A Novel Disproportionation Reaction That Occurs at a Multiply Bonded Dimetal Center. The Isolation of Dirhenium(IV,II) Alkoxide Complexes of the Type (RO)₂Cl₂ReReCl₂(PPh₃)₂ (R = Me, Et, or n-Pr)

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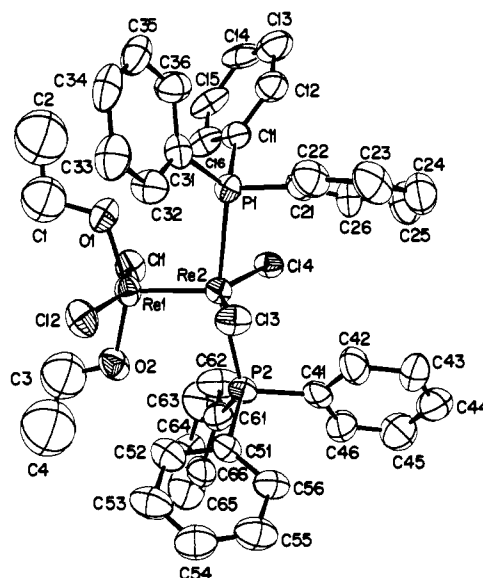*Department of Chemistry, Texas A&M University
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While the preparative and structural details of the dirhenium-(III,III) carboxylate complex Re₂Cl₄(O₂CCH₃)₂ and certain of its 1:2 adducts Re₂Cl₄(O₂CCH₃)₂L₂ (e.g., L = H₂O, py, DMF, and Me₂SO) have been quite thoroughly documented,[2-4] other aspects of the chemistry of these species, particularly their reaction chemistry, have remained largely unexplored. In our examination of the reactions of Re₂Cl₄(O₂CCH₃)₂L₂ (L = H₂O (**1**) or py (**2**)) toward monodentate tertiary phosphines, we have discovered what we believe to be a disproportionation reaction of a novel type in which a [Re(III)Re(III)] core is transformed into [Re(IV)Re(II)]. This constitutes an important development in the field of multiple-bond chemistry and may presage the discovery of other examples of this kind.

The reaction between **1** or **2**[5] and the phosphines PMe₃, PMe₂Ph, or PMePh₂ in refluxing ethanol for periods of 15–30 h gave the triply bonded dirhenium(II) complexes Re₂Cl₄(PR₃)₄ in yields of 60% or greater.[6] The course of these reactions resembles closely the conversion of (n-Bu₄N)₂Re₂Cl₈ to these same phosphine derivatives under comparable conditions.[8,9] However, the reaction of PPh₃ with **1** in refluxing ethanol for 20 h proceeded in a quite different fashion to afford a dark red crystalline solid of stoichiometry Re₂Cl₄(OEt)₂(PPh₃)₂.[10] When methanol and n-propanol were used as the reaction solvents (reaction times of 20 and 65 h, respectively) the related methoxide and n-propoxide derivatives were obtained in 49% and 60% yield, respectively.[11] Accordingly, these reactions provide a new class of rarely encountered alkoxide complexes of rhenium.[12]

The properties of the three complexes of the type Re₂Cl₄-(OR)₂(PPh₃)₂ (**3**: **a**, R = Me; **b**, R = Et; **c**, R = n-Pr) are so similar that we shall restrict ourselves primarily to a consideration

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(5) The preparative method used to obtain **1** and **2** has been described previously; see: Cotton, F. A.; Oldham, C.; Walton, R. A. *Inorg. Chem.* **1967**, *6*, 214.

(6) All reactions were performed under N₂(g) using deoxygenated solvents. These complexes crystallized directly from the reaction medium and were identified on the basis of their spectroscopic and electrochemical properties.[7,8]

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(10) Yield 54%. Anal. Calcd. for C₄₀H₄₀Cl₄O₂P₂Re₂: C, 42.55; H, 3.58; Cl, 12.56. Found: C, 42.15; H, 3.56; Cl, 12.57.

