

References and Notes

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Synthesis of "Skewered Complexes": Reaction of Rhenium Carbonyl Porphyrin Complexes with Antimony Pentachloride

Sir:

The syntheses and x-ray diffraction analyses of novel metalloporphyrin complexes in which the metal ions sit out of the plane of the porphyrin molecule have been previously reported by our laboratories.¹⁻⁴ Particular attention has been paid to metalloporphyrins of the type $[(CO)_3M]_2TPP$ ($M = Re, Tc$; $TPP = meso$ -tetraphenylporphyrin). The metal ions lie on either side of the macrocycle. In previous work the rhenium and technetium ions have been formally in the +1 oxidation state. It would be unlikely that a metal-metal bond would exist in this case and the observed M-M distances of 3.1 \AA ⁴ indicate that any interaction, if present, must be weak. We are at present investigating the reaction of these complexes with a variety of oxidizing agents in an attempt to further elucidate their chemical properties and to obtain new porphyrin complexes containing higher formal oxidation states of the metal ions. In such complexes a metal-metal bond could exist and would be evidenced by a shorter M-M distance than in the starting complexes. If a metal-metal bond were formed, it would necessarily pass through the center of the porphyrin core, resulting in a material that can be described as a "skewered complex".

In this paper, we wish to report the synthesis and characterization of a series of mono- and biscationic rhenium por-

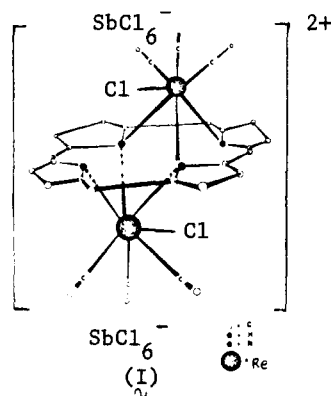


Figure 1. Proposed structure.

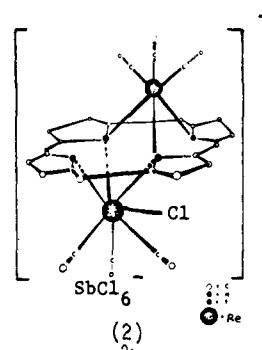
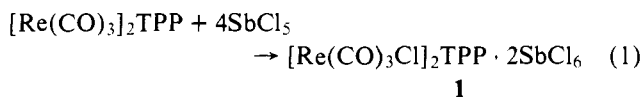


Figure 2.

phyrin species. In all of these antimony hexachloride serves as the anion. An x-ray determination of the structure of these complexes provides definite evidence for a "skewered complex", that is a metalloporphyrin in which a metal-metal bond exists through the "hole" of the macrocycle. A solution of antimony pentachloride (0.05 mmol) in dichloromethane (0.5 ml) was added dropwise to a solution of bis(tricarbonylrhenium)- μ -tetraphenylporphyrin (0.0125 mmol) in the same solvent (15 ml) kept below $-70^\circ C$. When the reaction mixture was allowed to stand overnight kept below $-60^\circ C$, a large quantity of a black substance crystallized out. This solid was separated by decantation at $-50^\circ C$, and then washed three times with 2-3 ml of dichloromethane and finally with a 1:1 mixture of dichloromethane-*n*-hexane. Very fine hexagonal crystals, identified as the salt **1**, were obtained in almost quantitative yield (eq 1).



A proposed structure of the salt **1** is suggested by visible and infrared spectra and by elemental analysis. Compound **1** has visible absorption maxima in dichloromethane at 405 (Soret band), 493, 532, and 590 nm, and four intense infrared absorption bands at 1990, 2010, 2040, and 2070 cm^{-1} due to metal carbonyl stretching vibrations, in the solid state. The elemental analysis⁵ of **1** gave results which exactly fit the suggested structure.

