an Yb–($\mu$-I) distance of 3.027 (1) Å. In this case, the difference, 0.432 Å, is close to that expected on the basis of the different size of the halide ligand. In both comparisons, I vs. II and II vs. III, the Sm–Cl distance in II is longer by 0.05–0.10 Å than the sum of ionic radii would predict.

In contrast to the large variation observed in metal–halide distances in I–III when metal and halide sizes are accounted for, the distances of the metal to the THF oxygen atom do not vary substantially from those expected. The Sm–O distances in II are similar to those in III. The difference between these distances and the Y–O distance in I is commensurate with the 0.06–0.08 Å difference in the radial sizes of these metals.

In summary, the overall structures of the complexes in this series of formally 8-coordinate $(C_5Me_5)_2LnX(THF)$ complexes are very similar as are the metal–carbon and metal–oxygen bond distances. However, the metal–halide distances vary substantially even when the sizes of the metal and halides are considered.

## Conclusion

The structural analysis of complexes I–III provides another example of the similarity of organoyttrium(III) and organolanthanide(III) complexes.[74] This study also shows how metrical data can vary in a series of closely related molecules. In addition to providing these structural data, the synthesis of these complexes generates useful precursors for further studies in organolanthanide chemistry.

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**Supplementary Material Available:** Figure showing numbering schemes for II and III and tables of bond distances and angles and thermal parameters (12 pages); tables of structure factor amplitudes (56 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

# Reactivity of the Dirhenium(III) Carboxylate Complexes $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl or Br) toward Monodentate Phosphines. A Novel Disproportionation Reaction Leading to Dirhenium(IV,II) Alkoxide Complexes of the Type $(RO)_2X_2ReReX_2(PPh_3)_2$ (X = Cl or Br; R = Me, Et, or Pr)

Akhil R. Chakravarty,[1a] F. Albert Cotton,*[1a] Ann R. Cutler,[1b] and Richard A. Walton*[1b]

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The reactions of quadruply bonded dirhenium(III) carboxylate complexes of the type $Re_2(O_2CR)_2X_4L_2$ (X = Cl or Br; R = $CH_3$ or $C_2H_5$; L = $H_2O$, py, DMF, or $Me_2SO$) with monodentate tertiary phosphines in alcohol solvents have been examined. Whereas $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = $H_2O$ or py) reacts with $PMe_3$, $PMe_2Ph$, and $PMePh_2$ in ethanol to give the dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$, the reactions between $Re_2(O_2CR)_2X_4L_2$ (X = Cl or Br; R = $CH_3$ or $C_2H_5$; L = $H_2O$, DMF, or $Me_2SO$) and $PPh_3$ in refluxing alcohol solvents ROH (R = Me, Et, *n*-Pr, or *i*-Pr) afford red crystalline, diamagnetic complexes of stoichiometry $Re_2(OR)_2X_4(PPh_3)_2$. The ethoxide derivative has been characterized by X-ray crystallography and shown to possess the novel structure $(EtO)_2Cl_2ReReCl_2(PPh_3)_2$. This is best described formally as a Re(IV)–Re(II) complex that has been derived from the Re(III)–Re(III) core by an intramolecular disproportionation. A comparison is made between the properties of these new mixed halide–alkoxide complexes and those of their symmetrical Re(III)–Re(III) halide analogues $Re_2X_6(PR_3)_2$. Crystal and structural data for $Re_2Cl_4(OEt)_2(PPh_3)_2$: space group $P2_1/c$ with $a$ = 10.782 (3) Å, $b$ = 14.330 (3) Å, $c$ = 26.924 (7) Å, $\beta$ = 96.98 (2)°, $V$ = 4129 (3) Å$^3$, $Z$ = 4. The Re–Re distance is 2.231 (1) Å.

## Introduction

The reaction of the octahalodirhenate dianions with simple carboxylic acids and/or their anhydrides yields one of three classes of compounds, viz., $Re_2(O_2CR)_4X_2$, $Re_2(O_2CR)_3X_3$, or $Re_2(O_2CR)_2X_4$.[2,3] These materials are related by a qualitatively similar electronic structure: each of them contains a quadruply bonded $Re_2^{6+}$ core. To date, only the reactivity of the tetracarboxylate species has been examined to any significant extent.[2,3]

While the preparation and structural details of the anhydrous dirhenium(III) carboxylates $Re_2(O_2CR)_2X_4$ (X = Cl or Br) and certain of their 1:2 adducts $Re_2(O_2CR)_2X_4L_2$ (e.g., L = $H_2O$, py, DMF, $Me_2SO$, and $Ph_3PO$) have been thoroughly documented,[2-5] few aspects of the reaction chemistry of these species have been explored. This may of course have reflected the expectation that little of note would be uncovered, but as we shall see, these compounds display some unusual and surprising reaction chemistry.

The present manuscript addresses two points: (1) the redox chemistry of the complexes $Re_2(O_2CCH_3)_2X_4L_2$ and (2) a study

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of the reactions of certain complexes of the type $Re_2(O_2CCH_3)_2X_4L_2$ (X = Cl or Br) toward monodentate tertiary phosphines in which a novel disproportionation reaction, namely, the transformation of a Re(III)–Re(III) core into Re(IV)–Re(II), has been encountered. A preliminary report describing a few of these results has been published previously.[6]

## Experimental Section

**Starting Materials.** The compounds $[(n\text{-}C_4H_9)_4N]_2Re_2X_8$ (X = Cl or Br) were prepared as described in the literature.[7,8] All common solvents were used as received from commercial sources. Triphenylphosphine was recrystallized twice from ethanol, and other phosphines were used as received without further purification.

**Reaction Procedures.** All syntheses were performed under an atmosphere of dry nitrogen, and all solvents were deoxygenated prior to use.

