H, 4.19. Found: C, 18.94; H, 4.19.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 81-21282 to R.R.S.) and, in part, the National Institutes of Health (Research Grant RR00317 to Professor Klaus Biemann). We thank Dr. Catherine Costello for obtaining FD mass spectra, Professor Satoru Masamune for use of his capillary GLC equipment, and Professor Robert H. Grubbs for permission to quote unpublished results.

Registry No. $1^+CF_3CO_2^-$, 86024-14-8; 1^+Cl^-, 86024-15-9; **2** (X = Cl), 86087-44-7; **2** (X = I), 86087-47-0; **3**, 86024-18-2; **4** (X = Cl), 86024-24-0; **4** (X = I), 86045-49-0; $TaCp^*(CHCMe_3)(H)(Cl)(PMe_3)$, 86087-43-6; $Ta(CDCMe_3)(D)(PMe_3)_3Cl_2$, 86087-45-8; $Ta(CHCMe_3)(D)(PMe_3)_3Cl_2$, 86024-16-0; $Ta(CDMe_3)(H)(PMe_3)_3Cl_2$, 86087-46-9; $Ta(CHCMe_3)(H)(PMe_3)_2(py)(OTF)_2$, 86024-20-6; $[NEt_4][Ta(CHCMe_3)(H)(PMe_3)_2Cl_3]$, 86024-23-9; $Ta(C_2H_4)(PMe_3)_2I_3$, 86024-25-1; $Ta(PMe_3)_3I_3$, 86024-26-2; $Ta(C_2H_4)Et(PMe_3)_2I_2$, 86024-27-3; $Ta(CHCMe_3)(dmpe)_2Cl$, 80559-92-8; $Ta(C_5Me_5)(CH_2CMe_3)Cl_3$, 68087-41-2; $Ta(CH_2CMe_3)Cl_4$, 71201-79-1; $Ta(CD_2CMe_3)Cl_4$, 75349-01-8; $Ta(CHDMe_3)Cl_4$, 86024-28-4; $Ta(CHCMe_3)(CH_2CH_3)(PMe_3)_2Cl_2$, 79839-93-3; $Ta(CH_2CMe_3)(CH_2CH_2)(PMe_3)_2Cl_2$, 79839-94-4; $Ta(CHCMe_3)(PMe_3)_2CD_3$, 70083-62-4; $Ta(C_2H_4)Et(PMe_3)_2Cl_2$, 79855-21-3; Me_3SiI, 16029-98-4; Me_3SiOTf, 27607-77-8; C_2H_4, 74-85-1; trifluoroacetic acid, 76-05-1; tetraethylammonium chloride, 56-34-8; neopentane, 463-82-1; 2,2-dimethylpentane, 590-35-2; 2,2-dimethylheptane, 1071-26-7; 2,2-dimethylnonane, 17302-14-6; 2,2-dimethylundecane, 17312-64-0; 2,2-dimethyltridecane, 61869-04-3; 2,2-dimethylbutane, 75-83-2.

Synthesis and Structural Characterization of $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$ (*n* = 0, 1, or 2): A Series of Complexes Possessing Metal–Metal Bond Orders of 4, 3.5, and 3 and the Dependence of Bond Length upon Bond Order

F. Albert Cotton,*[1a] Kim R. Dunbar,[1b] Larry R. Falvello,[1a] Milagros Tomas,[1a] and Richard A. Walton*[1b]

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

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Abstract: The following three compounds have been prepared in crystalline form and thoroughly characterized by chemical, electrochemical, magnetic, spectroscopic, and structural methods: $Re_2Cl_4(PMe_2Ph)_4$, **1**; $[Re_2Cl_4(PMe_2Ph)_4](PF_6)$, **2**; $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$, **3**. Compound **1** forms crystals in space group $C2/c$ with $a = 17.571$ (2) Å, $b = 9.991$ (1) Å, $c = 22.316$ (3) Å, $\beta = 107.47$ (1)°, $V = 3737$ (1) Å^3, and $Z = 4$. Olive green **2**, obtained by oxidation of **1** with $NOPF_6$, crystallizes in space group $P2_1/c$ with $a = 10.596$ (2) Å, $b = 33.129$ (6) Å, $c = 13.801$ (2) Å, $\beta = 111.16$ (1)°, $V = 4518$ (2) Å^3, and $Z = 4$. Compound **3**, also green and also obtained from **1** by oxidation with $NOPF_6$, crystallizes in space group $P2_1/c$ with $a = 24.317$ (8) Å, $b = 10.485$ (4) Å, $c = 20.284$ (7) Å, $\beta = 111.61$ (3)°, $V = 4808$ (3) Å^3, and $Z = 4$. Compounds **1**–**3** are reversibly electrochemically interconvertible with $E_{1/2}$ values of +0.85 and −0.26 V vs. SCE. **1** and **3** are diamagnetic while **2** has a magnetic moment of 1.35 μ_B (per Re_2 unit) and exhibits an ESR spectrum with $g_{\parallel} = 2.19$ and $g_{\perp} = 2.24$. Compound **2** has its $\delta \rightarrow \delta^*$ transition at 1360 nm. In going through the series **1** to **2** to **3**, the Re–Cl distances decrease (ca. 0.048 Å at each step), the Re–P distances increase (ca. 0.045 Å at each step), and the Re–Re distances change by −0.023 (2) Å from **1** to **2** and by −0.003 (2) Å (i.e., not significantly) from **2** to **3**. These bond length changes, which do not correlate simply with the bond order, are discussed and explanations proposed.