This reaction indicates a similarity between the reactions of bis(tricarbonyl)- μ -tetraphenyl compounds and on the analogous cyclopentadienyl metal carbonyl complexes (i.e., $CpM(CO)_3$, $M = W^6$ and Re^7) with antimony pentachloride. Although a search for further examples of reactions of this general type is difficult because of the limited number of out-of-plane metal carbonyl porphyrins, an analogous monocationic salt (**2**)⁸ is obtained from the reaction of 1:2 mole ratio of the bisrhenium porphyrin complex and antimony pentachloride (eq 2 and Figure 2).

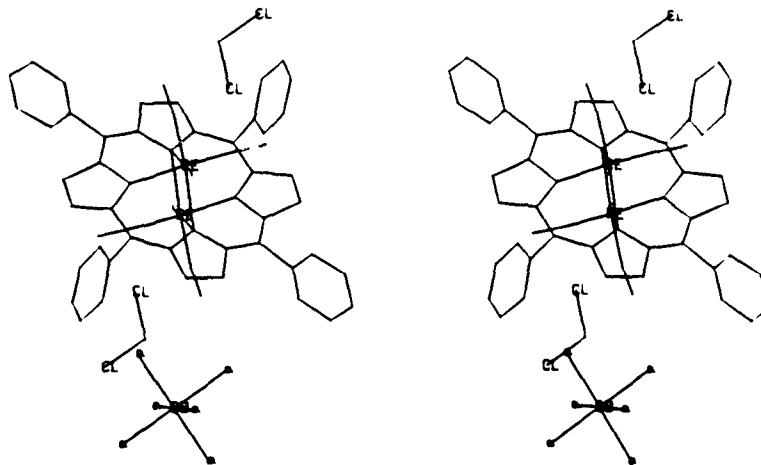
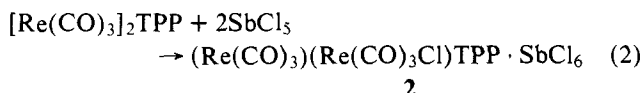
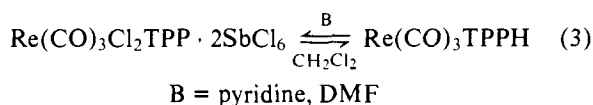


Figure 3. Stereoviews of the complex **3** as found in the solid state. The SbCl_6^- anion and dichloromethane solvent molecules are also shown.



The new compounds **1** and **2** are moisture sensitive and thermally unstable. However, in the solid state under dry argon, they can be kept over a week without decomposition. The salts also are fairly stable in dry dichloromethane or chloroform, but decompose readily in ether, THF, alcohols, acetone, or water to form the starting bisrhenium porphyrin complex. Interestingly, the addition of a small amount of DMF or pyridine to the salt **2** in dichloromethane leads to the monorhenium porphyrin complex (eq 3).



The salt **1** is not soluble in most organic solvents. However, large single crystals of this salt can be obtained by allowing the 4:1 reaction mixture of bis(tricarbonylrhenium)- μ -tetraphenylporphyrin and antimony pentachloride to sit at -30°C for a week. These crystals diffract x-rays very poorly, and repeated efforts to obtain suitable crystals for x-ray analysis have thus far failed. In one run, crystals of an entirely different habit were formed. These proved to be of excellent quality for x-ray analysis. However, these crystals proved to be a third compound; bis(tricarbonylrhenium)- μ -tetraphenylporphyrin hexachloroantimonate $[(\text{CO})_3\text{Re}]_2\text{TPP}^+\text{SbCl}_6^-$ (**3**). It has proved difficult to reproduce the synthesis of **3** in order to elucidate its formation pathway.