**A. Synthesis of the Bis(carboxylate) Complexes. (i) $Re_2(O_2CCH_3)_2X_4\cdot 2H_2O$ (X = Cl or Br).** The procedure described is a modification of that suggested by Cotton et al.[9] A sample of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (1.05 g, 0.92 mmol) was stirred in 15 mL of acetic anhydride under a nitrogen atmosphere. Aqueous $HBF_4$ (48%, 0.5 mL) was added by syringe and the resultant blue solution stirred for 2 h. The solution was then evaporated to dryness and the residue washed with $CH_2Cl_2$. It was then recrystallized from acetone/*n*-heptane to afford the complex as a blue powder; yield 0.60 g, 97%. Anal. Calcd for $C_4H_{10}Cl_4O_6Re_2$: C, 7.19; H, 1.51. Found: C, 7.76; H, 1.58. The IR and electronic absorption spectra of this product were in good agreement with literature data.[5f]

An analogous procedure was used to form $Re_2(O_2CCH_3)_2Br_4\cdot 2H_2O$ in similar yield. Anal. Calcd for $C_4H_{10}Br_4O_6Re_2$: C, 5.68; H, 1.19. Found: C, 6.60; H, 1.51. While the analytical data indicated some contamination by other carboxylate-containing species, its properties matched those described in the literature and its reactions (vide infra) were in accord with its identity as the bis(carboxylate).

**(ii) $Re_2(O_2CCH_2CH_3)_2Cl_4\cdot 2H_2O$.** A quantity of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.98 g, 0.86 mmol) was stirred with propionic anhydride (30 mL) and 48% aqueous $HBF_4$ (0.5 mL) under a nitrogen atmosphere for 1 h. The blue solution was evaporated to dryness and the sticky residue washed with $CH_2Cl_2$ and then extracted with acetone. The acetone extract was evaporated to again leave a gum. Since we were unable to dry this material, its identity is based upon its conversion to a 1:2 adduct with 4-methylpyridine (see section A part iii) and its other reactions.

**(iii) $Re_2(O_2CR)_2X_4L_2$ (R = $CH_3$ or $C_2H_5$; X = Cl or Br; L = py, 4-Mepy, DMF, or $Me_2SO$).** The procedure used is based upon that described by Misailova et al.[5f] A small quantity of $Re_2(O_2CR)_2X_4\cdot 2H_2O$ (R = $CH_3$ or $C_2H_5$; X = Cl or Br) was dissolved in acetone, and a few drops of the desired ligand (pyridine, 4-methylpyridine, *N*,*N*-dimethylformamide, or dimethyl sulfoxide) were added. The resulting solution was stirred and then concentrated by partial evaporation of the solvent. The green to blue microcrystals that formed were filtered off, washed sparingly with fresh acetone, and dried in vacuo; yields were close to quantitative. All complexes gave satisfactory microanalytical data.[10]

**B. Reactions of $Re_2(O_2CCH_3)_2Cl_4L_2$ with the Monodentate Tertiary Phosphines $PMe_{3-n}Ph_n$ ($n$ = 0, 1, or 2). (i) $Re_2Cl_4(PMe_3)_4$.** A quantity of $Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.10 g, 0.13 mmol) was refluxed with 0.3 mL of $PMe_3$ and 10 mL of ethanol for 30 h. The resulting green crystals were filtered off and washed with ethanol and ether; yield 0.06 g, 57%. The product was identified as $Re_2Cl_4(PMe_3)_4$ on the basis of its spectroscopic and electrochemical properties.[11,12]

**Table I.** Mixed Halide–Alkoxide Complexes of Dirhenium

| complex | yield, % | anal., % calcd C | calcd H | found C | found H |
|---|---|---|---|---|---|
| $Re_2(OMe)_2Cl_4(PPh_3)_2$[a] | 49 | 39.50 | 3.23 | 39.54 | 3.48 |
| $Re_2(OEt)_2Cl_4(PPh_3)_2$[b] | 54 | 42.55 | 3.58 | 42.15 | 3.56 |
| $Re_2(O\text{-}n\text{-}Pr)_2Cl_4(PPh_3)_2$ | 60 | 43.60 | 3.83 | 43.83 | 4.00 |
| $Re_2(O\text{-}i\text{-}Pr)_2Cl_4(PPh_3)_2$ | 23 | 43.60 | 3.83 | 43.03 | 3.74 |
| $Re_2(OMe)_2Br_4(PPh_3)_2$ | 63 | 35.70 | 2.84 | 35.46 | 3.05 |
| $Re_2(OEt)_2Br_4(PPh_3)_2$ | 43 | 36.77 | 3.09 | 36.87 | 3.11 |
| $Re_2(O\text{-}n\text{-}Pr)_2Br_4(PPh_3)_2$[a] | 31 | 36.38 | 3.27 | 36.79 | 3.10 |

[a] Microanalytical data are for the $CH_2Cl_2$ monosolvate of this complex. [b] Chlorine microanalysis: calcd, 12.56; found, 12.57.

**(ii) $Re_2Cl_4(PMe_2Ph)_4$.** The reaction between $Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.06 g, 0.08 mmol) and 0.6 mL of $PMe_2Ph$ in 30 mL of ethanol at room temperature for 24 h afforded insoluble $Re_2Cl_4(PMe_2Ph)_4$; yield 0.04 g, 47%. This same product was formed in 63% yield when the hydrate $Re_2(O_2CCH_3)_2Cl_4\cdot 2H_2O$ was reacted with $PMe_2Ph$ in ethanol. The identity of this complex was based upon its spectroscopic and electrochemical properties.[11,13]

**(iii) $Re_2Cl_4(PMePh_2)_4$.** A reaction similar to that described in section B part i between $Re_2(O_2CCH_3)_2Cl_4(py)_2$ (0.13 g, 0.16 mmol) and 0.4 mL of $PMePh_2$ was carried out for 16 h to give green $Re_2Cl_4(PMePh_2)_4$; yield 0.17 g, 81%. This product had the same spectroscopic and electrochemical properties as that of an authentic sample which we have recently prepared for the first time from the reaction of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$ with $PMePh_2$.[14] The new method described here is the superior one of the two.

**C. Reactions of $Re_2(O_2CR)_2X_4L_2$ with $PPh_3$ in Alcohol Solvents. Complexes of the Type $(RO)_2X_2ReReX_2(PPh_3)_2$ (X = Cl or Br; R = Me, Et, *n*-Pr, or *i*-Pr).** Since these complexes were prepared by the same general procedure, details of only one recipe will be given here. A mixture of $Re_2(O_2CCH_3)_2Cl_4\cdot 2H_2O$ (0.153 g, 0.23 mmol) and $PPh_3$ (0.120 g, 0.46 mmol) was refluxed in 10 mL of ethanol for 14 h. The reaction mixture was cooled, and the red crystals of the complex of stoichiometry $Re_2(OEt)_2Cl_4(PPh_3)_2$ were filtered off, washed with ethanol and diethyl ether, and dried in vacuo; yield 0.107, 41%. In some runs the product was contaminated by a trace of green powder. In this event, the desired complex can be recrystallized from $CH_2Cl_2$/ethanol. The green insoluble material was identified as $Re_2Cl_6(PPh_3)_2$ on the basis of its Nujol mull IR and electronic absorption spectral properties.

