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A Mixed-Valence Tetranuclear Rhenium Cluster with Re(I)-Re(III) Dative Bonds

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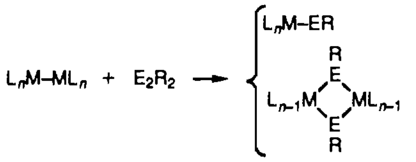
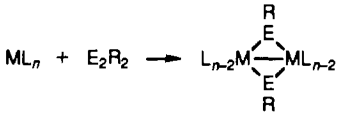
The reaction between $Re_2I_2(CO)_8$ and S_2Ph_2 gives $Re_4I_2(SPh)_6(CO)_8$ (**2**) under forcing conditions. The product has been characterized by X-ray diffractometry: triclinic, space group $P\bar{1}$, $a = 16.471$ (3) Å, $b = 15.044$ (3) Å, $c = 10.997$ (3) Å, $\alpha = 110.91$ (2)°, $\beta = 88.19$ (2)°, $\gamma = 101.83$ (2)°, $V = 2489$ (2) Å^3, $Z = 2$, and $R = 0.049$ for 2564 observed reflections. The structure consists of a central distorted edge-sharing bioctahedral $Re_2(SPh)_6I_2(CO)_2$ core with all the SPh groups in the equatorial plane and a syn arrangement of the two I and the two CO ligands in the axial positions. Two SPh and one I ligands in a relative cis configuration on each central rhenium atom bridge to lateral $Re(CO)_3$ moieties. The lateral Re(I) centers form dative bonds to the internal Re(III) centers, which are not bonded to each other. Reaction of **2** with PPh_3 or CyNC (Cy = cyclohexyl, C_6H_{11}) gives $Re_4I_2(SPh)_6(CO)_6L_2$ (L = PPh_3 (**3**), CyNC (**4**), where the carbonyls on the inner rhenium atoms have been selectively substituted. Reaction of **2** with CO gives rise to reductive elimination of S_2Ph_2 and formation of $ReI(CO)_5$ and $Re_2(SPh)_2(CO)_8$.

Introduction

The reactivity of E_2Ph_2 (E = S, Se, Te) toward transition-metal complexes has been the subject of a number of studies.[2-4] Either coordinative addition (reaction 1)[2] or oxidative addition (reactions 2 and 3)[3,4] of E_2Ph_2 to the metal center has been found to occur depending upon the nature of the metal system, the nature of R, and reaction conditions.

$$ML_n + E_2R_2 \longrightarrow \begin{cases} L_{n-1}M{-}E_2R_2 \\ L_{n-1}M{-}E_2R_2{-}ML_{n-1} \end{cases} \qquad (1)$$


(2)


(3)

Re(I) compounds have been previously found to react with E_2Ph_{2n} (E = S,[2i] Se,[2j] Te,[2k] $n = 1$; E = P, As, Sb, $n = 2$[5]) by coordinative addition (reaction 1) while diiodine failed to afford products of simple ligand displacement, the mixed-valence $Re_3I_6(CO)_6$ and $Re_4I_8(CO)_6$ being obtained instead.[6] We now report the oxidative addition of S_2Ph_2, the most oxidizing among the diphenyl dichalcogenides, to Re(I) under forcing conditions, and the structure and properties of a tetranuclear mixed-valence product that is a rare example of a compound with dative bonds between atoms of the same metal. This compound also allows new considerations to be made on the question of the metal-metal interaction in edge-sharing bioctahedral compounds of Re(III).

Experimental Section

Unless otherwise stated, all the operations were carried out under an atmosphere of prepurified dinitrogen or argon. Solvents were carefully dried by conventional methods and distilled under dinitrogen prior to use. IR spectra in the carbonyl stretching region were recorded on an expanded abscissa and calibrated with both CO and water vapor; the wavenumber values are believed to be accurate to ±1 cm^{-1}. Magnetic susceptibilities were measured with a magnetic balance equipped for the Faraday method using $CuSO_4{\cdot}5H_2O$ as calibrant. $ReI(CO)_5$,[2l] $Re_2I_2(CO)_8$,[2l] and $Re_2I_2(S_2Ph_2)(CO)_6$ (**1**)[2k] were prepared as previously described.

