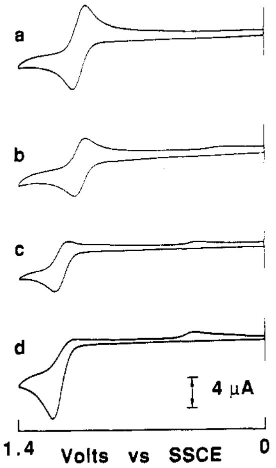

Figure 5. Cyclic voltammograms of (a) $[Ru(NO_2)(PEt_3)_2(trpy)](ClO_4)$, (b) *trans*-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$, (c) *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$, (d) *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ in 0.1 M Et_4NBF_4/CH_3CN at ice temperatures. All scans were conducted by using a platinum working electrode at scan rates of 100 mV/s.

The cyclic voltammograms of the *trans*-$[Ru(NO_2)(P(n\text{-}Bu)_3)_2(trpy)](ClO_4)$, *trans*-$[Ru(NO_2)(PBz_3)_2(trpy)](ClO_4)$, and *trans*-$[Ru(NO_2)(PPh_3)_2(trpy)](ClO_4)$ complexes indicate decomposition of the oxidized species, producing a new wave between +0.21 and +0.38 V. If the voltammogram is continually cycled, a reversible couple with an $E_{1/2}$ between +0.26 and +0.43 V is observed, corresponding to the $[Ru(NO)(PR_3)_2(trpy)]^{3+/2+}$ couple. This suggests that the $[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ complexes generated at the electrode surface decompose to the analogous $[Ru(NO)(PR_3)_2(trpy)]^{3+}$ or $[Ru(NO)(PR_3)_2(trpy)]^{2+}$ complexes. It should be noted that the authentically synthesized $[Ru(NO)(PR_3)_2(trpy)](ClO_4)_3$ complexes all displayed one reversible couple with $E_{1/2}$ values ranging between +0.26 and +0.43 V versus SSCE, in acetonitrile, where these values match the $E_{1/2}$ values measured for couples generated in situ from the decomposition of the unstable *trans*-$[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ complexes.

In our studies, the stabilities of the electrochemically generated (nitro)ruthenium(III) complexes do not appear to follow a trend based on the $E_{1/2}$ values of the complexes. If other types of (nitro)ruthenium complexes are examined, there still are no clear reasons for (nitro)ruthenium(III) stabilization. For example, (nitro)ruthenium complexes such as $[Ru(NH_3)(bpy)_2(NO_2)](PF_6)$[45] possess a lower $E_{p,a}$ value than the $E_{1/2}$ values of the electrochemically stable *trans*-$[Ru(NO_2)(PR_3)_2(trpy)]^{2+}$ complexes, yet the oxidation of $[Ru(NH_3)(bpy)_2(NO_2)](PF_6)$ is electrochemically irreversible. Also, the instabilities of the oxidized forms of $[Ru(bpy)_2(NO_2)(PPh_3)](PF_6)$[45] and $[Ru(bpy)_2(NO_2)(PMe_3)](ClO_4)$,[46] suggest that the presence of a single phosphine ligand is insufficient to stabilize the oxidized form. Our only clear observation is that the stabilization of (nitro)ruthenium(III) complexes requires the use of trans-trialkylphosphine ligands with alkyl groups of less than three carbon atoms, in conjunction with a terpyridine ligand.

Acknowledgment. This work was supported in part by the National Science Foundation (CHE 8814638), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the ARCO Chemical Co. We also acknowledge Mr. James G. Muller for his assistance with the NMR experiments.

Supplementary Material Available: Proton NMR spectrum (Figure 1) and proton decoupled carbon-13 NMR spectrum (Figure 2) of *trans*-$[Ru(NO_2)(P(n\text{-}Pr)_3)_2(trpy)](ClO_4)$ in $CDCl_3$ (2 pages). Ordering information is given on any current masthead page.

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(46) The cyclic voltammogram for $[Ru(bpy)_2(NO_2)(PMe_3)](ClO_4)$ is irreversible, with an $E_{p,a}$ of +1.14 V vs SSCE: Leising, R. A.; Kubow, S. A.; Takeuchi, K. J. Unpublished results.