Introduction

A fundamental question in the chemistry of dimetal species containing metal–metal multiple bonds[2] is not only how strong, in a thermodynamic sense, are such bonds, but how does the δ component affect the M–M bond length in compounds containing quadruple bonds (i.e., those possessing the $\sigma^2\pi^4\delta^2$ configuration)? While the presence or absence of the δ component is often critical in dictating the rotational conformation (eclipsed versus staggered) that may be present in such dimetal species, it is clear that this contribution is much weaker than the σ or π contributions to the M–M bond and thus its effect on the bond length is not easy to forecast.

In efforts over the years to elucidate this matter, structural studies have been carried out on pairs of complexes that possess *identical* ligand sets but differ in the population of the δ and δ^* orbitals. Of particular note in this regard are studies on the $[Tc_2Cl_8]^{2-}$ and $[Tc_2Cl_8]^{3-}$ anions,[3,4] possessing $\sigma^2\pi^4\delta^2$ and $\sigma^2\pi^4\delta^2\delta^{*1}$ configurations, respectively, and the sulfate- or phosphate-bridged anions $[Mo_2(SO_4)_4]^{4-}$, $[Mo_2(SO_4)_4]^{3-}$, and $[Mo_2(HPO_4)_4]^{2-}$[5,6] for which the ground-state electronic configurations are $\sigma^2\pi^4\delta^2$, $\sigma^2\pi^4\delta^1$, and $\sigma^2\pi^4$, respectively.

For the first time we have synthesized, and herein report the structural characterization of, a series of three complexes possessing M–M bonds of orders 4, 3.5, and 3 and identical sets of *monodentate* ligands. The isolation of the complexes $Re_2Cl_4(PMe_2Ph)_4$, $[Re_2Cl_4(PMe_2Ph)_4]PF_6$, and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ provides an ideal opportunity to study the variation of M–M bond length with changes in δ contribution to the bond in the absence of any special bonding constraints engendered by sets of *bridging* ligands.

Experimental Section

Starting Materials. The complexes $(n\text{-}Bu_4N)_2Re_2Cl_8$ and $Re_2Cl_4(PMe_2Ph)_4$ were prepared by previously reported methods.[7,8] The ligand

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dimethylphenylphosphine was purchased from Strem Chemicals, Inc., and used without further purification. Potassium perrhenate was obtained from Pressure Chemical Co. Nitrosonium hexafluorophosphate was supplied by Alfa Products. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by reacting tetra-*n*-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried at 90 °C.

Reaction Procedures. All reactions were performed under an atmosphere of dry nitrogen, and all solvents were deoxygenated with N_2. Acetonitrile was dried over CaH_2 and freshly distilled under N_2 prior to use.

Reactions of $Re_2Cl_4(PMe_2Ph)_4$ with $NOPF_6$. (i) $[Re_2Cl_4(PMe_2Ph)_4]PF_6$. In a typical reaction, 0.30 g (0.28 mmol) of $Re_2Cl_4(PMe_2Ph)_4$ was suspended in 10 mL of acetonitrile. Approximately 1 equiv of $NOPF_6$ (0.045 g, 0.30 mmol) was added to the suspension via a side-arm addition tube. A gas was evolved and the solution immediately turned emerald green but then changed quickly to an olive green color. After the reaction mixture was stirred for 10 min, a quantity of absolute diethyl ether (50 mL) was added. The solution was chilled to 0 °C for 24 h and filtered. The olive green crystals were washed with three 20-mL portions of diethyl ether. The reaction filtrate was reduced in volume, and ethanol was added. After being cooled to 0 °C, this solution yielded more product. The combined crops of crystals were then vacuum dried; yield 0.25 g (73%). Anal. Calcd for $C_{32}H_{44}Cl_4F_6P_5Re_2$: C, 31.72; H, 3.66. Found: C, 31.71; H, 3.34. An analogous procedure using tetrahydrofuran as the solvent gives the product in similar yields but in a less crystalline form.