(11) Some Re₂Cl₆(PPh₃)₂ was present as a byproduct in the reactions which gave Re₂Cl₄(OR)₂(PPh₃)₂. It was easily separated by extraction of the latter alkoxide complex into CH₂Cl₂, in which Re₂Cl₆(PPh₃)₂ is insoluble.

(12) The only previous example of a multiply bonded dirhenium complex that also contains a Re–OR bond is Re₂(μ-Cl)₂(μ-dppm)₂Cl₃(OR) (R = Me, Et, or n-Pr); see: Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

Figure 1. ORTEP drawing of the (EtO)₂Cl₂ReReCl₂(PPh₃)₂ molecule. Some important bond lengths (Å) and angles (deg): Re(1)–Re(2), 2.231 (1); Re(1)–Cl(1), 2.359 (3); Re(1)–Cl(2), 2.356 (3); Re(1)–O(1), 1.892 (8); Re(1)–O(2), 1.883 (8); Re(2)–Cl(3), 2.328 (2); Re(2)–Cl(4), 2.340 (2); Re(2)–P(1), 2.466 (3); Re(2)–P(2), 2.487(3); O(1)–C(1), 1.52 (2); O(2)–C(3), 1.47 (2) Å; Re(2)–Re(1)–Cl (1), 103.00 (8)°; Re(2)–Re(1)–Cl(2), 102.46 (8)°; Re(1)–Re(2)–Cl(3), 109.16 (8)°; Re(1)–Re(2)–Cl(4), 110.94 (7)°; Re(2)–Re(1)–O(1), 104.1 (2)°; Re(2)–Re(1)–O(2), 104.8 (2)°; Re(1)–Re(2)–P(1), 98.83 (7)°; Re(1)–Re(2)–P(2), 100.43 (7)°; Re(1)–O(1)–C(1), 120.7 (9)°; Re(1)–O(2)–C(3), 120 (1)°. Torsion angles: Cl(1)–Re(1)–Re(2)–Cl(4), 1.5°; Cl(2)–Re(1)–Re(2)–Cl(3), 1.5°; O(1)–Re(1)–Re(2)–P(1), 2.0°; O(2)–Re(1)–Re(2)–P(2), 0.5°.

of the representative ethoxide derivative **3b**. Their IR spectra (Nujol and halocarbon mulls) show bands arising from vibrations of the PPh₃ and OR ligands but none that can be attributed to ν(O–H) of any alcohol ligands. Their 200-MHz ¹H NMR spectra (in CDCl₃ or CD₂Cl₂) show resonances displaying the correct relative intensities for the alkoxide ligands (δ +0.66 (t, 3 H) and +1.79 (q, 2 H) for **3b**) and coordinated triphenylphosphine (δ +6.8 to +8.0 (30 H) for **3b**) but, once again, there was no spectroscopic evidence for hydroxyl protons.[13] This conclusion was further supported by monitoring the ¹H NMR spectra of solutions of **3b** in CD₂Cl₂ to which an excess of py or dry Me₂SO had been added. We found no evidence for the release of free ethanol which would have been expected had kinetically labile Re–HOR bonds been present.[14]

The electronic absorption spectra of CH₂Cl₂ solutions of these complexes were essentially the same, the most characteristic feature in each instance being an intense band at λmax = 1190 nm (ε 2800).[15] These spectra are in turn quite different from the related spectra of the quadruply bonded species Re₂Cl₆(PR₃)₂[2,8] and therefore imply a significant difference in electronic structure. This conclusion is further supported by electrochemical redox experiments. Cyclic voltammograms of solutions of **3b** in 0.2 M Bu₄NPF₆–CH₂Cl₂ show the presence of two couples, one of which corresponds to a one-electron oxidation ($E_{1/2}$ = +0.83 V vs. Ag/AgCl) the other to a one-electron reduction ($E_{1/2}$ = –0.61 V vs. Ag/AgCl).[16] While the couple at the more negative po-

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(13) Further evidence for this is seen by a careful examination of the methylene resonances of **3b**. The symmetric quartet shows no evidence for splitting by a hydroxyl proton.