Notes

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Preparation and Structure of $Re_2(\mu\text{-}SEt)_2Cl_4(3,6\text{-dithiaoctane})_2$: An Edge-Sharing Bioctahedron with an Unbuttressed Rhenium(III)-Rhenium(III) Double Bond

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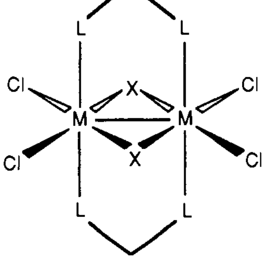
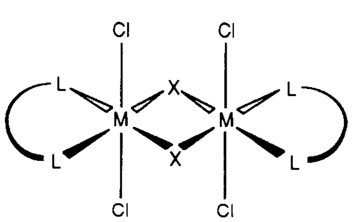
Introduction

Several years ago, it was shown that edge-sharing bioctahedral complexes with bridging thiolate ligands could be prepared by the oxidative addition of organic disulfides (RSSR) across the quadruple bond in $Mo_2Cl_4(LL)_2$ complexes.[1,2] The first compound to be synthesized in this manner was $Mo_2(\mu\text{-}SEt)_2Cl_4(3,6\text{-dithiaoctane})_2$, a dimolybdenum(III) molecule which was also prepared by the reaction of quadruply bonded $[Mo_2Cl_8]^{4-}$ with EtSSEt in the presence of dithiaoctane.[1] Herein, we report the preparation and characterization of the analogous dirhenium(III) complex.

A perplexing anomaly in the structures of edge-sharing bioctahedral complexes of the transition metals provided the impetus for our research. Of the four structurally characterized examples of d^4–d^4 $Re_2(\mu\text{-}X)_2Cl_4(LL)_2$ molecules, only one, $Re_2Cl_6(dppe)_2$, has no metal–metal bond. Three of the compounds[3-5] are diamagnetic and have structures of type I with four bridging ligands



I



II

and Re-Re double bonds, while $Re_2Cl_6(dppe)_2$[6] is paramagnetic and has a structure of type II with only two bridging ligands. Cotton has referred to these quadruply and doubly bridged geometries as the buttressed and unbuttressed arrangements, respectively.[7] In the same paper, it was noted that, although

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0020-1669/90/1329-4574$02.50/0

Table I. Crystallographic Data for $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$

chemical formula: $Re_2Cl_4S_6C_{16}H_{38}$	fw = 937.1
a = 19.561 (4) Å	space group: $I2/a$ (No. 15)
b = 17.795 (3) Å	T = 20 ± 1 °C
c = 20.478 (5) Å	λ = 0.71073 Å
β = 117.40 (1)°	ρ_{calcd} = 1.967 g/cm^3
V = 6329 (2) Å^3	μ = 84.8 cm^{-1}
Z = 8	R (F_o) = 0.0485
transm coeff = 0.215–0.679	$R_w(F_o^2)$ = 0.0564

buttressing has *no* effect in d^2–d^2 and d^3–d^3 compounds, in the case of two d^5–d^5 complexes, $Ru_2Cl_6(PBu_3)_4$ and $Ru_2Cl_6(dmpm)_2$, the unbuttressed molecule once again has no metal–metal bond while the buttressed compound has an Ru–Ru single bond. It was first pointed out by Shaik et al.[8] that repulsive forces between opposing axial ligands in edge-sharing bioctahedral complexes could be strong enough to prevent M–M bonding unless such ligands were "tied together" as in the case of bridging diphosphines. This appears to be consistent with the results obtained for the dirhenium(III) and diruthenium(III) cases, but not for the many d^2–d^2 and d^3–d^3 compounds that are presently known.

Because of the above cited work with Mo_2 compounds and the more recent report of the preparation of $Re_2(\mu\text{-}SePh)_2(\mu\text{-}dppm)_2Cl_4$ from the reaction of $Re_2Cl_4(dppm)_2$ with PhSeSePh,[5] we thought it might be possible to prepare unbuttressed dirhenium(III) complexes with Re–Re bonds by oxidative addition of disulfides to compounds of the type $Re_2Cl_4(LL)_2$, where the LL ligands are chelating and not bridging. It was assumed that, as in the case of the dimolybdenum(III) species,[2] the desired products would possess structures of type II. We have succeeded in preparing a molecule of the type $Re_2(\mu\text{-}SR)_2Cl_4(LL)_2$, although not by our originally intended method or with the expected ligand arrangement.