Preparation of $Re_2(SPh)_2(CO)_8$. $Re_2(CO)_{10}$ (2.55 g, 3.91 mmol) and S_2Ph_2 (0.89 g, 4.06 mmol) were dissolved in toluene (100 mL), and the resulting colorless solution was irradiated with a UV lamp at room temperature until the reaction was complete (by IR monitoring in the carbonyl stretching region, ca. 10 h). Most of the solvent was then removed by evaporation under reduced pressure, and the precipitation of the product was completed by the addition of 50 mL of *n*-heptane. Yield: 2.40 g (75%). The spectroscopic properties of this material correspond to those reported in the literature[7] for $Re_2(SPh)_2(CO)_8$. The compound was used directly without further purification.

Preparation of Hexakis(μ-phenyl sulfido)-1:2κ²*S*;1:2κ²*S*;2:3κ²*S*;-2:3κ²*S*;3:4κ²*S*;3:4κ²*S*-bis(μ-iodo)-1:2κ²*I*;3:4κ²*I*-octacarbonyl-1κ³*C*,2κ*C*,3κ*C*,4κ³*C*-tetrarhenium, $Re_4I_2(SPh)_6(CO)_8$ (2). (a) From $Re_2I_2(CO)_8$ and S_2Ph_2. $Re_2I_2(CO)_8$ (1.28 g, 1.51 mmol) and S_2Ph_2 (0.67 g, 3.09 mmol) were refluxed in toluene (100 mL) for 6 days. In a few hours the colorless solution gradually turned red, while the refluxing toluene assumed a pink color; this gradually disappeared within 24 h. The final mixture was set at 0 °C overnight and then filtered to give 0.364 g (26% yield) of the black microcrystalline, air-stable product. This was recrystallized from hot toluene to give well-formed crystals of pure product, one of which was used for the X-ray analysis.

Compound **2** is moderately soluble in CH_2Cl_2, THF, and toluene and completely insoluble in saturated hydrocarbons and CCl_4. Anal. Calcd for $C_{44}H_{30}I_2O_8Re_4S_6$: C, 28.2; H, 1.6; S, 10.2. Found: C, 28.3; H, 1.6; S, 10.0. IR (cm^{-1}): CH_2Cl_2, 2059 s, 2004 m, 1948 m-s, 1903 m; Nujol mull, 3050 w, 2040 vs, 2000 vs, 1950 vs, 1890 vs, 1575 m, 1440 s, 1305 w, 1180 w, 1160 w, 1070 m, 1020 m, 1000 m, 840 w, 735 s, 685 m-s, 600

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Table I. Crystal Data for Compound **2**[a]

formula	$C_{44}H_{30}I_2O_8Re_4S_6$	V, Å^3	2489 (2)
fw	1877.71	Z	2
space group	$P\bar{1}$	d_{calc}, g/cm^3	2.503
a, Å	16.471 (3)	μ (Mo Kα), cm^{-1}	112.52
b, Å	15.044 (3)	transm factors: max, min	0.99, 0.78
c, Å	10.997 (3)		
α, deg	110.91 (2)	R[b]	0.049
β, deg	88.19 (2)	R_w[c]	0.051
γ, deg	101.83 (2)		

[a] A nonconventional setting of $P\bar{1}$ was chosen. The conventional setting would be a = 10.997 Å, b = 15.044 Å, c = 16.471 Å, α = 78.17°, β = 88.19°, and γ = 69.09°. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma^2(|F_o|) + 0.0010|F_o|^2]^{-1}$.

m, 585 m, 550 m, 500 w, 485 m, 470 w, 435 m.

(b) From $Re_2I_2(CO)_6(S_2Ph_2)$ (1) and S_2Ph_2. Compound **1** (0.16 g, 0.16 mmol) and S_2Ph_2 (0.036 g, 0.165 mmol) were refluxed in toluene (20 mL) for 7 h. After cooling, filtration of the mixture gave 0.016 g (11% yield) of product, which was identical with that obtained by the procedure described above as evidenced by its spectroscopic properties.

(c) From $ReI(CO)_5$, $Re_2(SPh)_2(CO)_8$, and S_2Ph_2 in a 2:1:2 Ratio. $ReI(CO)_5$ (0.39 g, 0.85 mmol), $Re_2(SPh)_2(CO)_8$ (0.36 g, 0.44 mmol), and S_2Ph_2 (0.20 g, 0.91 mmol) were dissolved in toluene (30 mL) and refluxed for 2 days. After cooling, black microcrystals of **2** formed, which were collected by filtration. Yield: 0.16 g (20%).