The other methoxide and ethoxide complexes of this type were prepared by this same procedure using reflux periods of from 12 to 20 h. For the preparation of the *n*- and *iso*-propoxide complexes, the reactions were heated to just below reflux and maintained at this temperature for from 1 to 6 days. Since these derivatives are apparently more air-sensitive than the methoxide and ethoxide complexes when in solution, more stringent air- and moisture-free conditions were used in the workup of these products. Microanalytical data and product yields for all of these complexes are compiled in Table I.

The complex of stoichiometry $Re_2(OEt)_2Cl_4(PPh_3)_2$ was also prepared by the use of other complexes of the type $Re_2(O_2CR)_2Cl_4L_2$ as starting materials through their reaction with $PPh_3$ in refluxing ethanol. The starting materials (with product yields in parentheses) are as follows: $Re_2(O_2CCH_3)_2Cl_4(DMF)_2$ (52%), $Re_2(O_2CCH_3)_2Cl_4(Me_2SO)_2$ (12%), and $Re_2(O_2CC_2H_5)_2Cl_4\cdot 2H_2O$ (52%).

**Single Crystals of $(EtO)_2Cl_2ReReCl_2(PPh_3)_2$.** Suitable single crystals of this complex were obtained directly from the reaction mixture as described in the preceding section, C.

**X-ray Crystal Structure Analysis.**[15,16] A small cuboidal crystal was mounted in a capillary and aligned on a CAD-4 diffractometer. Preliminary examination showed that the crystal diffracted well, and from the systematic absences, the space group was unambiguously identified as $P2_1/c$. The collection of data and the solution and refinement of the

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**Table II.** Crystallographic Data

| | |
|---|---|
| formula | $Re_2Cl_4(OEt)_2(PPh_3)_2$ |
| fw | 1128.92 |
| space group | $P2_1/c$ (No. 14) |
| syst absences | $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $00l$, $l = 2n + 1$ |
| $a$, Å | 10.782 (3) |
| $b$, Å | 14.330 (3) |
| $c$, Å | 26.924 (7) |
| $\alpha$, deg | 90.0 |
| $\beta$, deg | 96.98 (2) |
| $\gamma$, deg | 90.0 (2) |
| $V$, Å$^3$ | 4129 (3) |
| $Z$ | 4 |
| $d_{calcd}$, g/cm$^3$ | 1.816 |
| cryst size, mm | 0.3 × 0.2 × 0.2 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 63.09 |
| data collcn instrum | Enraf-Nonius CAD-4 |
| radiation monochromated in incident beam | Mo K$\alpha$ (0.71073) |
| orientation reflcns: no.; range ($2\theta$), deg | 25; 12–32 |
| temp, °C | 25 |
| scan method | $\omega$ |
| data collcn range ($2\theta$), deg | 5–50 |
| no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$ | 6823, 4150 |
| no. of params refined | 431 |
| transmissn factors, max, min, av | 99.91, 65.34, 84.32 |
| $R^a$ | 0.040 |
| $R_w{}^b$ | 0.048 |
| quality-of-fit indicator$^c$ | 1.166 |
| largest shift/esd, final cycle | 0.19 |
| largest peak, e/Å$^3$ | 1.223 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

**Table III.** Positional Parameters and Their Estimated Standard Deviations for $Re_2Cl_4(OEt)_2(PPh_3)_2$

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|
| Re1 | 0.20734 (4) | 0.11164 (4) | 0.08108 (2) | 3.69 (1) |
| Re2 | 0.24057 (4) | 0.24130 (3) | 0.12664 (2) | 2.953 (8) |
| Cl1 | 0.0041 (3) | 0.1342 (2) | 0.0394 (1) | 4.82 (7) |
| Cl2 | 0.3965 (3) | 0.0297 (2) | 0.1006 (1) | 4.95 (7) |
| Cl3 | 0.4419 (2) | 0.2374 (2) | 0.1691 (1) | 3.98 (6) |
| Cl4 | 0.0653 (2) | 0.3389 (2) | 0.1160 (1) | 3.55 (6) |
| P1 | 0.1667 (3) | 0.1859 (2) | 0.2047 (1) | 3.28 (6) |
| P2 | 0.3316 (3) | 0.3439 (2) | 0.0659 (1) | 3.42 (6) |
| O1 | 0.1348 (7) | 0.0281 (5) | 0.1237 (3) | 4.7 (2) |
| O2 | 0.2645 (7) | 0.1401 (6) | 0.0195 (3) | 4.9 (2) |
| C1 | 0.108 (2) | −0.073 (1) | 0.1082 (7) | 9.6 (5)* |
| C2 | 0.041 (2) | −0.113 (2) | 0.146 (1) | 13.4 (8)* |
| C3 | 0.239 (2) | 0.075 (2) | −0.0226 (8) | 10.7 (6)* |
| C4 | 0.326 (2) | 0.078 (2) | −0.053 (1) | 15.2 (9)* |
| C11 | −0.000 (1) | 0.1893 (8) | 0.2097 (4) | 3.8 (3) |
| C12 | −0.042 (1) | 0.2121 (9) | 0.2554 (5) | 4.6 (3) |
| C13 | −0.168 (1) | 0.209 (1) | 0.2607 (6) | 5.9 (3) |
| C14 | −0.254 (1) | 0.1838 (9) | 0.2191 (5) | 6.0 (3) |
| C15 | −0.214 (1) | 0.1630 (9) | 0.1730 (5) | 5.7 (3) |
| C16 | −0.086 (1) | 0.1633 (8) | 0.1684 (5) | 4.5 (3) |
| C21 | 0.230 (1) | 0.2742 (8) | 0.2499 (4) | 3.7 (3) |
| C22 | 0.328 (1) | 0.257 (1) | 0.2871 (5) | 5.3 (3) |
| C23 | 0.377 (1) | 0.331 (1) | 0.3175 (5) | 6.2 (4) |
| C24 | 0.329 (1) | 0.420 (1) | 0.3118 (5) | 6.2 (4) |
| C25 | 0.233 (1) | 0.439 (1) | 0.2740 (5) | 6.0 (4) |
| C26 | 0.180 (1) | 0.3672 (9) | 0.2430 (5) | 5.4 (3) |
| C31 | 0.219 (1) | 0.0746 (8) | 0.2345 (4) | 3.7 (3) |
| C32 | 0.338 (1) | 0.0394 (9) | 0.2280 (5) | 4.6 (3) |
| C33 | 0.384 (1) | −0.039 (1) | 0.2544 (5) | 5.7 (3) |
| C34 | 0.313 (1) | −0.0818 (9) | 0.2898 (5) | 5.3 (3) |
| C35 | 0.196 (1) | −0.0480 (9) | 0.2947 (5) | 5.0 (3) |
| C36 | 0.148 (1) | 0.032 (1) | 0.2685 (5) | 4.9 (3) |
| C41 | 0.3278 (9) | 0.4624 (8) | 0.0889 (4) | 3.8 (3) |
| C42 | 0.355 (1) | 0.480 (1) | 0.1406 (5) | 5.4 (3) |
| C43 | 0.361 (1) | 0.572 (1) | 0.1592 (5) | 5.7 (3) |
| C44 | 0.336 (1) | 0.645 (1) | 0.1269 (6) | 6.3 (4) |
| C45 | 0.310 (1) | 0.630 (1) | 0.0760 (6) | 6.9 (4) |
| C46 | 0.304 (1) | 0.5390 (9) | 0.0570 (5) | 5.2 (3) |
| C51 | 0.4973 (9) | 0.3251 (8) | 0.0611 (4) | 3.6 (2) |
| C52 | 0.533 (1) | 0.2360 (9) | 0.0460 (5) | 5.0 (3) |
| C53 | 0.659 (1) | 0.219 (1) | 0.0409 (5) | 5.9 (4) |
| C54 | 0.749 (1) | 0.289 (1) | 0.0542 (5) | 5.7 (3) |
| C55 | 0.712 (1) | 0.377 (1) | 0.0691 (5) | 5.6 (4) |
| C56 | 0.586 (1) | 0.3953 (9) | 0.0742 (4) | 4.5 (3) |
| C61 | 0.258 (1) | 0.3518 (9) | 0.0020 (4) | 4.5 (3) |
| C62 | 0.129 (1) | 0.357 (1) | −0.0080 (5) | 6.5 (4) |
| C63 | 0.070 (1) | 0.363 (1) | −0.0571 (6) | 8.0 (5) |
| C64 | 0.142 (2) | 0.369 (1) | −0.0971 (5) | 7.3 (4) |
| C65 | 0.272 (2) | 0.368 (1) | −0.0877 (5) | 7.5 (5) |
| C66 | 0.330 (1) | 0.3580 (9) | −0.0386 (5) | 5.3 (3) |