Crystal Data: A single-crystal x-ray diffraction analysis was carried out on **3**: $[\text{C}_{50}\text{H}_{28}\text{N}_4\text{O}_6\text{Re}_2]^+\text{SbCl}_6^- \cdot 2\text{CH}_2\text{Cl}_2$; $M = 1657.8$ daltons; space group $P\bar{1}$; $a = 12.938$ (1), $b = 10.438$ (1), $c = 11.347$ (1) Å; $\alpha = 82.98$ (1) $^\circ$, $\beta = 100.08$ (1) $^\circ$, $\gamma = 111.61$ (1) $^\circ$; $V = 1399.8$ Å 3 ; $Z = 1$; $d_c = 1.96$ g cm $^{-3}$; linear absorption coefficient, μ , for Cu $K\alpha$ radiation is 169.1 cm $^{-1}$. Three-dimensional data were collected using pyrolytic graphite monochromatized Cu $K\alpha$ radiation (λ 1.541 78 Å) on a Datex-Syntex automated diffractometer. A total of 1691 independent reflections were measured out to 2θ ca. 80° . Of these 1513 were considered observed and were used in the analysis. Absorption corrections were applied to the data.

The structure was solved by Patterson and Fourier methods and refined by block-diagonal least-squares techniques to the present discrepancy indices of $R = 0.080$ and weighted $R = 0.087$.

At the present stage of refinement, the thermal motion for all atoms has been assumed to be isotropic. Hydrogen ions have

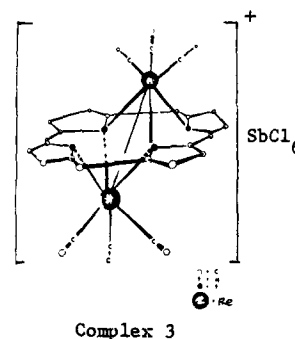


Figure 4.

not been found and are omitted from the structure factor calculations.

A stereoview of the structure is shown in Figure 3. It is shown schematically in Figure 4. Unlike the suggested structures for **I** and **II** there are no Re-Cl bonds. Instead the monocationic porphyrin species, which is providing a radical, has a structure very similar to that of the neutral starting material, $[(\text{CO})_3\text{Re}]_2\text{TPP}$.

The metal ions are not positioned directly over the center of the macrocycle, but are set to one side so that each metal ion is bonded to three of the four nitrogen atoms of the porphyrin. Three carbonyl groups on each metal ion complete the octahedral coordination. The most dramatic difference is the shorter Re-Re distance. One electron has been lost. One possible formulation would be to give each metal ion a formal oxidation state of 1.5. One might thus expect a metal-metal bond of one-half bond order through the porphyrin "core" forming a "skewered complex". The Re-Re distance is 2.95 Å (0.18 Å shorter than in the neutral species), a distance which is indicative of definite metal-metal interaction.⁹

As in the neutral Re(I)-Re(I) species the two Re-N bonds to nitrogen atoms shared by both metal ions are considerably longer than the third Re-N bond (2.35 and 2.36 Å vs. 2.11 Å). The average Re-C distance of 1.97 Å is considerably longer in the present case.

The macrocycle is distorted in a manner similar to the neutral compound. The two pyrrole rings containing nitrogen atoms shared by both metal ions are approximately coplanar with the mean plane of the macrocycle while the other two rings are tilted toward the metal ion to which they are coordinated.

The average Sb-Cl distance in the regular octahedral SbCl_6^- anion is 2.35 Å, which is normal. There are two dichloromethane solvent molecules per formula unit.

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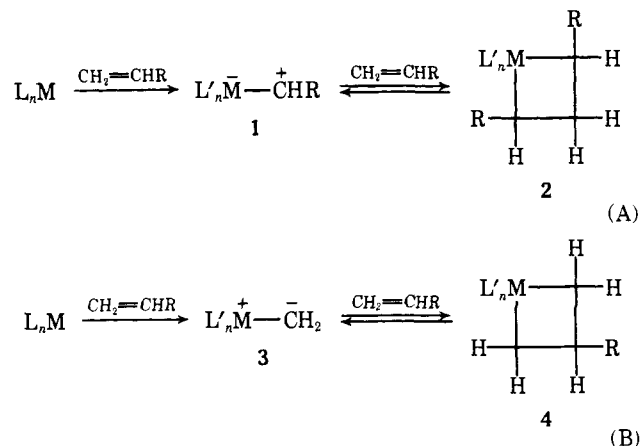
The Relationship of Polarization in Metal-Carbene Complexes to the Degenerate Metathesis of Terminal Olefins¹