Reaction between $Re_2(SPh)_2(CO)_8$ and I_2. $Re_2(SPh)_2(CO)_8$ (0.60 g, 0.74 mmol) and I_2 (0.20 g, 0.80 mmol) were refluxed in toluene (100 mL) for 24 h with IR monitoring in the carbonyl stretching region. The final solution showed the presence of compound **2** and of $Re_2I_2(CO)_8$, by comparison with the IR spectra of pure samples.

Reaction of Compound 2 with PPh_3. Preparation of $Re_4I_2(SPh)_6(CO)(PPh_3)_2$ (3). Compound **2** (0.38 g, 0.20 mmol) and PPh_3 (0.11 g, 0.42 mmol) were refluxed in toluene (25 mL). The reaction was monitored by IR in the carbonyl stretching region. After ca. 50 h the starting material was no longer present. The solution was filtered, concentrated to half its original volume, and treated with 25 mL of *n*-heptane. The resulting pale green solid was filtered out, washed with *n*-heptane, and dried in vacuo. Yield: 0.24 g (50%). Anal. Calcd for $C_{78}H_{60}I_2O_6P_2Re_4S_6$: C, 39.4; H, 2.5; I, 10.7; S, 8.1. Found: C, 39.6; H, 2.4; I, 11.0; S, 8.3. IR (cm^{-1}): toluene, 1995 s, 1915 sh, 1896 vs, ca. 1880 sh, ca. 1860 sh; Nujol mull, 2060 w, 1995 s, 1900 s, 1575 w, 1440 m, 1090 w, 1070 vw, 1020 w, 1000 w, 735 m, 690 m, 650 w, 580 w, 520 m, 490 w, 475 w, 450 w.

Reaction of Compound 2 with CyNC. Preparation of $Re_4I_2(SPh)_6(CO)_6(CyNC)_2$ (4). Compound **2** (0.971 g, 0.38 mmol) and CyNC (81 μL, 0.66 mmol) were refluxed in toluene (50 mL) with IR monitoring for ca. 36 h. The final solution was concentrated by evaporation to about 10 mL and treated with 30 mL of *n*-heptane. The resulting pale green solid was filtered out, washed with *n*-heptane, and dried in vacuo. Yield: 0.55 g (71%). The product was purified by dissolution in toluene and reprecipitation by addition of *n*-heptane. Anal. Calcd for $C_{56}H_{52}I_2N_2O_6Re_4S_6$: C, 32.5; H, 2.5; I, 12.3; N, 1.4; S, 9.3. Found: C, 33.2; H, 2.3; I, 13.0; N, 1.2; S, 9.3. IR (cm^{-1}): toluene, 2172 s, 2047 w, 2013 s, 1917 vs, 1903 vs; Nujol mull, 3050 w, 2170 s, 2040 m, 2000 s, 1915 vs, 1575 m, 1365 m, 1350 m, 1320 m, 1270 w, 1175 w, 1155 w, 1125 w, 1065 w, 1020 m, 1000 w, 890 w, 860 w, 740 s, 680 m-s, 650 w, 585 m, 520 w, 480 m, 450 w.

Reaction of Compound 2 with CO. A THF (5 mL) solution of compound **2** (27 mg) was stirred at room temperature under CO at atmospheric pressure with IR monitoring in the carbonyl stretching region. After ca. 5 days the IR spectrum showed bands at 2145 w, 2096 m, 2038 vs, 2015 s, 1990 s, and 1951 cm^{-1} s, corresponding to a mixture of $ReI(CO)_5$ and $Re_2(SPh)_2(CO)_8$, and did not change further over longer exposure to CO.

X-ray Data Collection, Structure Determination, and Refinement for Compound 2. A crystal with dimensions 0.18 × 0.09 × 0.08 mm^3 was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). The crystal system is triclinic. Cell parameters are reported in Table I together with other relevant crystal data.