[a] Values marked with an asterisk indicate that the atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

**Table IV.** Cyclic Voltammetric Data for the Dirhenium(III) Carboxylate Complexes $Re_2(O_2CR)_2X_4L_2$[a]

| R | L | Cl | Br |
|---|---|---|---|
| $CH_3$ | $H_2O$ | −0.38 (85) | −0.27 (80) |
| $CH_3$ | py | −0.43 (120) | −0.29 (85) |
| $CH_3$ | 4-Mepy | −0.42 (100)[b] | −0.30 (110) |
| $CH_3$ | DMF | −0.43 (100)[c,d] | −0.28 (80) |
| $CH_3$ | $Me_2SO$ | −0.44 (95) | −0.30 (90) |
| $C_2H_5$ | 4-Mepy | −0.47 (110) | |

[a] $E_{1/2}$ values are in volts vs. Ag/AgCl. Recorded in 0.1 M TBAH–$CH_3CN$ by using a Pt-bead electrode unless otherwise stated. Data obtained at $\nu$ = 200 mV/s. $E_{p,c} - E_{p,a}$ values (i.e. $\Delta E_p$) are given in parentheses. [b] $E_{1/2}$ = −0.43 V vs. Ag/AgCl ($\Delta E_p$ = 130 mV at $\nu$ = 200 mV/s) for a solution in 0.1 M TBAH–$CH_2Cl_2$. [c] Recorded in 0.1 M TBAH–$CH_2Cl_2$. [d] This process is irreversible in 0.1 M TBAH–$CH_3CN$; $E_{p,c}$ = −0.47 V vs. Ag/AgCl ($i_{p,c}/i_{p,a} \gg 1$ at $\nu$ = 200 mV/s).

structure proceeded smoothly. Absorption corrections were based on azimuthal scans ($\psi$-scans) of nine reflections having the angle $\chi$ near 90°. The crystallographic details are presented in Table II. There was no indication of disorder anywhere in the structure. Table III provides a list of the atomic positional parameters and the isotropic or equivalent isotropic displacement parameters for the structure.

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls on an IBM Instruments IR/32 Fourier transform spectrometer (4800–400 cm$^{-1}$). Electronic absorption spectra were recorded on a Cary 17D (1800–900 nm) or IBM Instruments 9420 (900–300 nm) UV-visible spectrophotometer. Electrochemical data were obtained on $CH_2Cl_2$ or $CH_3CN$ solutions of the complexes that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to a Ag/AgCl electrode at room temperature, and the measurements are uncorrected for junction potentials. A Bioanalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B X-Y recorder was used for voltammetric measurements. X-Band ESR spectra were recorded at −160 °C on frozen $CH_2Cl_2$ solutions with a Varian E-109 spectrometer. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Varian XL-200 spectrometer. Resonances for the $^1H$ NMR spectra were referenced internally to the residual protons in the deuterated solvent. The $^{31}P\{^1H\}$ NMR were obtained with the spectrometer operated at 80.98 MHz using an internal deuterium lock and 85% $H_3PO_4$ as an external standard.

**Analytical Procedures.** Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

## Results and Discussion

**(a) Properties and Reactivities of the Dirhenium(III) Carboxylates $Re_2(O_2CR)_2X_4L_2$.** Our initial objective in preparing a selection of complexes of the type $Re_2(O_2CR)_2X_4L_2$ (R = $CH_3$ or $C_2H_5$; X = Cl or Br; L = $H_2O$, py, 4-Mepy, DMF, or $Me_2SO$) had been to examine their redox properties and compare them with the related behavior of the dirhenium(III) carboxylates of stoichiometry $Re_2(O_2CR)_4X_2$.[17] The cyclic voltammetric data for solutions of these complexes in 0.1 M TBAH–$CH_3CN$ and/or 0.1 M TBAH–$CH_2Cl_2$ are presented in Table IV. Each complex possesses a one-electron couple, corresponding to a reduction of the bulk complex, at a potential (in the range −0.27 to −0.44 V

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[17] Srinivasan, V.; Walton, R. A. *Inorg. Chem.* **1980**, *19*, 1635.