(ii) **$[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$.** A reaction procedure similar to that described above, but using 0.50 g (0.469 mmol) of $Re_2Cl_4(PMe_2Ph)_4$, 10 mL of acetonitrile, and 3.5 equiv of $NOPF_6$ (0.236 g, 1.64 mmol), afforded a deep emerald-green solution. After this was stirred for 3 min, 80 mL of absolute diethyl ether was added to the reaction solution in 5-mL aliquots over a period of 15 min. This slow addition of diethyl ether resulted in a crystalline product rather than the fine powder produced by rapid precipitation. The emerald green crystals were collected under N_2, washed with diethyl ether, and vacuum dried; yield 0.59 g (90%). Anal. Calcd for $C_{32}H_{44}Cl_4F_{12}P_6Re_2$: C, 28.33; H, 3.27. Found: C, 28.61; H, 3.46. The compound is soluble in common solvents, e.g., acetone and dichloromethane, but it is difficult to recrystallize because it is quickly reduced to the monocation in solution. In the solid state, the compound slowly decomposes in air over the period of several days. The major decomposition product is $Re_2Cl_5(PMe_2Ph)_3$, which cyclic voltammetry showed was also present as a minor contaminant in the crystalline product obtained from the reaction solution.

Reaction of $Re_2Cl_4(PMe_2Ph)_4$ with Tropylium Hexafluorophosphate. A quantity of $Re_2Cl_4(PMe_2Ph)_4$, (0.1 g, 0.094 mmol) was suspended in 5 mL of acetonitrile to which was added 0.025 g (0.106 mmol) of $(C_7H_7)PF_6$. The reaction mixture was stirred for 5 min at which time 5 mL of diethyl ether was added via a syringe. The solution was refrigerated for 24 h and then filtered. The crop of dark olive green crystals of $[Re_2Cl_4(PMe_2Ph)_4]PF_6$ was washed with several portions of diethyl ether and dried under reduced pressure; yield 0.08 g (70%).

Preparation of Single Crystals of $Re_2Cl_4(PMe_2Ph)_4$ and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_n$ (n = 1 or 2). Crystals of $Re_2Cl_4(PMe_2Ph)_4$, which were of a quality suitable for an X-ray structure analysis, were grown directly from the reaction solution.[8] In the case of $[Re_2Cl_4(PMe_2Ph)_4PF_6$, good quality crystals were obtained by the addition of tetrahydrofuran–diethyl ether mixtures to an acetonitrile solution of the compound. Emerald green platelike crystals of $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2$ were grown by the slow addition of diethyl ether to the reaction solution. Attempts to grow crystals of the latter complex by other procedures were thwarted by the ease of reduction of the dication to $[Re_2Cl_4(PMe_2Ph)_4]PF_6$.

X-ray Crystallographic Procedures. The structures of single crystals containing the complexes $[Re_2Cl_4(PMe_2Ph)_4]^{n+}$, in which n = 0, 1, and 2 (structures **1**, **2**, and **3**, respectively), were determined by application of general procedures which have already been fully described elsewhere.[9] A detailed description of the diffractometer data collection,[9a,b] empirical absorption corrections,[9c] and computational procedures[9d] is available as supplementary material. The crystal parameters and basic information about data collection and structure refinement are summarized in Table I.

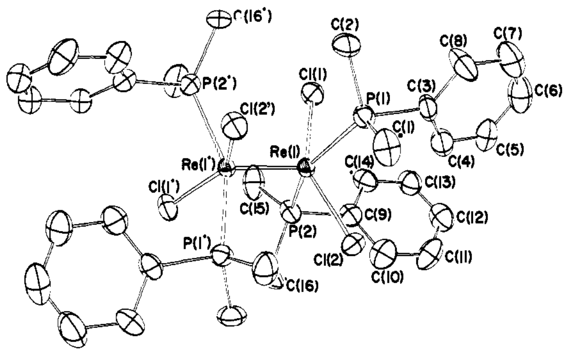

Figure 1. Structure and labeling scheme for the neutral complex $Re_2Cl_4(PMe_2Ph)_4$. Atoms are represented by their 50% probability ellipsoids. The molecule resides on a twofold axis of symmetry.

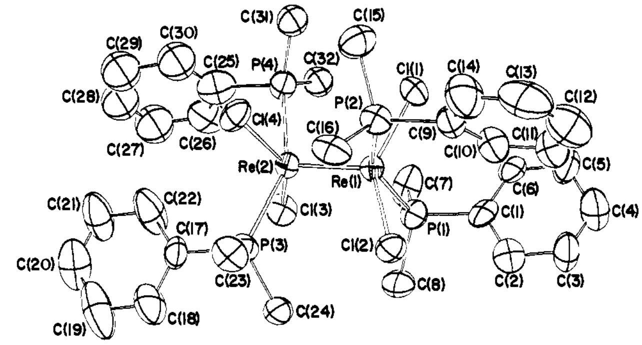

Figure 2. Structure and atom labeling scheme for the complex cation $[Re_2Cl_4(PMe_2Ph)_4]^+$. Atoms are represented by their 50% probability ellipsoids.