Experimental Section

Materials and Methods. The reaction was carried out in a nitrogen atmosphere with use of standard air-free techniques. HPLC-grade ethanol in a "Sure|Seal" bottle was used as obtained from Aldrich. The reagents 3,6-dithiaoctane (dto) and ethyl disulfide were purchased from Pfaltz & Bauer and Aldrich, respectively, and used as received. The dirhenate compound $(n\text{-}Bu_4N)_2Re_2Cl_8$ was prepared by a published procedure.[9]

Preparation of $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$. Ethanol (20 mL) was added to 0.304 g (0.266 mmol) of $(n\text{-}Bu_4N)_2Re_2Cl_8$ in a round-bottom flask equipped with a stir bar. Ethyl disulfide (0.15 mL, 1.2 mmol) was then added, followed immediately by 3,6-dithiaoctane (0.080 mL, 1.3 mmol). The mixture was stirred and refluxed for 17 h. The resulting brown solid was filtered off and washed with ethanol and diethyl ether and allowed to dry in air. Yield: 0.138 g (55.4%). UV–vis spectrum (CH_2Cl_2; λ_{max}, nm): 468, 337. IR spectrum (CsI pellet; cm^{-1}): 1490 w, sh; 1448 vs; 1410 vs; 1375 s, sh; 1290 w, sh; 1268 m; 1245 m; 1168 w; 1125 m; 1050 s; 971 s; 920 m; 853 m; 768 s; 699 m; 636 w; 461 w; 334 m, sh; 301 s; 265 m, sh.

Single crystals of $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ for analysis by X-ray diffraction were obtained by layering a CH_2Cl_2 solution of the compound with hexane. After several days of slow diffusion, suitable green-brown crystals had formed.

X-ray Crystallography. Information relating to data collection and structure refinement is summarized in Table I. Data collection was performed by Crystalytics Co. of Lincoln, NE, with use of a Nicolet autodiffractometer. An empirical absorption correction based on ψ scans for five reflections was applied to the data. The structure was solved by analysis of a Patterson map in the space group $C2/c$. In order to use the most reduced representation of the lattice, the cell setting was then changed from a = 34.189 (5), b = 17.805 (3), c = 19.533 (4), β = 147.92 (1)° to a = 19.561 (4), b = 17.795 (3), c = 20.478 (5), β = 117.40 (1)°. The space group was changed to $I2/a$ to match the new setting. Full-matrix least-squares refinement proceeded straightforwardly with use of the SDPVAX software package on a VAX-11/785 computer at ACU. All non-hydrogen atoms were refined anisotropically, and no attempt was made to include hydrogen atoms. The 12 largest peaks (with heights ranging from 1.1 to 1.8 e/Å^3) in a final difference Fourier map were all within 1.22 Å of a Re atom. All other final peaks were smaller than 0.86 e/Å^3. Final atomic positional and isotropic equivalent displacement parameters are listed in Table II.

Table II. Atomic Positional and Isotropic Equivalent Thermal Parameters for $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$