**Table V.** Electrochemical and Spectroscopic Data for Mixed Halide–Alkoxide Complexes of Dirhenium

| complex | voltammetric half-wave potentials,[a] V | | electronic abs spectrum, nm | $^1$H NMR,[c] $\delta$ |
|---|---|---|---|---|
| | oxid | redn | | |
| $Re_2(OMe)_2Cl_4(PPh_3)_2$ | +0.84 | −0.52 | 1190 (2400) | 1.69 (s, $CH_3$) |
| $Re_2(OEt)_2Cl_4(PPh_3)_2$ | +0.83 | −0.61 | 1190 (2800) | 1.81 (q, $CH_2$), 0.66 (t, $CH_3$) |
| $Re_2(O\text{-}n\text{-}Pr)_2Cl_4(PPh_3)_2$ | +0.82 | −0.60 | 1190 (2800) | 1.67 (t, $CH_2$), 1.02 (m, $CH_2$), 0.46 (t, $CH_3$) |
| $Re_2(O\text{-}i\text{-}Pr)_2Cl_4(PPh_3)_2$ | +0.80 | −0.63 | 1190 (2200) | 2.73 (m, CH), 0.65 (d, $CH_3$) |
| $Re_2(OMe)_2Br_4(PPh_3)_2$ | +0.93 | −0.49 | 1210 (3400) | 1.66 (s, $CH_3$) |
| $Re_2(OEt)_2Br_4(PPh_3)_2$ | +0.93 | −0.46 | 1210 (3100) | 1.67 (q, $CH_2$), 0.66 (t, $CH_3$) |
| $Re_2(O\text{-}n\text{-}Pr)_2Br_4(PPh_3)_2$ | +0.83 | −0.59 | 1210 (3600) | 1.63 (br, $CH_2$), 1.01 (m, $CH_2$), 0.47 (t, $CH_3$) |

[a] In volts vs. Ag/AgCl. Recorded on solutions in 0.1 M TBAH–$CH_2Cl_2$ by using a Pt-bead electrode. Data obtained at $v$ = 200 mV/s. [b] Measured in $CH_2Cl_2$; $\epsilon_{max}$ values in parentheses. [c] 200-MHz spectra measured in $CDCl_3$. Phenyl resonances not included. Abbreviations are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

vs. Ag/AgCl) similar to those reported for the $Re_2(O_2CR)_4X_2$ complexes.[17] As expected, the $E_{1/2}$ values for the bromides are less negative (i.e. the bromides being more easily reduced to $[Re_2(O_2CR)_2X_4L_2]^-$) than their chloride analogues but there is little, if any, discernible dependence on the nature of L. This reflects the absence of a significant effect of the weakly bound axial ligands L upon the energy of the metal-based LUMO. Each of the couples listed in Table IV is characterized by a $i_{p,c}/i_{p,a}$ ratio close to unity and a constant $i_p/v^{1/2}$ ratio for sweep rates ($v$) of between 50 and 400 mV/s. The potential separation between the coupled cathodic and anodic peaks, $\Delta E_p$, ranged between 80 and 130 mV for a sweep rate of 200 mV/s and increased slightly with an increase in sweep rate. These properties are (with these solvent systems and our cell configuration) consistent with an electron-transfer process that approaches reversibility.[18]

The preceding results prompted us to attempt the isolation of the corresponding tertiary phosphine adducts $Re_2(O_2CR)_2X_4(PR_3)_2$ in order to determine the influence, if any, of a range of phosphine ligands upon the $E_{1/2}$ values. To our initial surprise we were unable to prepare these adducts. Instead, the reactions of $Re_2(O_2CCH_3)_2Cl_4{\cdot}2L$ (L = $H_2O$ or py) with $PMePh_2$, $PMe_2Ph$, or $PMe_3$ readily yield the complexes $Re_2Cl_4(PR_3)_4$.[11-14] In each case, the phosphine is sufficiently basic not only to replace the axially coordinated ligands L but also to reduce the dirhenium(III) unit; the reactions involve a reduction of a quadruply bonded $Re_2^{6+}$ core of electronic configuration $\sigma^2\pi^4\delta^2$ to a triply bonded $Re_2^{4+}$ core ($\sigma^2\pi^4\delta^2\delta^{*2}$). Of special note is our isolation of $Re_2Cl_4(PMePh_2)_4$ by this method because while $PMe_3$ and $PMe_2Ph$ are known to reduce the $[Re_2Cl_8]^{2-}$ ion to the $Re_2Cl_4(PR_3)_4$ complexes, the analogous reaction with $PMePh_2$ produces paramagnetic $Re_2Cl_5(PMePh_2)_3$.[11] The present synthesis of $Re_2Cl_4(PMePh_2)_4$, which demonstrates the effectiveness of acetate as a leaving group in $Re_2(O_2CCH_3)_2X_4L_2$, is a preferred procedure to the only alternative synthetic method, namely, the reaction of $[(\eta^5\text{-}C_5H_5)_2Co][Re_2Cl_5(PMePh_2)_3]$ with $PMePh_2$.[14]

The corresponding reaction of $Re_2(O_2CCH_3)_2Cl_4{\cdot}2H_2O$ with $PPh_3$ in refluxing ethanol for 14 h produced red crystals of stoichiometry $Re_2(OEt)_2Cl_4(PPh_3)_2$. Through the use of the bromide analogue $Re_2(O_2CCH_3)_2Br_4{\cdot}2H_2O$ and the use of other alcohol solvents (in addition to ethanol), we were able to prepare a range of complexes with the stoichiometry $Re_2(OR)_2X_4(PPh_3)_2$ (X = Cl or Br; R = Me, Et, *n*-Pr, or *i*-Pr; see Table I). The preparation of the ethoxide $Re_2(OEt)_2Cl_4(PPh_3)_2$ could also be accomplished by using the propionate $Re_2(O_2CC_2H_5)_2Cl_4{\cdot}2H_2O$ and the DMF and $Me_2SO$ adducts $Re_2(O_2CCH_3)_2Cl_4L_2$ as starting materials, thereby demonstrating the generality of these reactions (eq 1).[19]

$$Re_2(O_2CR')_2X_4L_2 + 2PPh_3 + 2ROH \rightarrow Re_2(OR)_2X_4(PPh_3)_2 + 2R'CO_2H + 2L \quad (1)$$