(14) When "wet" Me₂SO was used, some hydrolysis of the Re–OEt bonds of **3b** occurred thereby leading to the slow release of ethanol. Under such conditions, the ratio of coordinated ethoxide (in unchanged **3b**) to free ethanol was ca. 3:1 after 10 h. The addition of PMe₃ to a CD₂Cl₂ solution of **3b** resulted in a redox reaction in which Re₂Cl₄(PMe₃)₄ was one of the principal products.

(15) A scan in the spectral region 1600–300 nm for a CH₂Cl₂ solution of **3b** revealed the following features (λmax nm, εmax in parentheses): 1190 (ε 2800), ∼560 sh, 480 (ε 300), 420 (ε 650), 340 (ε 2900).

tential was chemically irreversible (as judged by bulk electrolysis at −0.65 V), oxidation at +0.90 V generated a green solution of the ESR-active monocation [3b][+].[17] This redox behavior differs considerably from that reported for $Re_2Cl_6(PR_3)_2$ compounds,[7] for which two one-electron reductions both occur at potentials more negative than +0.1 V. The $^{31}P\{^1H\}$ NMR spectrum of **3b** (in $CDCl_3$) shows a singlet at δ −6.18 (vs. 85% aqueous H_3PO_4 with positive chemical shifts downfield) in accord with magnetically and chemically equivalent phosphine ligands. A clue to the structure of this Re_2^{6+} core complex was provided by an analysis of the 200-MHz ^1H NMR spectra of the phenyl rings of the PPh_3 ligands. There are two groups of resonances (intensity ratio 2:1), the upfield set of which (comprising two apparent triplets and an apparent quartet) can be attributed to a unique phenyl ring of each PPh_3 ligand.[18] A series of decoupling experiments showed that the ortho protons of these two sets of rings (δ +7.90 and +6.46) are coupled to two trans phosphorus nuclei. This implies that these compounds possess the unsymmetrical and entirely unexpected structure $(RO)_2Cl_2ReReCl_2(PPh_3)_2$, a conclusion that we have confirmed by an X-ray structure analysis on crystals of **3b**.

The structure of a single crystal of **3b** was determined[19] by following general procedures described elsewhere.[20,21] The compound crystallizes in the monoclinic space group $P2_1/c$, with one complete molecule in the crystallographic asymmetric unit. The molecule, shown in Figure 1, consists of a strongly bonded dirhenium unit with an unsymmetrical distribution of unidentate ligands on the metal centers. The effective C_2 axis lies along the Re(1)–Re(2) axis. The conformation of the molecule is essentially eclipsed and the Re(1)–Re(2) distance in **3b** is 2.231 (1) Å. The Re(1)–O distances, 1.892 (8) and 1.883 (8) Å, are short compared to the Re–O distance of 2.085 (14) Å observed[12] in Re_2Cl_5-(OEt)(dppm)$_2$. The shortening of the Re–O bond lengths in **3b** could be due to extensive interaction of an oxygen $p\pi$ orbital perpendicular to the C–O–Re(1) plane and the Re(1) atom. The Re(1)–O–C angles are 120.7 (9)° and 120 (1)°. Although strong π-interaction normally tends to involve both oxygen lone pairs thus leading to M–O–C angles greater than the Re–O–C angles in **3b**, any increase of this angle is opposed by a repulsive interaction between the ethyl group of EtO and the phenyl groups of PPh_3. The Re(1)–Cl distances (average value of 2.358 [3] Å) in **3b** are slightly longer than the Re(2)–Cl bond lengths (average value of 2.334 [2] Å). This could be due to the presence of strong Re–O bonds. The Re(2)–P distances of 2.466 (3) and 2.487 (3) Å are normal.[9,12]