atom	x	y	z	B,[a] Å^2
Re(1)	–0.03311 (5)	–0.18527 (4)	–0.12372 (4)	3.64 (2)
Re(2)	–0.02202 (5)	–0.26088 (4)	–0.22665 (3)	3.52 (2)
Cl(1)	–0.0018 (4)	–0.0601 (3)	–0.1458 (3)	5.5 (1)
Cl(2)	0.0452 (3)	–0.1526 (3)	0.0051 (2)	5.0 (1)
Cl(3)	0.0188 (3)	–0.1659 (3)	–0.2847 (3)	5.2 (1)
Cl (4)	–0.1003 (3)	–0.3082 (3)	–0.3530 (2)	4.9 (1)
S(b1)	–0.1359 (3)	–0.2015 (3)	–0.2438 (2)	3.8 (1)
S(b2)	0.0808 (3)	–0.2417 (3)	–0.1084 (2)	4.1 (1)
S(1)	–0.1418 (3)	–0.1166 (3)	–0.1152 (3)	4.7 (1)
S(2)	–0.0751 (3)	–0.2879 (3)	–0.0762 (2)	4.5 (1)
S(3)	0.0878 (3)	–0.3332 (3)	–0.2271 (3)	4.3 (1)
S(4)	–0.0515 (3)	–0.3793 (3)	–0.1902 (2)	4.2 (1)
C(1)	–0.190 (1)	–0.192 (1)	–0.090 (1)	4.5 (5)
C(2)	–0.126 (1)	–0.241 (1)	–0.0307 (9)	4.9 (4)
C(3)	–0.104 (1)	–0.053 (1)	–0.033 (1)	7.2 (6)
C(4)	–0.180 (2)	–0.014 (1)	–0.037 (1)	7.9 (7)
C(5)	–0.002 (1)	–0.332 (1)	0.001 (1)	4.9 (5)
C(6)	–0.029 (2)	–0.404 (2)	0.028 (1)	9 (1)
C(7)	0.080 (1)	–0.427 (1)	–0.194 (1)	5.2 (6)
C(8)	–0.007 (1)	–0.450 (1)	–0.224 (1)	5.3 (6)
C(9)	0.076 (1)	–0.355 (1)	–0.320 (1)	5.4 (5)
C(10)	0.148 (2)	–0.389 (2)	–0.313 (1)	8.5 (9)
C(11)	–0.154 (1)	–0.407 (1)	–0.246 (1)	6.1 (6)
C(12)	–0.167 (2)	–0.486 (1)	–0.220 (2)	8.4 (9)
C(13)	–0.154 (1)	–0.114 (1)	–0.297 (1)	5.0 (6)
C(14)	–0.209 (2)	–0.129 (2)	–0.375 (1)	7.5 (9)
C(15)	0.149 (1)	–0.170 (1)	–0.106 (1)	7.2 (7)
C(16)	0.221 (2)	–0.205 (2)	–0.106 (2)	9 (1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement 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 III. Selected Bond Distances and Angles for $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$

Distances (Å)

Re(1)–Re(2)	2.5925 (9)	Re(2)–Cl(3)	2.405 (5)
Re(1)–Cl(1)	2.407 (5)	Re(2)–Cl(4)	2.471 (5)
Re(1)–Cl(2)	2.435 (5)	Re(2)–S(b1)	2.342 (6)
Re(1)–S(b1)	2.371 (6)	Re(2)–S(b2)	2.354 (5)
Re(1)–S(b2)	2.330 (6)	Re(2)–S(3)	2.508 (6)
Re(1)–S(1)	2.528 (6)	Re(2)–S(4)	2.393 (5)
Re(1)–S(2)	2.386 (5)		

Angles (deg)

Re(2)–Re(1)–Cl(1)	101.7 (1)	S(1)–Re(1)–Cl(2)	86.5 (2)
Re(2)–Re(1)–Cl(2)	139.4 (2)	Cl(1)–Re(1)–Cl(2)	84.0 (2)
Re(2)–Re(1)–S(1)	134.0 (1)	S(b1)–Re(2)–S(b2)	113.1 (2)
Re(2)–Re(1)–S(2)	96.2 (1)	S(b1)–Re(2)–S(4)	95.4 (2)
Re(1)–Re(2)–Cl(3)	102.0 (1)	S(b1)–Re(2)–Cl(3)	96.8 (2)
Re(1)–Re(2)–Cl(4)	141.7 (1)	S(b1)–Re(2)–Cl(4)	84.7 (2)
Re(1)–Re(2)–S(3)	131.4 (1)	S(b2)–Re(2)–S(3)	75.5 (2)
Re(1)–Re(2)–S(4)	94.6 (1)	S(b2)–Re(2)–S(4)	91.2 (2)
S(b1)–Re(1)–S(b2)	112.9 (2)	S(b2)–Re(2)–Cl(3)	94.9 (2)
S(b1)–Re(1)–S(1)	78.0 (2)	S(3)–Re(2)–S(4)	83.1 (2)
S(b1)–Re(1)–S(2)	92.5 (2)	S(3)–Re(2)–Cl(3)	83.0 (2)
S(b1)–Re(1)–Cl(1)	94.9 (2)	S(3)–Re(2)–Cl(4)	86.6 (2)
S(b2)–Re(1)–S(2)	95.9 (2)	S(4)–Re(2)–Cl(4)	84.5 (2)
S(b2)–Re(1)–Cl(1)	96.5 (2)	Cl(3)–Re(2)–Cl(4)	84.8 (2)
S(b2)–Re(1)–Cl(2)	82.6 (2)	Re(1)–S(b1)–Re(2)	66.7 (2)
S(1)–Re(1)–S(2)	83.3 (2)	Re(1)–S(b2)–Re(2)	67.2 (2)
S(1)–Re(1)–Cl(1)	82.0 (2)		