X = Cl, Br; R = Me, Et, *n*-Pr, *i*-Pr; R′ = $CH_3$, $C_2H_5$; L = $H_2O$, DMF, $Me_2SO$

**(b) Preliminary Characterization of $Re_2(OR)_2X_4(PPh_3)_2$.** The properties of these complexes are very similar (Table V), thereby confirming their close structural similarity to one another. Their IR spectra (Nujol and halocarbon mulls) show bands arising from vibrations of the $PPh_3$ and alkoxide ligands but none that can be attributed to $\nu$(O–H) of any alcohol ligands. The 200-MHz $^1$H NMR spectra (recorded on $CDCl_3$ solutions) show resonances displaying the correct relative intensities for the alkoxide ligands (Table V) and coordinated $PPh_3$, but there was no direct spectroscopic evidence for hydroxyl protons. Further support for this conclusion is seen through a careful examination of the methylene resonances of the coordinated ethoxide ligands in $Re_2(OEt)_2Cl_4(PPh_3)_2$. The symmetric quartet (Table V) shows no evidence for splitting by a hydroxyl proton.

If alcohol rather than alkoxide ligands were present, we would expect the Re–HOR bonds to be kinetically labile. By monitoring the $^1$H NMR spectrum of solutions of $Re_2(OEt)_2Cl_4(PPh_3)_2$ in $CD_2Cl_2$ to which an excess of pyridine or dry $Me_2SO$ had been added, we were able to prove that free ethanol was not released even after extended periods of time (3–7 h). This complex could be recovered unchanged from such solutions.[20]

A clue to the structure of these complexes is provided by an analysis of the 200-MHz $^1$H NMR spectra of the phenyl rings of the $PPh_3$ ligands. All seven complexes possess remarkably similar spectra with two sets of resonances (intensity ratio 2:1) in the region from $\delta$ = +8.0 to $\delta$ = +6.8. In the case of the ethoxide derivative $Re_2(OEt)_2Cl_4(PPh_3)_2$ these resonances (measured in $CD_2Cl_2$) are as follows: $\delta$ = +7.90 (quartet, 4 H) and ca. +7.50 (multiplet, 6 H), +7.31 (triplet, 1 H), +7.12 (triplet, 2 H), +6.46 (quartet, 2 H). The upfield set of three resonances (comprising two apparent triplets and an apparent quartet) can be attributed to a unique phenyl ring of each $PPh_3$ ligand. A series of decoupling experiments (carried out on this ethoxide and on its methoxide analogue) showed that the ortho protons of the two sets of rings (resonances at $\delta$ = +7.90 and +6.46) are coupled to two trans phosphorus nuclei—in each case decoupling of the meta protons gave a triplet for both of the ortho proton resonances. This result was unexpected, for it implies that both $PPh_3$ ligands are bound to the same rhenium atom[21] and that these complexes are the mixed-valence species $(RO)_2Cl_2ReReCl_2(PPh_3)_2$. However, this formulation was subsequently confirmed by a single-crystal X-ray structure determination on $Re_2(OEt)_2Cl_4(PPh_3)_2$.

**(c) Crystal Structure of $Re_2(OEt)_2Cl_4(PPh_3)_2$.** The structure consists of $Re_2Cl_4(OEt)_2(PPh_3)_2$ molecules, shown in Figure 1,

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(18) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, 20, 947.

(19) Interestingly, the reaction between $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = py or 4-Mepy) and $PPh_3$ in refluxing ethanol does not yield $Re_2(OEt)_2Cl_4(PPh_3)_2$. The course of these reactions is being investigated further.

(20) However, when "wet" $Me_2SO$ was used, some hydrolysis of the Re–OEt bonds occurred, thereby leading to the slow release of ethanol. Under such conditions, the ratio of coordinated ethoxide in the original complex to free ethanol was ca. 3:1 after 10 h. The addition of $PMe_3$ to a $CD_2Cl_2$ solution of this same ethoxide complex resulted in a redox reaction in which $Re_2Cl_4(PMe_3)_4$ was one of the principal products.

(21) The $^{31}P\{^1H\}$ NMR spectrum of $Re_2(OEt)_2Cl_4(PPh_3)_2$ (in $CDCl_3$) shows a singlet at $\delta$ = −6.18 (vs. 85% aqueous $H_3PO_4$ with positive chemical shifts downfield), in accord with magnetically and chemically equivalent phosphine ligands.

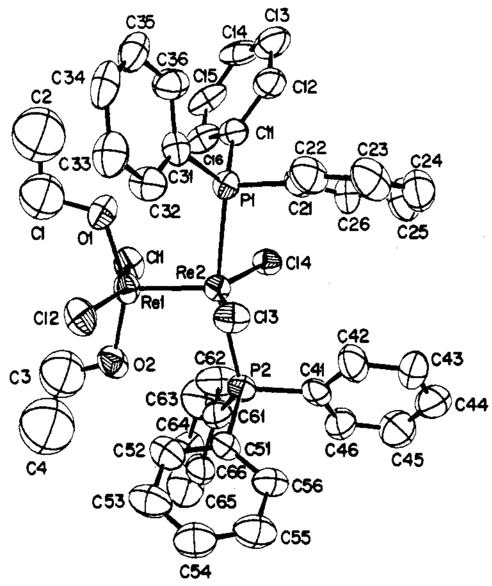

**Figure 1.** Drawing of the $Re_2Cl_4(OEt)_2(PPh_3)_2$ molecule in which the atoms are represented by their ellipsoids of thermal vibration scaled at the 50% level and each atom labeled as in the tables.