The intensities were collected up to 2θ = 40°; the ω–2θ scan technique was employed, the scan range being 1.4° and the speed 0.05° s^{-1}. A total of 4650 independent reflections were measured, of which 2082 having $I \leq 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement. Three standard reflections, which were measured periodically, showed no apparent variation in intensity during data collection. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North et al.[8]

Table II. Fractional Atomic Coordinates in Compound **2**[a]

atom	x/a	y/b	z/c
Re(1)	0.3479 (1)	−0.3534 (1)	0.0623 (2)
Re(2)	0.2802 (1)	−0.1888 (1)	0.1986 (1)
Re(3)	0.2807 (1)	0.0874 (1)	0.3620 (1)
Re(4)	0.3425 (1)	0.2882 (1)	0.4123 (2)
I(1)	0.4315 (1)	−0.1685 (2)	0.0614 (3)
I(2)	0.4227 (1)	0.1513 (2)	0.2310 (2)
S(1)	0.2403 (6)	−0.2901 (7)	−0.018 (1)
S(2)	0.3618 (6)	−0.2558 (7)	0.2968 (9)
S(3)	0.2360 (5)	−0.0544 (6)	0.1592 (9)
S(4)	0.3451 (5)	−0.0402 (6)	0.3822 (9)
S(5)	0.2235 (6)	0.1782 (7)	0.2642 (9)
S(6)	0.3676 (5)	0.1908 (7)	0.5416 (9)
O(1)	0.227 (2)	−0.528 (2)	0.078 (3)
O(2)	0.381 (2)	−0.456 (2)	−0.228 (3)
O(3)	0.492 (2)	−0.425 (2)	0.137 (3)
O(4)	0.118 (2)	−0.257 (2)	0.308 (3)
O(5)	0.143 (2)	0.047 (2)	0.532 (3)
O(6)	0.502 (2)	0.427 (2)	0.565 (3)
O(7)	0.351 (2)	0.420 (2)	0.245 (3)
O(8)	0.230 (2)	0.406 (2)	0.596 (3)
C(1)	0.275 (2)	−0.464 (3)	0.074 (4)
C(2)	0.367 (3)	−0.421 (3)	−0.120 (5)
C(3)	0.436 (3)	−0.396 (3)	0.102 (4)
C(4)	0.180 (2)	−0.228 (3)	0.274 (4)
C(5)	0.197 (2)	0.060 (2)	0.466 (3)
C(6)	0.444 (3)	0.376 (3)	0.513 (5)
C(7)	0.347 (2)	0.373 (3)	0.308 (4)
C(8)	0.279 (2)	0.359 (3)	0.529 (4)
C(9)	0.141 (1)	−0.371 (2)	−0.055 (2)
C(10)	0.067 (1)	−0.338 (2)	−0.020 (2)
C(11)	−0.009 (1)	−0.399 (2)	−0.074 (2)
C(12)	−0.011 (1)	−0.493 (2)	−0.162 (2)
C(13)	0.063 (1)	−0.526 (2)	−0.197 (2)
C(14)	0.139 (1)	−0.465 (2)	−0.144 (2)
C(15)	0.318 (2)	−0.318 (2)	0.402 (3)
C(16)	0.364 (2)	−0.290 (2)	0.519 (3)
C(17)	0.330 (2)	−0.321 (2)	0.618 (3)
C(18)	0.251 (2)	−0.380 (2)	0.601 (3)
C(19)	0.205 (2)	−0.408 (2)	0.484 (3)
C(20)	0.238 (2)	−0.377 (2)	0.384 (3)
C(21)	0.129 (1)	−0.076 (2)	0.128 (2)
C(22)	0.105 (1)	−0.084 (2)	0.003 (2)
C(23)	0.021 (1)	−0.106 (2)	−0.036 (2)
C(24)	−0.039 (1)	−0.120 (2)	0.052 (2)
C(25)	−0.016 (1)	−0.111 (2)	0.177 (2)
C(26)	0.068 (1)	−0.089 (2)	0.215 (2)
C(27)	0.324 (1)	−0.053 (2)	0.537 (2)
C(28)	0.245 (1)	−0.088 (2)	0.572 (2)
C(29)	0.234 (1)	−0.096 (2)	0.694 (2)
C(30)	0.301 (1)	−0.069 (2)	0.782 (2)
C(31)	0.380 (1)	−0.035 (2)	0.747 (2)
C(32)	0.392 (1)	−0.027 (2)	0.625 (2)
C(33)	0.128 (1)	0.215 (2)	0.322 (3)
C(34)	0.116 (1)	0.301 (2)	0.312 (3)
C(35)	0.043 (1)	0.334 (2)	0.355 (3)
C(36)	−0.017 (1)	0.281 (2)	0.408 (3)
C(37)	−0.005 (1)	0.195 (2)	0.419 (3)
C(38)	0.068 (1)	0.162 (2)	0.376 (3)
C(39)	0.324 (1)	0.213 (2)	0.694 (2)
C(40)	0.246 (1)	0.238 (2)	0.720 (2)
C(41)	0.217 (1)	0.261 (2)	0.846 (2)
C(42)	0.266 (1)	0.259 (2)	0.946 (2)
C(43)	0.344 (1)	0.235 (2)	0.920 (2)
C(44)	0.373 (1)	0.212 (2)	0.794 (2)

[a] Estimated standard deviations in parentheses refer to the last digit.