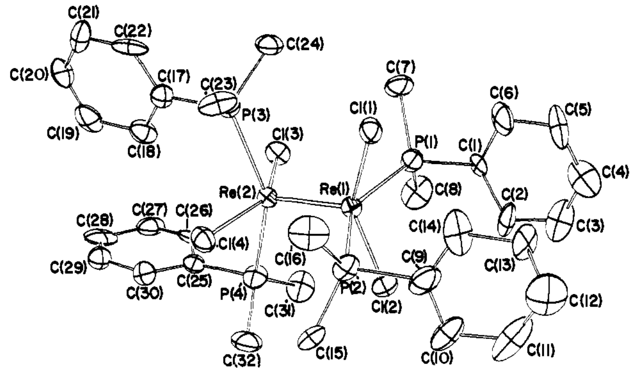

Figure 3. Structure and labeling scheme for the complex cation $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$. Atoms are represented by their 40% probability ellipsoids. Atom C(17) is shown as its isotropic equivalent.

Tables II, III, and IV list the atomic coordinates for structures **1**, **2**, and **3**, respectively; and Tables V and VI give the important bond distances and angles, respectively, for the three structures. Complete tables of anisotropic thermal parameters, bond distances, bond angles, and structure factor data are available as supplementary material. Figures 1, 2, and 3 show the structures and atom numbering schemes for the three dinuclear complexes.

Other Physical Measurements. Infrared spectra of Nujol mulls on polyethylene plates were recorded in the region 400–50 cm^{-1} by using a Digilab FTS-20B spectrophotometer and in the region 4000–600 cm^{-1} by using a Beckman IR-12 spectrophotometer. Electronic absorption spectra of acetonitrile solutions were recorded on a Cary 14 spectrophotometer. Magnetic susceptibility measurements were done by the Evans method[11,12] in dichloromethane on a 90-MHz Perkin-Elmer R32 spectrometer. X-Band ESR spectra of dichloromethane–toluene glasses were recorded at −160 °C with a Varian E-109 spectrometer. Electro-

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(10) The estimated deviation in square brackets is calculated as [ ] = $[\Sigma_n\Delta_i^2/n(n-1)]^{1/2}$, in which Δ_i is the deviation of the ith of n values from the arithmetic mean of the set.

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Table I. Summary of Crystal Data, Data Collection Parameters, and Least-Squares Residuals for $Re_2Cl_4(PMe_2Ph)_4$, 1, $[Re_2Cl_4(PMe_2Ph)_4](PF_6)\cdot{}^1/_2THF$, 2, and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2\cdot CH_3CN$, 3

	1	2	3
formula	$Re_2Cl_4P_4C_{32}H_{44}$	$Re_2Cl_4P_5F_6C_{32}H_{44}\cdot{}^1/_2(C_4H_8O)$	$Re_2Cl_4P_6F_{12}C_{34}H_{47}N$
fw	1066.8	1247.8	1397.8
space group	*C*2/*c*	*P*2₁/*c*	*P*2₁/*c*
a, Å	17.571 (2)	10.596 (2)	24.317 (8)
b, Å	9.991 (1)	33.129 (6)	10.485 (4)
c, Å	22.316 (3)	13.801 (2)	20.284 (7)
α, deg	90	90	90
β, deg	107.47 (1)	111.16 (1)	111.61 (3)
γ, deg	90	90	90
V, Å^3	3737 (1)	4518 (2)	4808 (3)
Z	4	4	4
d_{calcd}, g/cm^3	1.896	1.834	1.931
cryst size, mm	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.1	0.55 × 0.20 × 0.02
μ(Mo Kα), cm^{-1}	73.2	61.3	58.2
data collection instrument	Enraf-Nonius CAD-4	CAD-4	Syntex P$\bar{1}$
radiation	Mo Kα ($\lambda\bar{\alpha}$ = 0.710 73 Å); graphite monochromated		
scan method	ω-2θ	ω scan	ω scan
data collection range	4 ≤ 2θ ≤ 50°	4 ≤ 2θ ≤ 50°	4 ≤ 2θ ≤ 50°
no. of unique data, $F_o^2 \geq 3\sigma(F_o^2)$	2826	3749	2927
no. of parameters refined	194	418	467
R^a	0.0279	0.0477	0.0560
$R_w{}^b$	0.0454	0.0551	0.0666
quality-of-fit indicator^c	1.412	1.220	1.045
largest shift/esd, final cycle	0.10	0.26	0.36

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

Table V. Table of Important Bond Distances (Å) and Their Estimated Standard Deviations for $Re_2Cl_4(PMe_2Ph)_4$, 1, $[Re_2Cl_4(PMe_2Ph)_4](PF_6)\cdot{}^1/_2THF$, 2, and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2\cdot CH_3CN$, 3[a]