The X-ray structure of **3b** and other data suggest that molecules of type **3** are quadruply bonded, mixed-valence dirhenium compounds $(RO)_2Cl_2Re^{IV}Re^{II}Cl_2(PPh_3)_2$. The only known[22,23] dirhenium complex with an asymmetric arrangement of ligands is $Cl_4ReRe(dth)_2Cl$, dth = 2,5-dithiahexane, which has a staggered conformation of ligands around the Re_2 unit and a Re–Re bond order of 3. In **3b**, the electronic configurations of Re(1) and Re(2) are d^3 and d^5, respectively, and the ground electronic configuration of this eclipsed molecule can be written as $(\sigma)^2(\pi)^4(\delta)^2$. The quadruple bond, however, is different from those previously known in that one component is formally dative in character.

Supplementary Material Available: Tables of crystallographic data and atomic positional parameters for $Re_2Cl_4(PPh_3)_2(OEt)_2$ (3 pages). Ordering information is given on any current masthead page.

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Norhalichondrin A: An Antitumor Polyether Macrolide from a Marine Sponge[1]

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In our continuing search for physiologically active substances from marine sources, we recently found several antitumor compounds from *Halichondria okadai* Kadota.[2] One of them, norhalichondrin A, is a new type macrolide; in this report, we describe the structure determination of norhalichondrin A, a major component in a series of halichondrins.[3]

Halichondria okadai Kadota is a common, widely distributed sponge in the Pacific coast of Japan. Prior studies by Scheuer

(16) CV's were measured at a Pt-bead electrode. For details of our experimental procedure, see: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947. For both couples, the separation between the coupled anodic and cathodic peaks (ΔE_p) was 105 mV at v = 200 mV/s, and the $i_{p,a}/i_{p,c}$ ratios were close to unity. Under these same experimental conditions, the ferricinium/ferrocene couple has an $E_{1/2}$ value of +0.47 V vs. Ag/AgCl.
(17) This solution possessed a CV with couples at $E_{1/2}$ = +0.79 and −0.59 V vs. Ag/AgCl, both of which correspond to one-electron reductions. The X-band ESR spectrum (CH_2Cl_2 solution at −160 °C) gave a broad complex signal between 2000 and 5500 G.
(18) The ^1H NMR spectrum of the phenyl resonances of **3b** (recorded in CD_2Cl_2) can be described as follows: δ +7.90 (q, 4 H) and ca. +7.50 (m, 6 H), +7.31 (t, 1 H), +7.12 (t, 2 H), +6.46 (q, 2 H).
(19) Crystal data for $Re_2Cl_4(PPh_3)_2(OEt)_2$: monoclinic, $P2_1/c$; a = 10.782 (3) Å, b = 14.330 (3) Å, c = 26.924 (7) Å, $\alpha = \gamma = 90°$, β = 96.98 (2) °, V = 4129 (3) Å^3, Z = 4, d_{calcd} = 1.816 g/cm^3; μ(Mo Kα) = 63.09 cm^{-1}. An automated diffractometer Enraf-Nonius CAD-4 was used to collect 4150 data with $F_o^2 > 3\sigma(F_o^2)$ by using ω-scan technique. An empirical absorption correction was based on azimuthal scans of nine reflections. The positions of two independent Re atoms in the crystallographic asymmetric unit were derived from a three-dimensional Patterson map and refined by least squares. The structure was refined to residuals of R = 0.040 and R_w = 0.048 and a quality of fit index of 1.166 with a largest shift/esd = 0.19.
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(21) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, with a VAX-SDP software package.

(1) This work was presented at the 50th Annual Meeting of the Chemical Society of Japan, Tokyo, Japan, April 1, 1985.
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(3) The name halichondrin B was given to the most potent antitumor constituent in this series. Bioactivity of halichondrin B was about 50 times that of norhalichondrin A. Actually, halichondrin B shows high T/C % against L-1210 leukemia, P-388 leukemia, and B-16 melanoma in vivo. These data involving the structure of halichondrin B will be published very soon by D. Uemura, K. Takahashi, T. Yamamoto, Y. Tsukitani, H. Kikuchi, and Y. Hirata.