Results

The structure of $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ is illustrated in Figure 1. Important bond distances and angles are given in Table III. No crystallographic symmetry is imposed on the molecule, but its effective symmetry (including only the atoms that comprise the immediate coordination sphere of the Re atoms) is C_2. Since both metal atoms are in distorted octahedral environments, the molecule is best described as an edge-sharing bioctahedron with

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[7] Cotton, F. A.; Dunbar, K. R.; Eagle, C. T.; Falvello, L. R.; Price, A. C. *Inorg. Chem.* **1989**, *28*, 1754.

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Table IV. Important Structural Features of $Re_2(\mu\text{-}X)_2Cl_4(LL)_2$ Compounds[a]

dist, Å or angle, deg	$Cl_2(dppe)_2$[6]	$Cl_2(dppm)_2$[3]	$Cl_2(dmpm)_2$[4]	$(SePh)_2(dppm)_2$[5]	$(SEt)_2(dto)_2$[b]
Re-Re	3.809 (1)	2.616 (1)	2.5807 (4)	2.656 (1)	2.5925 (9)
av Re-X	2.499 (3)	2.391 (2)	2.369 (1)	2.462 (1)	2.349 (15)
av Re-Cl	2.314 (7)	2.388 (5)	2.408 (2)	2.451 (9)	2.43 (2)
av Re-L	2.370 (1)	2.475 (5)	2.437 (1)	2.474 (8)	2.45 (6)
Re-X-Re	99.48 (13)	66.33 (5)	66.01 (5)	65.28 (4)	67.0 (3)
X-Re-X'	80.71 (14)	113.67 (5)	113.99 (7)	114.72 (4)	113.0 (1)

[a] Only the $(\mu\text{-}X)_2(LL)_2$ portions of the molecules are used to identify the compounds. [b] This work.

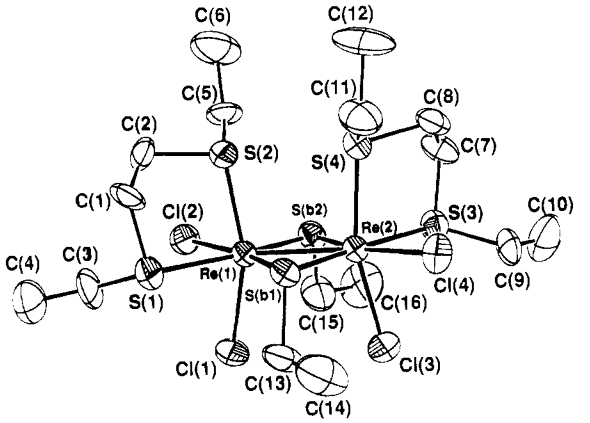

Figure 1. ORTEP view of the $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ molecule. Thermal ellipsoids are at the 50% probability level.

two bridging ethyl thiolate ligands. Two of the chloride ligands are coordinated in axial positions, while the other two are bound in trans equatorial positions. Both dto ligands are coordinated in an axial/equatorial fashion and are positioned on the same side (the top in Figure 1) of the molecule. Similarly, the ethyl groups of the thiolate ligands are located on the same side of the molecule (pointing downward in Figure 1), i.e. in a syn conformation. There is a surprisingly large dissimilarity among the $Re-S_{terminal}$ distances; the axial sulfur atoms are an average of 0.13 Å closer to the rhenium atoms than the equatorial sulfur atoms.

The most significant feature of the structure is the short Re-Re bond length of 2.5925 (9) Å. A comparison of this value to those of other dirhenium(III) bioctahedral complexes is given in Table IV, along with several other structural parameters for these compounds. Despite the fact that there is no buttressing of the Re-Re unit in $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$, there is definitely an Re-Re bond, and it is shorter than those in most of the other structurally characterized $Re_2(\mu\text{-}X)_2Cl_4(LL)_2$ molecules.

