Cl$_1$, 116.3 ± 0.2°; Re–Re–Cl$_2$, 104.0 ± 0.2°; Re–Re–Cl$_3$, 103.0 ± 0.2°; Re–Re–P, 97.4 ± 0.2°. While the significant difference in Re–Cl distances may be explained in terms of the *trans* effect, there is no immediately apparent reason for the observed angular distortions.

This is the first substitution product (not involving oxidation or reduction) of an $Re_2X_8^{2-}$ ion which has

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[1] (a) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **4**, 330 (1965); (b) V. G. Kuznetzov and P. A. Koz'min, *Zh. Strukt. Khim.*, **4**, 55 (1963); (c) V. G. Koz'min, V. G. Kuznetzov, and Z. V. Popova, *ibid.*, **6**, 651 (1965); (d) W. R. Robinson, Thesis, MIT, 1966.

[2] F. A. Cotton, *Inorg. Chem.*, **4**, 334 (1965).

[3] (a) F. A. Cotton, N. F. Curtis, and W. R. Robinson, *ibid.*, **4**, 1696 (1965); (b) F. A. Cotton, N. F. Curtis, B. F. G. Johnson, and W. R. Robinson, *ibid.*, **4**, 326 (1965); (c) F. A. Cotton, C. Oldham, and W. R. Robinson, *ibid.*, **5**, 1798 (1966).

[4] F. A. Cotton, S. J. Lippard, and J. T. Mague, *ibid.*, **4**, 508 (1965).

[5] Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

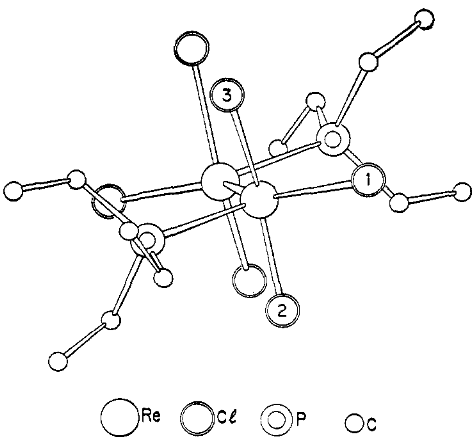

Figure 1. The structure of $Re_2Cl_6[P(C_2H_5)_3]_2$.

been structurally characterized in a direct and definitive way. It shows that such substitutions can indeed be carried out with preservation of the Re-to-Re quadruple bond with its attendant structural consequences. This result is to be compared with the extensive structural changes (see below) which are sometimes found when $Re_2X_8^{2-}$ species are subjected to redox reactions.

It has recently been reported that a crystalline form of rhenium(IV) chloride exists, from which many chemical reactions produce the $Re_2Cl_8^{2-}$ ion or derivatives thereof.[6] These observations would suggest that the rhenium(IV) chloride contains dinuclear structural units, and one interesting possibility is that such a unit might have a structure similar to that of $Re_2Cl_8^{2-}$ except that the rotational configuration would be staggered and the Re–Re bond longer because of the absence of a δ bond, as in the recently reported[7] structure of $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$. A single-crystal X-ray study of the structure of the rhenium(IV) chloride has been undertaken. Though dinuclear units are present, they are of an entirely different structure, being of the $W_2Cl_9^{3-}$ type, strung together in infinite chains *via* bridging by one of each set of terminal Cl atoms. Thus, conversion of rhenium(IV) chloride to $Re_2Cl_8^{2-}$ and its derivatives takes place with very extensive rearrangement, *but* the Re–Re unit remains intact.

Rhenium(IV) chloride forms monoclinic crystals belonging to one of the space groups Pc or P2/c. Unit cell dimensions are $a = 6.366 \pm 0.005$, $b = 6.282 \pm 0.006$, $c = 12.165 \pm 0.006$ A; $\beta = 93.17 \pm 0.10°$. Three-dimensional data were collected using nickel-filtered Cu Kα radiation on a GE XRD-5 diffractometer, within the sphere limited by $2\theta \leq 101°$. The 425 significant reflections were corrected for Lorentz-polarization effects and absorption. Conventional Patterson and Fourier techniques revealed the structure shown in Figure 2.

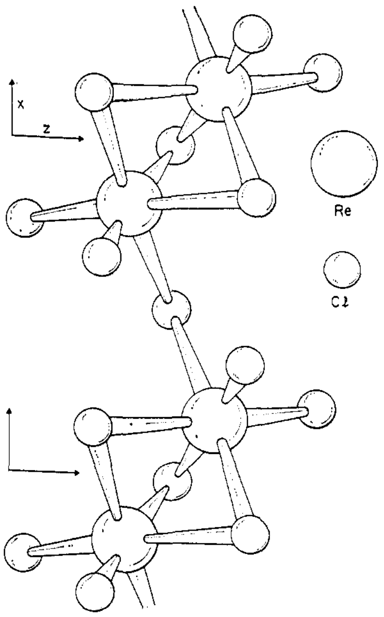

Figure 2. A portion of the $ReCl_4$ structure projected down the *b* axis.

Refinement of this structure has been hampered by several severe and seemingly inescapable difficulties, although there is no reason to doubt that, qualitatively, this structure is correct. As reported[6] before, the $ReCl_4$ crystals are only metastable and the preparation of them has not been successfully duplicated. The available crystals are relatively large (giving transmission factors for Cu Kα radiation ranging from 0.027 to 0.160) and irregularly shaped so that absorption corrections could not be accurately applied. Attempts to reduce the size or improve the shape of the crystals using either solvents or mechanical grinding failed because of their chemical instability and brittleness. There is also evidence in Laué photographs for disorder. Difference Fourier maps have contained too much noise ($\sim 2e/A^3$) to allow an unambiguous test of the several disorder models which have been postulated. Two independent sets of data on different crystals have been used, each refining (full-matrix, least-squares, P2/c) to $R \sim 18\%$. Use of the average of the two sets leads to $R = 17\%$. Use of space group Pc makes no significant difference in the course of the refinement. It is possible that by recollecting the data using Mo Kα radiation, absorption errors might be minimized enough to permit clarification of the disorder.

The Re–Re distance presently available is 2.73 ± 0.03 A, which indicates metal–metal bonding. This distance and in fact the entire structure is in marked contrast to that of $TcCl_4$. The latter[8] also contains polymeric chains of MX_6 octahedra, but joined on edges with Tc–Tc distances of 3.62 A. Moreover, the Tc atoms are actually displaced away from each other, a good sign[9] that there is no metal–metal bonding. Thus for the four-valent group VII metals, the tendency to form metal–metal bonds becomes dominant only with the third-row metals. However, even a slight lowering of the oxidation state causes Tc as well as Re to form such bonds, as in the $Tc_2Cl_8^{3-}$ ion.[10,11]

[6] F. A. Cotton, W. R. Robinson, and R. A. Walton, *Inorg. Chem.*, **6**, 223 (1967).

[7] M. J. Bennett, F. A. Cotton, and R. A. Walton, *J. Am. Chem. Soc.*, **88**, 3866 (1966).

[8] M. Elder and B. R. Penfold, *Inorg. Chem.*, **5**, 1197 (1966).

[9] F. A. Cotton, *Rev. Pure Appl. Chem.*, in press.

[10] F. A. Cotton and W. K. Bratton, *J. Am. Chem. Soc.*, 87, 921 (1965).

[11] These studies were supported, in part, by Contract No. AT(30-1)-1965 with the U. S. Atomic Energy Commission.

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