Sir:

Differing explanations have appeared for the degeneracy observed in the metathesis² of terminal olefins. We now wish to report experimental evidence which supports the contention that, at least in the case of certain tungsten-based catalysts, the degenerate metathesis of terminal olefins is due to the polarization of the chain-carrying metal-carbene complex. In addition, we suggest that this polarization results in nucleophilic character on carbon and significant positive charge distribution to the metal.

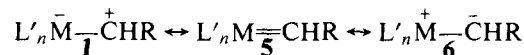
The degenerate nature of the metathesis of terminal olefins has been well established by the excellent use of isotopic labeling experiments.³ Not only have these olefins been shown to metathesize in a degenerate manner, but it has been demonstrated that they metathesize so rapidly that the presence of terminal olefins may effectively inhibit the metathesis of internal olefins.⁴ The degeneracy of terminal olefin metathesis has been discussed in terms of steric interactions.^{4,5} Alternately,

it has been implied that this degeneracy is the result of a highly selective addition of a polarized intermediate to a terminal olefin.^{5,6} The latter rationalization has been viewed in terms of process A,^{5,6} which occurs with intermediate formation of **2** via addition of **1** to a terminal olefin.⁷ At least as attractive is process B, which involves the addition of **3** to a terminal olefin to produce the intermediate **4**.⁸ Distinguishing between process A and process B amounts to distinguishing between electrophilic and nucleophilic addition to a terminal



olefin.⁹ It also amounts to determining whether the transition metal complex reacts with the terminal olefin to form **1** or **3** in the generation of the initial metal-carbene complex.

If a simple method were available which would permit experimental determination of the polar character of **5**, that is, whether **6** or **1** was the major resonance contributor, the



problem could be readily solved.¹⁰ In principle, this could be accomplished through a cross-metathesis reaction between 2-butene and a terminal olefin. In practice, the metathesis of the terminal olefins was so rapid that effective cross-metathesis with internal olefins was not readily observed.^{4,11} Thus, an alternate method was needed for the generation of significant amounts of **5** in the presence of a terminal olefin. If this could be accomplished, examination of the products of the reaction would allow a distinction to be made between the various mechanistic possibilities. Formation of **7**, which would not be expected to metathesize in the presence of a terminal olefin, would require **8** as a precursor. The formation of **8** would be inconsistent with either a sterically controlled mechanism or with process A. Furthermore, it would only be consistent with **6** being the major resonance contributor. If only **9** were observed, **10** would be implicated as the crucial intermediate and either process A or a sterically controlled mechanism would be required.

Fortunately, our recent discovery of phenyltungsten trichloride-aluminum trichloride promoted retro-carbene additions¹² offered an attractive possibility for the generation of

Table I. Product Yields Obtained in the Cross Metathesis Reaction of C-Alkyl Substituted Metal-Carbene Complexes with Terminal Olefins

Terminal olefin	3-Olefin formed	% yield ^a	% yield ^b	Trans/cis
1-Butene	3-Hexene	35	c	3.4
1-Pentene	3-Heptene	30 ^{d,e}	71	3.5
1-Hexene	3-Octene	29 ^{d,e}	74	3.5

^a Yield based on 1-olefin. All yields are determined by GLC analysis vs. cyclododecane as an internal standard. ^b Yield based on unrecovered 1-olefin. ^c Since 1-butene was generated from the ethylcyclopropane, this value was meaningless. ^d In addition, 4% of 3-hexene was formed. ^e Trace amounts of 4-octene and 5-decene were also observed in the experiments which utilized 3-heptene and 3-octene, respectively.