The structure was solved by direct methods and refined by the full-matrix least-squares method with the SHELX-76 package of programs.[9] The phenyl groups were constrained to perfect hexagons (C–C = 1.395

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Table III. Selected Distances (Å) and Angles (deg) for Compound **2**

(a) Distances

Re(1)–I(1)	2.843 (2)	Re(3)–S(4)	2.452 (6)
Re(1)–S(1)	2.495 (8)	Re(3)–S(5)	2.356 (8)
Re(1)–S(2)	2.461 (9)	Re(3)–S(6)	2.333 (8)
Re(1)–C(1)	1.89 (3)	Re(3)–C(5)	1.84 (3)
Re(1)–C(2)	1.94 (5)	Re(4)–I(2)	2.825 (2)
Re(1)–C(3)	1.82 (4)	Re(4)–S(5)	2.486 (8)
Re(2)–I(1)	2.891 (2)	Re(4)–S(6)	2.472 (8)
Re(2)–S(1)	2.352 (10)	Re(4)–C(6)	1.98 (4)
Re(2)–S(2)	2.327 (8)	Re(4)–C(7)	1.98 (3)
Re(2)–S(3)	2.461 (6)	Re(4)–C(8)	1.81 (4)
Re(2)–S(4)	2.480 (8)	Re(1)–Re(2)	2.828 (2)
Re(2)–C(4)	1.90 (3)	Re(3)–Re(4)	2.838 (2)
Re(3)–I(2)	2.885 (2)	Re(2)···Re(3)	3.892 (2)
Re(3)–S(3)	2.476 (8)		

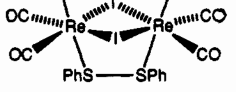
(b) Angles

I(1)–Re(1)–S(1)	75.3 (2)	I(2)–Re(3)–C(5)	172.2 (8)
I(1)–Re(1)–S(2)	78.6 (2)	S(3)–Re(3)–S(4)	75.2 (2)
I(1)–Re(1)–C(1)	168.8 (9)	S(3)–Re(3)–S(5)	86.7 (3)
I(1)–Re(1)–C(2)	93.7 (11)	S(3)–Re(3)–S(6)	157.1 (2)
I(1)–Re(1)–C(3)	99.4 (12)	S(3)–Re(3)–C(5)	98.9 (8)
S(1)–Re(1)–S(2)	102.8 (3)	S(4)–Re(3)–S(5)	159.6 (3)
S(1)–Re(1)–C(1)	95.7 (9)	S(4)–Re(3)–S(6)	85.0 (2)
S(1)–Re(1)–C(2)	86.6 (11)	S(4)–Re(3)–C(5)	90.4 (8)
S(1)–Re(1)–C(3)	171.5 (12)	S(5)–Re(3)–S(6)	110.5 (3)
S(2)–Re(1)–C(1)	97.3 (9)	S(5)–Re(3)–C(5)	101.8 (8)
S(2)–Re(1)–C(2)	165.7 (11)	S(6)–Re(3)–C(5)	92.4 (8)
S(2)–Re(1)–C(3)	82.3 (12)	I(2)–Re(4)–S(5)	78.8 (2)
C(1)–Re(1)–C(2)	92.4 (14)	I(2)–Re(4)–S(6)	79.0 (2)
C(1)–Re(1)–C(3)	90.3 (15)	I(2)–Re(4)–C(6)	97.0 (11)
C(2)–Re(1)–C(3)	87.1 (16)	I(2)–Re(4)–C(7)	95.7 (8)
I(1)–Re(2)–S(1)	76.4 (2)	I(2)–Re(4)–C(8)	170.8 (11)
I(1)–Re(2)–S(2)	79.7 (2)	S(5)–Re(4)–S(6)	101.9 (2)
I(1)–Re(2)–S(3)	93.2 (2)	S(5)–Re(4)–C(6)	173.9 (12)
I(1)–Re(2)–S(4)	88.5 (2)	S(5)–Re(4)–C(7)	86.7 (9)
I(1)–Re(2)–C(4)	169.2 (10)	S(5)–Re(4)–C(8)	94.8 (11)
S(1)–Re(2)–S(2)	111.8 (3)	S(6)–Re(4)–C(6)	81.3 (11)
S(1)–Re(2)–S(3)	89.8 (3)	S(6)–Re(4)–C(7)	168.6 (9)
S(1)–Re(2)–S(4)	158.0 (3)	S(6)–Re(4)–C(8)	96.1 (11)
S(1)–Re(2)–C(4)	96.9 (10)	C(6)–Re(4)–C(7)	89.5 (14)
S(2)–Re(2)–S(3)	154.6 (3)	C(6)–Re(4)–C(8)	89.9 (16)
S(2)–Re(2)–S(4)	80.5 (3)	C(7)–Re(4)–C(8)	90.5 (13)
S(2)–Re(2)–C(4)	95.3 (10)	Re(1)–I(1)–Re(2)	59.1 (0)
S(3)–Re(2)–S(4)	74.9 (2)	Re(3)–I(2)–Re(4)	59.6 (0)
S(3)–Re(2)–C(4)	95.3 (10)	Re(1)–S(1)–Re(2)	71.3 (2)
S(4)–Re(2)–C(4)	100.1 (10)	Re(1)–S(2)–Re(2)	72.4 (2)
I(2)–Re(3)–S(3)	88.8 (2)	Re(2)–S(3)–Re(3)	104.1 (2)
I(2)–Re(3)–S(4)	90.6 (2)	Re(2)–S(4)–Re(3)	104.2 (2)
I(2)–Re(3)–S(5)	79.6 (2)	Re(3)–S(5)–Re(4)	71.7 (2)
I(2)–Re(3)–S(6)	80.0 (2)	Re(3)–S(6)–Re(4)	72.3 (2)