	1[b]	2	3
Re-Re	2.241 (1)	2.218 (1)	2.215 (2)
Re(1)-Cl(1)	2.390 (1)	2.336 (4)	2.294 (7)
-Cl(2)	2.384 (1)	2.331 (4)	2.287 (7)
-P(1)	2.433 (1)	2.446 (5)	2.496 (8)
-P(2)	2.403 (1)	2.461 (5)	2.502 (7)
Re(2)-Cl(3)		2.321 (4)	2.279 (7)
-Cl(4)		2.331 (4)	2.302 (8)
-P(3)		2.476 (4)	2.520 (7)
-P(4)		2.458 (4)	2.514 (7)
$[Re-Cl]_{av}{}^c$	2.387 [3]	2.330 [3]	2.291 [5]
$[Re-P]_{av}{}^c$	2.418 [15]	2.460 [6]	2.508 [5]
$[P-C_{phenyl}]_{av}{}^c$	1.828 [2]	1.83 [1]	1.81 [1]
$[P-C_{methyl}]_{av}{}^c$	1.826 [6]	1.83 [1]	1.84 [1]

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits. [b] In structure 1 the complex resides on a crystallographic diad axis, and so the unique unit is half of the chemical moiety. Also, the minor (2% occupancy) disordered component is not treated in this table. Its derived parameters (Re-Re = 2.23 (4) Å) are treated fully in the supplementary tables. [c] The estimated deviation in square brackets is defined in ref 10.

chemical measurements were made in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values were determined as $(E_{p,a} + E_{p,c})/2$ and are referenced to the saturated potassium chloride calomel electrode (SCE) at room temperature. Voltammetric experiments were performed by using a BioAnalytical Systems, Inc., Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

Table VI. Table of Important Bond Angles (deg) and Their Estimated Standard Deviations for $Re_2Cl_4(PMe_2Ph)_4$, 1, $[Re_2Cl_4(PMe_2Ph)_4](PF_6)\cdot{}^1/_2THF$, **2**, and $[Re_2Cl_4(PMe_2Ph)_4](PF_6)_2\cdot CH_3CN$, 3[a]

	1[b]	2	3
Re-Re(1)-Cl(1)	109.27 (3)	108.1 (1)	107.6 (2)
-Cl(2)	107.16 (3)	110.1 (1)	106.7 (2)
-P(1)	104.04 (3)	103.4 (1)	106.8 (2)
-P(2)	103.12 (3)	104.8 (1)	107.6 (2)
Cl(1)-Re(1)-Cl(2)	143.54 (5)	141.8 (2)	145.6 (3)
-P(1)	84.75 (5)	86.1 (2)	85.1 (3)
-P(2)	85.66 (5)	86.2 (2)	85.8 (3)
Cl(2)-Re(1)-P(1)	85.10 (5)	86.2 (2)	85.9 (3)
-P(2)	87.66 (5)	83.2 (2)	83.1 (3)
P(1)-Re(1)-P(2)	152.83 (5)	151.7 (2)	145.6 (3)
Re(1)-Re(2)-Cl(3)		108.9 (1)	106.9 (2)
-Cl(4)		108.2 (1)	108.0 (2)
-P(3)		105.5 (1)	106.4 (2)
-P(4)		104.1 (1)	104.8 (2)
Cl(3)-Re(2)-Cl(4)		142.9 (2)	145.1 (3)
-P(3)		83.8 (2)	85.9 (3)
-P(4)		87.3 (2)	85.6 (3)
Cl(4)-Re(2)-P(3)		85.6 (2)	84.0 (3)
-P(4)		84.7 (2)	86.0 (3)
P(3)-Re(2)-P(4)		150.4 (2)	148.8 (3)
$[Re-Re-Cl]_{av}{}^c$	108 [1]	108.8 [5]	107.3 [3]
$[Re-Re-P]_{av}{}^c$	103.6 [5]	104.5 [5]	106.4 [6]
$[Cl-Re-Cl]_{av}{}^c$		142.4 [6]	145.4 [3]
$[P-Re-P]_{av}{}^c$		151.1 [7]	147 [2]
$[Cl-Re-P]_{av}{}^c$	85.8 [7]	85.4 [5]	85.2 [4]
$[Re-P-C_{methyl}]_{av}{}^c$	119.7 [7]	117.8 [6]	116 [1]
$[Re-P-C_{phenyl}]_{av}{}^c$	106 [2]	106 [2]	104 [2]
$[C_{methyl}-P-C_{methyl}]_{av}{}^c$	103.5 [6]	104.9 [4]	107 [1]
$[C_{methyl}-P-C_{phenyl}]_{av}{}^c$	102.8 [5]	105 [1]	107 [1]

[a] Estimated standard deviations of individual angles are given in parentheses for the least significant digits. [b] In structure 1 the complex sits across a crystallographic two fold axis, and so the unique portion comprises half of the molecule. Also, the minor (2% occupancy) disordered component is not considered in this table; derived parameters involving it are available in the supplementary tables. [c] The estimated deviation in square brackets is defined in ref 10.