**Table VI.** Selected Bond Lengths (Å) in $Re_2Cl_4(OEt)_2(PPh_3)_2$

| | | | |
|---|---|---|---|
| Re(1)–Re(2) | 2.231 (1) | Re(2)–Cl(3) | 2.328 (2) |
| Re(1)–Cl(1) | 2.359 (3) | Re(2)–Cl(4) | 2.340 (2) |
| Re(1)–Cl(2) | 2.356 (3) | Re(2)–P(1) | 2.466 (3) |
| Re(1)–O(1) | 1.892 (8) | Re(2)–P(2) | 2.487 (3) |
| Re(1)–O(2) | 1.883 (8) | | |

**Table VII.** Selected Bond Angles (deg) in $Re_2Cl_4(OEt)_2(PPh_3)_2$

| | | | |
|---|---|---|---|
| Re(2)–Re(1)–Cl(1) | 103.00 (8) | Re(1)–Re(2)–Cl(3) | 109.16 (8) |
| Re(2)–Re(1)–Cl(2) | 102.46 (8) | Re(1)–Re(2)–Cl(4) | 110.94 (7) |
| Re(2)–Re(1)–O(1) | 104.1 (2) | Re(1)–Re(2)–P(1) | 98.83 (7) |
| Re(2)–Re(1)–O(2) | 104.8 (2) | Re(1)–Re(2)–P(2) | 100.43 (7) |
| Cl(1)–Re(1)–Cl(2) | 154.5 (1) | Cl(3)–Re(2)–Cl(4) | 139.9 (1) |
| O(1)–Re(1)–O(2) | 151.0 (4) | P(1)–Re(2)–P(2) | 160.7 (1) |
| Re(1)–O(1)–C(1) | 120.7 (9) | | |
| Re(1)–O(2)–C(3) | 120.0 (10) | | |

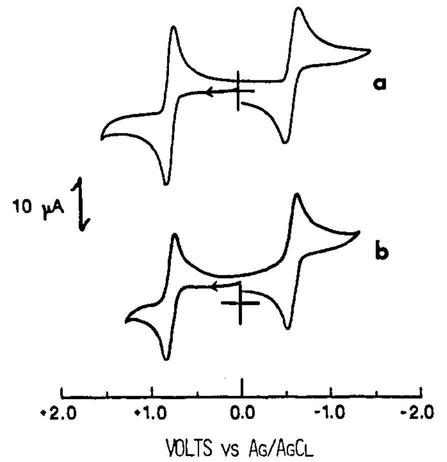

**Figure 2.** Cyclic voltammograms (recorded at $v$ = 200 mV/s by using a Pt-bead electrode) for 0.1 M TBAH–$CH_2Cl_2$ solutions of (a) $Re_2(OEt)_2Cl_4(PPh_3)_2$ and (b) solution a following exhaustive electrolysis at +0.90 V vs. Ag/AgCl.

packed with no unusual contacts. No crystallographic symmetry is imposed on the molecule, but the central portion comes close to having *mm* symmetry, where the approximate symmetry planes would be (1) one that included Re(1), Re(2), and the four chlorine atoms and (2) another including Re(1), Re(2), O(1), O(2), P(1), and P(2). The slight deviations from exact *mm* symmetry in this central region are primarily in the existence of the following nonzero 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°. The more important interatomic distances and angles are listed in Tables VI and VII. Complete lists are available in the supplementary material.

The essentially eclipsed conformation and the Re–Re bond distance of 2.231 (1) Å are both indicative of a Re–Re quadruple bond. However, the way the ligands are distributed over the $Re_2^{6+}$ core requires us to formulate this somewhat differently than the conventional, homopolar quadruple bonds found in $Re_2Cl_8^{2-}$, $Re_2Cl_6(PR_3)_2$, etc. From a purely formal point of view, Re(1) is in oxidation state IV and Re(2) is in oxidation state II, and we would then say, again formally, that one component of the bond must be dative in character in the Re(2)→Re(1) direction. This is doubtless an oversimplification because the alkoxide ligands on Re(2) are good $\pi$-donors and this will help to offset some of the formal charge separation just described.

The Re–O bonds are indeed very short, as a comparison with $Re_2Cl_5(OEt)(dppm)_2$[22] shows. In the present case they are ca. 1.88 Å, while in the comparison compound the Re–O distance is ca. 2.09 Å. While strong RO to metal $\pi$-donor bonding usually leads also to an opening of the M–O–C angle, that is not the case here. This can probably be attributed to the fact that the steric requirements of the large $Ph_3P$ ligands do not permit the ethyl groups to move out. As a result, the strong O→Re $\pi$-donation takes place mainly from one oxygen p$\pi$ orbital, namely, the one whose nodal plane is the C–O–Re plane.

The fact that the Re(1) to Cl distances are slightly longer (by ca. 0.02 Å) than the Re(2)–Cl distances shows that the effective (as opposed to formal) charge at Re(1) cannot be appreciably higher than that at Re(2), or else the opposite relationship would be expected. Thus, the combination of oxygen p$\pi$ donor bonding to Re(1) and Re(2)→Re(1) dative bonding effectively equalize the charge distribution. The fact that the Re(1)–O bonds are short may actually make close approach of the chlorine atoms to Re(1) more difficult sterically.

The concept of a donor–acceptor metal–metal bond is not, of course, a new one,[23] but this is the first instance, to our knowledge, where such a bond has been invoked as part of a strong, multiple metal–metal bond.

**(d) Spectroscopic and Redox Properties of $Re_2(OR)_2X_4(PPh_3)_2$.** The structural differences that exist between these mixed halide–alkoxides and analogous halide complexes of the type $Re_2X_6(PR_3)_2$[2,11] are reflected by differences in their spectroscopic and electrochemical properties (Table V). The most characteristic feature in the electronic absorption spectra of these complexes (measured in $CH_2Cl_2$) is an intense band at $\lambda_{max}$ ~1200 nm ($\epsilon$ ~3000), which can be attributed to a metal-based "mixed-valence" transition. The spectra of all the complexes are very similar in the region from 1500 to 300 nm; the spectrum of $Re_2(OEt)_2Cl_4(PPh_3)_2$ (which is representative of these species) shows additional features at $\lambda_{max}$ ($\epsilon_{max}$ in parentheses) of ~560 sh, 480 (300), 420 (650), and 340 (2900) nm. These spectra are in turn quite different from the related spectra of the quadruply bonded species $Re_2Cl_6(PR_3)_2$[2,11] and therefore imply a significant difference in electronic structure. This conclusion is further supported by electrochemical redox experiments. Cyclic voltammograms of solutions in 0.1 M TBAH–$CH_2Cl_2$ show the presence of two couples (see Table V and Figure 2a), one of which corresponds to a one-electron oxidation ($E_{1/2} \simeq +0.85$ V vs. Ag/AgCl) and the other to a one-electron reduction ($E_{1/2} \simeq -0.55$ V vs. Ag/AgCl). For both couples, the separation between the coupled anodic and cathodic peaks ($\Delta E_p$) was in the range 90–120 mV at $v$ = 200 mV/s, and the $i_{p,a}/i_{p,c}$ ratios were close to unity. Oxidation at +0.90 V generated a green solution of the ESR-active monocation (Figure 2b),[24] while the couple at the more negative

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[22] Barder, T. J.; Cotton, F. A.; Lewis, D.; Schwotzer, W.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 2882.