Å) and refined as rigid groups. The hydrogen atoms were included at calculated positions (C–H = 1.08 Å) with overall isotropic parameter *U* = 0.13 Å^2. Anisotropic thermal parameters were refined for the Re, I, and S atoms. The atomic scattering factors were taken from ref 9 for S, O, C, and H and from ref 10 for Re and I; the correction for anomalous dispersion was included. Non-hydrogen atomic coordinates are listed in Table II, and relevant bond distances and angles are collected in Table III.

Results

(a) Synthesis. Previous studies[2k] have shown that ReI(CO)$_5$ or Re$_2$I$_2$(CO)$_8$ reacts with S$_2$Ph$_2$ in refluxing toluene to form, among other uncharacterized products, low yields of Re$_2$I$_2$(CO)$_6$(S$_2$Ph$_2$) (**1**), where the disulfide ligand has coordinatively



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added to the metal centers. On the other hand, similar reactions with Se$_2$Ph$_2$ and Te$_2$Ph$_2$[2k] and those of ReBr(CO)$_5$ with E$_2$Ph$_2$ (E = S,[2i] Se,[2j] Te[2k]) afford the corresponding Re$_2$X$_2$(CO)$_6$(E$_2$Ph$_2$) selectively.

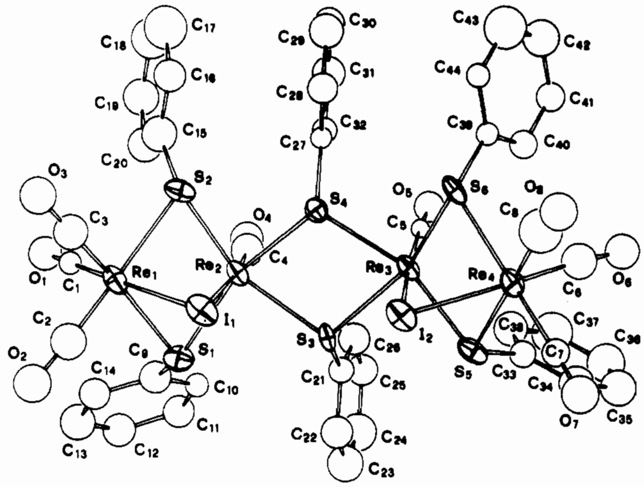

Figure 1. View of the molecular structure of compound **2** with the numbering scheme adopted.