Synthesis and Spectroscopic, Magnetic, and Electrochemical Characterization of the Species $[Re_2Cl_4(PMe_2Ph)_4]^{0,1+,2+}$. Previous electrochemical studies[13,14] have demonstrated that complexes of the type $Re_2X_4(PR_3)_4$ (X = Cl, Br, and I) possess two reversible one-electron oxidations, the first of which is very accessible ($E_{1/2}$ value between −0.22 and −0.44 V vs. SCE).[14] Use of $NOPF_6$ as a chemical oxidant led to isolation of the crystalline salts $[Re_2X_4(PEt_3)_4]PF_6$ (X = Cl and Br), but we were, at the time,

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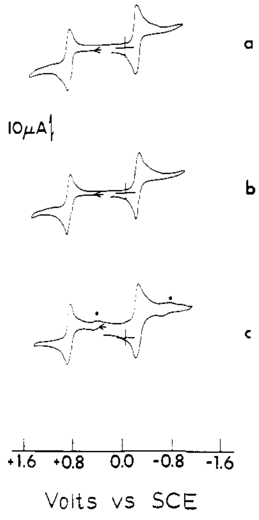

Figure 4. Cyclic voltammograms (scan rate 200 mV/s at a Pt bead electrode) in 0.2M TBAH–CH$_2$Cl$_2$: (a) Re$_2$Cl$_4$(PMe$_2$Ph)$_4$; (b) [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]PF$_6$; (c) [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)$_2$ (couples due to the presence of the contaminant Re$_2$Cl$_5$(PMe$_2$Ph)$_3$ are marked with an asterisk).

unable to achieve the second oxidation to [Re$_2$X$_4$(PEt$_3$)$_4$]$^{2+}$ using NOPF$_6$.[14] One explanation for this was that the redox potential of the NO$^+$/NO couple (estimated to be between +1.00 and +0.85 V in acetonitrile vs. Ag$^+$/Ag)[15] was insufficient to bring about this second oxidation. However, that this is not the case with all dirhenium complexes of this type is demonstrated by our isolation, in the present study, of the crystalline salts [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]PF$_6$ and [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)$_2$ using this same oxidant.

Cyclic voltammograms of the neutral and the chemically oxidized species are shown in Figure 4. The three complexes exhibit identical $E_{1/2}$ values (+0.85 and −0.26 V vs. SCE), with the neutral complex having two reversible oxidations (Figure 4a), the monocation possessing a reversible oxidation and a reversible reduction (Figure 4b), and the dication exhibiting two reversible reductions (Figure 4c). A simple electrochemical experiment involving addition of free Cl$^-$ to solutions of either [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]PF$_6$ or [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)$_2$ confirms the previously postulated EECC and ECEC mechanisms[14] for the formation of Re$_2$Cl$_5$(PR$_3$)$_3$ and Re$_2$Cl$_6$(PR$_3$)$_2$ in electrochemically oxidized solutions of Re$_2$Cl$_4$(PR$_3$)$_4$, through the reactions [Re$_2$Cl$_4$(PR$_3$)$_4$]$^+$ + Cl$^-$ → Re$_2$Cl$_5$(PR$_3$)$_3$ + PR$_3$ and [Re$_2$Cl$_4$(PR$_3$)$_4$]$^{2+}$ + 2Cl$^-$ → Re$_2$Cl$_6$(PR$_3$)$_2$ + 2PR$_3$. These reactions were confirmed by monitoring the formation of Re$_2$Cl$_5$(PMe$_2$Ph)$_3$ ($E_{1/2}$(ox.) = +0.46 V and $E_{1/2}$(red.) = −0.65 V vs. SCE) and Re$_2$Cl$_6$(PMe$_2$Ph)$_2$ ($E_{1/2}$(red.) = −0.05 V and $E_{1/2}$(red.) = −0.92 V vs. SCE) by cyclic voltammetry.

The spectroscopic and magnetic properties of the hexafluorophosphate salts of the oxidized dirhenium cations are summarized in Table VII. The data for [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]PF$_6$ correlate very well with that previously reported for [Re$_2$Cl$_4$(PEt$_3$)$_4$]PF$_6$.[14] The IR spectrum is typical of coordinated PMe$_2$Ph and exhibits a strong absorption at ~840 cm^{-1} due to the ν(P–F) mode of PF$_6^-$. The ν(Re–Cl) stretches are at 348 (s) and 304 (s) cm^{-1}. An acetonitrile solution of [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]PF$_6$ has an intense, broad band at 1360 nm (7350 cm^{-1}) in its electronic absorption spectrum, characteristic of a Re$_2^{5+}$ core possessing a $\sigma^2\pi^4\delta^2\delta^{*1}$ ground-state electronic configuration.[8,16,17] This band is assigned to the $\delta \rightarrow \delta^*$ transition.[18] The paramagnetic nature of this complex was confirmed by a determination of its magnetic moment (1.35 μ_B/Re$_2$ unit) by the Evans method.[11,12] The X-band ESR spectrum of this complex (Table VII) is typical of those obtained for other dirhenium phosphine complexes containing Re–Re bonds of order 3.5.[13,14]