[23] See, for example: Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K.; Rushman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 345.

potential was chemically irreversible (as judged by bulk electrolysis at −0.65 V). An attempt to generate a solution of the monoanion using cobaltocene as the reducing agent failed to yield a pure product. The redox behavior observed for $Re_2(OR)_2X_4(PPh_3)_2$ differs considerably from that reported for $Re_2X_6(PR_3)_2$ compounds,[25] for which two one-electron reductions occur at potentials more negative than +0.1 V.

**(e) Concluding Remarks.** In our examination of the reactions of $Re_2(O_2CR)_2X_4L_2$ (X = Cl or Br; R = $CH_3$ or $C_2H_5$) toward monodentate tertiary phosphines, we have discovered a novel type of disproportionation reaction in which a Re(III)–Re(III) core is transformed into Re(IV)–Re(II), namely, in the complexes of stoichiometry $Re_2(OR)_2X_4(PPh_3)_2$. This constitutes an important development in the field of multiple-bond chemistry and may presage the discovery of other examples of this kind. The only previous example of this type of reaction was encountered many years ago; the $Re_2Cl_8^{2-}$ ion was found to react with the 2,5-dithiahexane ligand ($CH_3SCH_2CH_2SCH_3$, dth) to afford the triply bonded paramagnetic complex $Cl_4ReRe(dth)_2Cl$.[26] The present discovery is much more significant in terms of its potential scope. Furthermore, these reactions are of additional significance, for they provide a route to a new class of rarely encountered alkoxide complexes of rhenium.[27] Our studies are continuing into the reactivity patterns of the dirhenium(III) carboxylates $Re_2(O_2CR)_2X_4L_2$.

**Acknowledgment.** We thank the National Science Foundation (Grant No. CHE82-06117 and CHE85-06702 to R.A.W. and Grant No. CHE82-11407 to F.A.C.) for research support. The assistance of Stephen M. Tetrick in recording and interpreting of the NMR is gratefully acknowledged.

**Supplementary Material Available:** Tables of complete bond distances and angles, anisotropic thermal parameters, and root-mean-square amplitudes of thermal vibration (9 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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(24) This solution possessed a cyclic voltammogram with couples at $E_{1/2}$ = +0.81 and −0.60 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. We have not yet analyzed this spectrum in detail.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

# Thermal Reaction of $Mo_2I_4(CO)_8$ with $PMe_2Ph$, $PEt_2Ph$, and Pyridine. Formation of Metal–Metal Quadruple Bonds vs. Disproportionation. X-ray Crystal Structures of $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ and $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$

F. Albert Cotton* and Rinaldo Poli

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The thermal reactions of $Mo_2I_4(CO)_8$ with $PMe_2Ph$, $PEt_2Ph$, and pyridine (py) have been studied. The reaction with pyridine leads to disproportionation with formation of $Mo(CO)_3(py)_3$ and $MoI_3(py)_3$. The reactions with the two phosphines in toluene as solvent lead to disproportionation as well as to the formation of the $Mo_2I_4L_4$ (L = $PMe_2Ph$, $PEt_2Ph$) dimers with metal–metal quadruple bonds. The use of THF as solvent in the $PEt_2Ph$ reaction suppresses the formation of the molybdenum(II) dimer in favor of disproportionation. Compounds $Mo_2I_4(PMe_2Ph)_4$ (**1**) and $MoI_3(PMe_2Ph)_2(POMe_2Ph)$ (**2**) have been isolated from the $PMe_2Ph$ reaction in toluene, while the compound $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$ (**3**) has been obtained from the $PEt_2Ph$ reaction in THF. Compounds **2** and **3** have been structually characterized by X-ray diffraction methods. Compound **2**: space group $Pmn2_1$, $a$ = 13.801 (3) Å, $b$ = 12.303 (3) Å, $c$ = 9.298 (1) Å, $V$ = 1578.7 (8) Å$^3$, $Z$ = 2, $R$ = 0.0516 ($R_w$ = 0.0622) for 1038 data with $F_o^2 > 3\sigma(F_o^2)$. Compound **3**: space group $P2_1/c$, $a$ = 20.144 (6) Å, $b$ = 10.368 (2) Å, $c$ = 19.822 (3) Å, $\beta$ = 109.37°, $V$ = 3904 (3) Å$^3$, $Z$ = 4, $R$ = 0.0371 ($R_w$ = 0.0540) for 3902 data with $F_o^2 > 3\sigma(F_o^2)$. A possible mechanism that interrelates the two different pathways is discussed.

## Introduction

The recent development[1] of a convenient synthesis of $Mo_2I_4(CO)_8$[2] has permitted more reactivity studies to be carried out on this molecule. As a result, a new route to the quadruply bonded dimolybdenum(II) tetraiodide complexes has been recently found in this laboratory.[3] In particular, $Mo_2I_4(PMe_3)_4$,[3a] $Mo_2I_4(dppm)_2$,[3a,b] and $Mo_2I_4(dmpm)_2$[3c] could be produced upon reaction of $Mo_2I_4(CO)_8$ with the appropriate phosphine in refluxing toluene. To probe the possible application of this method to the preparation of a wider variety of dimolybdenum(II) molecules, we have investigated the same reaction with different systems. We report here the results obtained by using $PMe_2Ph$, $PEt_2Ph$, and pyridine (py) as ligands, which show this reaction to be far more complicated than expected.

## Experimental Section

All operations were carried out under an atmosphere of prepurfied argon. Solvents were dried by conventional methods and distilled under dinitrogen. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer; the solution spectra were recorded on expanded abscissa and calibrated with both CO(g) and water vapor. Elemental analyses were by Galbraith Laboratories, Knoxville, TN. $PMe_2Ph$ and $PEt_2Ph$ were purchased from Strem Chemicals and used without further purification. $Mo_2I_4(CO)_8$ was prepared as previously described.[1]

**Reaction of $Mo_2I_4(CO)_8$ with $PMe_2Ph$.** $Mo_2I_4(CO)_8$ (0.38 g, 0.41 mmol) was treated at room temperature with $PMe_2Ph$ (0.23 mL, 1.6 mmol) in 20 mL of toluene as solvent. Vigorous gas evolution occurred,

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