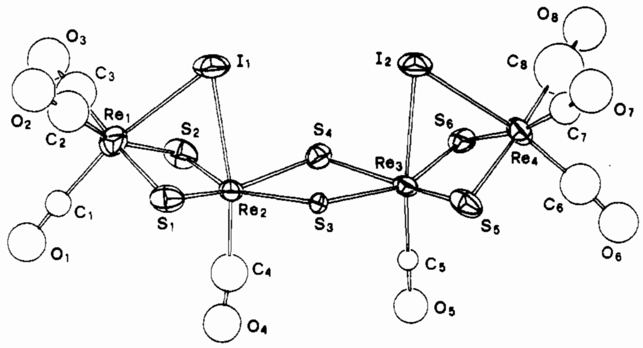

Figure 2. Simplified view of compound **2** emphasizing the coordination geometries around the central metal atoms. Phenyl groups are omitted for clarity.

The major side product in the Re$_2$I$_2$(CO)$_8$–S$_2$Ph$_2$ reaction is a black microcrystalline material, **2**. Iodine also formed along the products, as evidenced by the refluxing toluene assuming a pale pink color. The spectroscopic and solubility properties of compound **2** are indicative of higher nuclearity, and the results of the elemental analysis, suggesting the formulation Re$_4$I$_2$(SPh)$_6$(CO)$_8$, did not provide much structural insight. It was therefore decided to carry out a single-crystal X-ray analysis, which confirmed the above given formulation as a tetranuclear cluster (see structural results below). A possible stoichiometry for the formation of **2** from Re$_2$I$_2$(CO)$_8$ and S$_2$Ph$_2$ is shown in eq 4. Compound **2** can also be obtained from the interaction of preformed **1** with S$_2$Ph$_2$; see eq 5.

$$2Re_2I_2(CO)_8 + 3S_2Ph_2 \rightarrow Re_4I_2(SPh)_6(CO)_8 + I_2 + 8CO \quad (4)$$

$$2Re_2I_2(CO)_6(S_2Ph_2) + S_2Ph_2 \rightarrow Re_4I_2(SPh)_6(CO)_8 + I_2 + 4CO \quad (5)$$

(b) Structure. The crystal structure of **2** consists of discrete Re$_4$I$_2$(SPh)$_6$(CO)$_8$ molecules. Figure 1 shows the shape of these molecules as well as the atomic numbering scheme. As it is better appreciated in the simplified view of Figure 2, the molecule can be described as derived from the condensation of four octahedra. The two lateral pairs of octahedra [around Re(1):Re(2) and Re(3):Re(4)] share a face that consists of the triangle delineated by two bridging sulfur and one bridging iodine atoms, whereas the two internal octahedra [around Re(2):Re(3)] share the edge that is the vector joining the two bridging S(3) and S(4) atoms. The coordination is completed by three terminal CO ligands on each lateral rhenium atom and one terminal CO ligand on each internal rhenium atom. The molecule exhibits an approximate C_{2v} symmetry, the 2-fold axis being normal to the Re(2)–S-

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(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(3)–S(4)–Re(3) plane and the mirrors passing through this axis and through Re(1), Re(2), Re(3), and Re(4) and perpendicularly through S(3) and S(4). Selected bond lengths and angles are listed in Table III.

It is obvious from the metal–metal distances that a bonding interactions exist between Re(1) and Re(2) and between Re(3) and Re(4) [2.828 (2) and 2.838 (2) Å, respectively], whereas the two inner rhenium atoms are not directly bonded to each other [Re(2)···Re(3) = 3.892 (2) Å]. This situation reflects in the observed distortions of the octahedral geometries around each rhenium atom. For instance, the S(3)–Re(n)–S(4) (n = 2, 3) angles are smaller and the Re(2)–S(n)–Re(3) (n = 3, 4) angles greater than the undistorted value of 90° for an edge-sharing bioctahedral structure in agreement with a net repulsion between the Re(2) and Re(3) atoms. Conversely, the S(1)–Re(n)–S(2) (n = 1, 2) and S(5)–Re(n)–S(6) (n = 3, 4) angles are greater than 90°, consistent with attraction between each pair of lateral Re atoms. Interestingly, all the S–Re–I angles are *smaller* than 90° although one might expect them to be greater in analogy to the S–Re–S angles because of the metal–metal bonding interaction. This effect may be caused by the electronic requirements of the metal–metal interactions. The metal–metal bonding involves orbitals of Re(2) and Re(3) that are in the equatorial plane of the edge-sharing bioctahedral inner core (see discussion of bonding below). These interactions tend to bend the tetranuclear structure, as indicated by the fact that the Re(1)–Re(2)–Re(3) and Re(2)–Re(3)–Re(4) angles [average 155.3 (5)°] are larger than the theoretical value of 125.26°, ultimately orienting the Re–Re bonds closer to the equatorial plane of the internal edge-sharing bioctahedron. This causes a selective S–Re–S angle widening and, indirectly, a S–Re–I angle narrowing. Another effect of this distortion is the small [average 59.4 (3)°] Re–I–Re angle.