Table VII. Spectroscopic and Magnetic Properties of the Complexes [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]PF$_6$ and [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)$_2$

	[Re$_2$Cl$_4$-(PMe$_2$Ph)$_4$]$^+$	[Re$_2$Cl$_4$-(PMe$_2$Ph)$_4$]$^{2+}$
characteristic IR absorptions, cm^{-1}	840 (vs) 348 (s), 304 (s)	843 (vs) 368 (s), 314 (m)
electronic absorption spectra,^{a} nm	440 (s), 585 (w) 1360 (s, br)	435 (s), 720 (vs) 1395 (s, br)^b
ESR (CH$_2$Cl$_2$/toluene glass)^c		
$g_\parallel$ ($A_\parallel$)	2.19 (300)	no signal
$g_\perp$ ($A_\perp$)	2.24 (120)	
magnetic moment,^{d} μ_{obsd}	1.35	diamagnetic

^{a} Electronic absorption spectra were measured in CH$_3$CN solution. ^{b} This peak is due to an overlap of the $\delta \rightarrow \delta^*$ transition of Re$_2$Cl$_5$(PMe$_2$Ph)$_3$ present as an impurity and of the [Re$_2$Cl$_4$-(PMe$_2$Ph)$_4$]$^+$ species which forms due to the spontaneous reduction of [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]$^{2+}$ in solution. ^{c} The values for $A_\parallel$ and $A_\perp$ are given in Gauss and are approximate values. ^{d} Magnetic moments were determined on dichloromethane solutions by the Evans method.

The corresponding properties of [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$](PF$_6$)$_2$ are those which are expected for a diamagnetic complex possessing a $\sigma^2\pi^4\delta^2$ configuration. The diamagnetism of this salt was confirmed by the lack of an ESR signal as well as the absence of a shift in the ^{1}H NMR spectrum of dichloromethane by the Evans method. The electronic spectrum of this complex resembles those of [Re$_2$Cl$_8$]$^{2-}$ and Re$_2$Cl$_6$(PR$_3$)$_2$ in showing an intense sharp band at 720 nm (13 900 cm^{-1}), assigned to the $\delta \rightarrow \delta^*$ transition.[2,19] However, the additional presence of an absorption band at 1395 nm (Table VII) is easily explained by the presence of Re$_2$Cl$_5$(PMe$_2$Ph)$_3$ as an impurity and also some [Re$_2$Cl$_4$(PMe$_2$Ph)$_4$]$^+$ which is formed in CH$_3$CN solution from the spontaneous reduction of the 2+ complex. This is not unexpected in view of the high positive potential for the 1+/2+ couple ($E_{1/2}$ = +0.85 V vs. SCE). A similar spontaneous reduction does not occur as readily or as rapidly in the CH$_2$Cl$_2$–toluene glass used for the EPR examination of **3**.

Structural Results and Interpretation. The central Re$_2$Cl$_4$P$_4$ unit in each case has essentially the same structure, in which the total conformation about the Re–Re bond is eclipsed, but the Cl and P subsets are staggered. The virtual symmetry is thus D_{2d}. In the case of **1** there is a crystallographic twofold axis perpendicular to the Re–Re axis, while in **2** and **3** there is no crystallographic symmetry imposed on the cations. While there are small bond angle changes in going from the dirhenium unit in **1** to that in **2** and then **3**, the most important and significant information is to be gleaned from the changes in bond distances. Table V gives the values of these distances, including average values for D_{2d} symmetry.

Let us look first at the trends in metal–ligand distances. As we go through the series from the neutral Re(II)–Re(II) compound to the Re(III)–Re(III) ion, the Re–Cl distances decrease first by 0.057 (4) Å and then 0.039 (6) Å. Each of these changes is statistically significant and the average value of the two is 0.048 Å. This trend presumably reflects the decreasing bond radius of the metal atoms as their formal charge changes from +2.0 to +2.5 to +3.0. A comparable change, 0.044 Å, was seen on going from [Tc$_2$Cl$_8$]$^{3-}$ to [Tc$_2$Cl$_8$]$^{2-}$.[3,4] The decreases in bond radius could be attributed to contraction of the metal valence orbitals, the increased electrostatic attraction as the metal charge increases, or both.

For the Re–P bonds the opposite trend is seen. The mean bond lengths increase, by 0.042 (16) Å from **1** to **2** and by 0.048 (8) Å from **2** to **3**. Presumably this trend reflects the fact that Re

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Table VIII. Some Re-Re Bond Lengths and Bond Orders

	bond length, Å	configuration	order	ref
1. $Re_2Cl_4(PMe_2Ph)_4$	2.241 (1)	$\sigma^2\pi^4\delta^2\delta^{*2}$	3.0	*a*
2. $[Re_2Cl_4(PMe_2Ph)_4]^+$	2.218 (1)	$\sigma^2\pi^4\delta^2\delta^*$	3.5	*a*
3. $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$	2.215 (2)	$\sigma^2\pi^4\delta^2$	4.0	*a*
4. $Re_2Cl_4(PEt_3)_4$	2.232 (6)	$\sigma^2\pi^4\delta^2\delta^{*2}$	3.0	2
5. $Re_2Cl_6(PEt_3)_2$	2.222 (3)	$\delta^2\pi^4\delta^2$	4.0	20

[a] This work.