Discussion

Synthesis. As mentioned in the Introduction, we originally intended to synthesize $Re_2(\mu\text{-}SR)_2Cl_4(LL)_2$ complexes with chelating LL ligands by oxidative addition of organic disulfides across the triple bond in $Re_2Cl_4(LL)_2$ compounds.[5] Dithioethers (SS) were chosen as the bidentate LL ligands because of their demonstrated ability to chelate, but not bridge in dimolybdenum and dirhenium compounds.[10,11] However, our efforts to prepare $Re_2Cl_4(SS)_2$ complexes from $[Re_2Cl_8]^{2-}$ have not been successful when SS is 2,5-dithiahexane or 3,6-dithiaoctane.[12]

We have also attempted to prepare $Re_2(\mu\text{-}SR)_2Cl_4(PP)_2$ complexes, in which PP is a chelating diphosphine, but so far no reaction has occurred between $Re_2Cl_4(PP)_2$ species and RSSR, where R is Me, Et, or Ph. Thus only by reacting quadruply bonded $[Re_2Cl_8]^{2-}$ with a mixture of a dithioether and a disulfide were we successful in synthesizing a compound of the desired type.

Structure. Clearly, the metal-metal distance in $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ is consistent with an Re-Re bond order of 2. Thus this compound contains the first example of an unbuttressed Re-Re double bond in dirhenium(III) complexes of this type. The electronic configuration for this electron-rich bond is probably $\sigma^2\pi^2\delta^{*2}\delta^2$, although it is difficult to determine the correct order for the δ and δ^* orbitals.[5]

To our knowledge, the ligand arrangement in $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ is unique among edge-sharing bioctahedra. Perhaps among unbuttressed compounds this new geometry is more favorable for metal-metal bond formation than that (see II above) adopted by $Re_2Cl_6(dppe)_2$.[3] It is noteworthy, however, that the analogous dimolybdenum compound $Mo_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ contains an Mo-Mo bond with length 2.682 (1) Å, even though it has a structure of the $Re_2Cl_6(dppe)_2$ type so that all chloride ligands occupy axial positions and the dto ligands occupy equatorial positions.[2]

The nature of the bridging ligands is probably a more important factor influencing the metal-metal distance in such complexes. Excluding the diphosphine ligands, there are three different types of bridging ligands among the compounds listed in Table IV. Of these, the SePh ligand undoubtedly contains the largest bridging atom. Comparison of $Re_2Cl_6(dppm)_2$ with $Re_2(\mu\text{-}SePh)_2Cl_4(dppm)_2$ reveals that the Re-Re distance lengthens by 0.04 Å upon going from bridging Cl to bridging SePh. The smaller values of Re-X and X-Re-X' for $Re_2(\mu\text{-}SEt)_2Cl_4(dto)_2$ indicate that the bridging sulfur atoms take up a little less space than bridging chlorine atoms. On the basis of this factor alone, it is not particularly surprising that the title complex should have a short Re-Re distance. We are not, however, convinced that bridging ligands smaller than chloride are necessary for metal-metal bond formation in unbuttressed complexes of this type.

We intend to synthesize and characterize several more examples of both buttressed and unbuttressed $Re_2(\mu\text{-}X)_2Y_4(LL)_2$ complexes in order to better understand all factors responsible for metal-metal bond formation. Obviously, it is desirable to compare complexes with a minimum of differences. It is conceivable that a change in terminal LL ligands alone, such as from dppe to dto, might determine whether or not an Re-Re bond is formed.

Acknowledgment. We are grateful to The Robert A. Welch Foundation for financial support.

Supplementary Material Available: Details of the structure analysis, and tables of crystal data, bond distances, bond angles, and anisotropic thermal parameters (6 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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(12) Heyen, B. J.; Jennings, J. G.; Powell, G. L. To be submitted for publication in *Inorg. Chem.*

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Intramolecular Bridging Ligand Exchange in [2,2-Bis((phenylthio)methyl)-1-(diphenylphosphino)propane]palladium(II) Chloride

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Due to the geometrical rigidity of tripodal ligands, complexation studies concerning the triphos **1a** and the related sulfur analogue

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