→ P π bonding is important for **1**, is less so but still exists for **2**, and is still less so for **3**. These results are consistent with the SCF-Xα-SW calculations[18] reported for the model compound $Re_2Cl_4(PH_3)_4$. It was shown that as δ* electrons are lost, metal-based MO's drop in energy while ligand-based orbitals are hardly affected. Thus, Re–P π bonding would be expected to decrease through the series **1**, **2**, **3** not primarily because of the decreasing number of δ* electrons (which themselves appear to play little if any role in Re–P π bonding) but because the Re–Re δ and π electrons become lower in energy and thus less available. In summary, the observed trend in Re–P distances is well accounted for—even predicted—by the SCF-Xα-SW calculations.

We turn now to the centerpiece of this study, namely, the behavior of the Re–Re bond length through this series of compounds. The question we are dealing with was first addressed in our studies of the $[Tc_2Cl_8]^{3-}$ and $[Tc_2Cl_8]^{2-}$ ions,[3,4] where it was found that the latter with a higher bond order (4.0) than the former (3.5) has the longer bond, by ca. 0.04 Å. It was proposed that the change from $[Tc_2Cl_8]^{3-}$ to $[Tc_2Cl_8]^{2-}$ not only raises the bond order (which would, by itself, tend to shorten the bond) but also causes a contraction of the valence orbitals of the metal atoms and this has the effect of lengthening the bond because it weakens the σ and π overlaps. In the case of the two technetium ions, the orbital contraction due to increased effective charge on the metal atoms dominates, thus giving a net increase in the Tc–Tc bond length. The steady increase of Mo–Mo bond distance in the series $[Mo_2(SO_4)_4]^{4-}$, $[Mo_2(SO_4)_4]^{3-}$, $[Mo_2(HPO_4)_4]^{2-}$ was then seen to be inevitable because both the bond order change and the charge effects work in the same direction.

At an even earlier date[20,21] a comparison of the structures of $Re_2Cl_4(PEt_3)_4$ (**4**) and $Re_2Cl_6(PEt_3)_2$ (**5**) had revealed essentially no change in the Re–Re distance despite the change of one unit of bond order, as shown in Table VIII. This result was not understood at that time, and it was even suggested[21] that perhaps electrons beyond the $\sigma^2\pi^4\delta^2$ set in $Re_2Cl_4(PEt_3)_4$ were not occupying the δ* orbital. However, our recent theoretical and spectroscopic study[18] disposes of that suggestion, and it is now evident that in this case the opposing effects of bond order change and charge increase are approximately offsetting.

However, a comparison of these two compounds is far from ideal since the ligand sets are different; magnitudes of nonbonded attractions and repulsions are not likely to cancel out to the maximum practical extent. The present study was designed to achieve the latter goal; moreover, we now have a series of three compounds covering bond orders of 3.0, 3.5, and 4.0, instead of just 3.0 and 4.0. As shown in Table VIII, by comparison of compounds **1** and **4**, a change of ~0.01 Å can occur between two compounds with the same bond order that differ only in the identity of the phosphine.

The comparison of Re–Re bond lengths in compounds **1**, **2**, and **3** shows that the effect of increasing the bond order (which should shorten the bond) is largely (**1** to **2**) or even completely (**2** to **3**) offset by a second effect which, as before, we assume to be a lessening of σ and/or π bonding resulting from orbital contraction with increasing charge. In going from **1** to **2** there is a contraction of 0.023 (2) Å, suggesting that the bond order increase is slightly dominant. However, in going from **2** to **3** there is no statistically significant change, 0.003 (2) Å, indicating that the bond order effect is exactly nullified by the opposing effect.

In conclusion, we believe that the results of our present, purposely designed and more complete study show that for dinuclear systems with M–M bond orders in the range of 3.0–4.0 the M–M distance does not respond in a simple and direct way to δ bond order increases when these are effected by removal of electrons from the dimetal unit. There are other methods of altering the δ bond order without changing the formal state of ionization of the metal atoms,[22] and for these the expected relationship (distance inversely proportional to bond order) is regularly observed.

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Registry No. **1**, 85993-34-6; **2**, 85939-70-4; **3**, 85939-73-7; $NOPF_6$, 16921-91-8; tropylium hexafluorophosphate, 29663-54-5.

Supplementary Material Available: Tables of structure factors, anisotropic thermal parameters, and less important bond lengths and angles for all three structures, Tables II–IV containing the atomic positional parameters, and detailed descriptions of the crystallographic procedures (69 pages). Ordering information is given on any current masthead page.

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