The metal–metal bond pattern of the molecule excludes the assignment of the metal oxidation states as I–III–III–I with a central double-bond interaction ($\sigma^2\pi^2\delta^{*2}\delta^2$) between the two inner, 16-electron, d^4 Re(III) centers. An alternative possibility is the II–II–II–II oxidation state assignment with two single bonds between each pair of lateral Re atoms. However, no example appears to be reported of a dinuclear Re(II) compound, either with a face-sharing bioctahedral or with any other coordination geometry, containing a single bond between the two d^5 centers. In all cases found, Re(II) dimers assume a geometry arising from the condensation of two square-planar ReX$_2$L$_2$ units and contain a Re–Re triple ($\sigma^2\pi^4\delta^2\delta^{*2}$) bond.[11] In addition, carbonyl complexes of Re(II) are rather elusive, an example being ReX$_2$(CO)$_2$(PR$_3$)$_2$.[12] No rhenium(II) carbonyl compound containing the Re(CO)$_3$ moiety appears to be known. The oxidation state assignment that we propose for the four rhenium centers in compound **2** is I–III–III–I with the inner Re atoms achieving a closed-shell electronic configuration through Re(I)→Re(III) dative bonds rather than through Re(III)–Re(III) double bonds. In agreement with this oxidation state assignment, the Re–S bond lengths involving the lateral Re atoms [average 2.478 (8) Å] are longer than those involving the inner Re atoms. Of these, the bond lengths involving the bridging S atoms of the face-sharing units average 2.342 (8) Å, whereas those involving the bridging S atoms of the edge-sharing unit average 2.467 (7) Å. This difference is likely to be the result of the different metal–metal interactions (attractive in one case, repulsive in the other). These distances are to be compared with 2.53 (1) Å (average)[13] in Re$_2$(CO)$_8$[μ-SRe(CO)$_5$][μ-SSnMe$_3$] and 2.50 (1) Å (average)[14] in [Re(CO)$_3$(μ_3-SMe)]$_4$, for what concerns compounds of Re(I), and with 2.35 (1) Å (average) for the distances to the bridging sulfur atoms in the metal–metal bonded Re(III) dimer Re$_2$(μ-SEt)$_2$Cl$_4$(dto)$_2$ (dto = 3,6-dithiaoctane).[15]

The Re–I bond lengths have an opposite pattern with respect to the Re–S bond lengths: those involving the lateral Re(I) atoms [average 2.834 (9) Å] are significantly shorter than those involving the two inner Re(III) atoms [average 2.888 (4) Å]. However, all these are longer than any of the Re(I)–(μ-I) distances reported in the literature, which are in the 2.79–2.82-Å range.[6,16] We attribute this effect to the higher distortion around the Re(III) centers.

(c) Reactivity. Compound **2** is unaffected by Lewis bases at room temperature, but it slowly reacts in refluxing toluene with 2 equiv of PPh$_3$ or CyNC according to eq 6.

$$\mathrm{Re_4I_2(SPh)_6(CO)_8 + 2L \rightarrow Re_4I_2(SPh)_6(CO)_6L_2 + 2CO} \quad (6)$$
$$\mathrm{L = PPh_3\ (3),\ CyNC\ (4)}$$

The stoichiometry of the substitution reaction and the structure of the parent compound **2** would suggest that selective substitution of the two CO ligands bonded to the inner Re(III) atoms has taken place. The IR spectroscopic properties of the two new compounds, which are discussed in the next section together with those of the parent compound **2**, are in agreement with this view and indicate that the structure of the two new compounds is identical with that of **2**, including the oxidation state assignment.

If **2** were a homogeneous-valence Re(II) compound, the CO groups on the external Re(CO)$_3$ moieties would be expected to be the most labile toward substitution because the higher CO/σ-donor ligand ratio on these metal centers would make π back-bonding to the lateral CO ligands weaker. According to the mixed-valence formulation, on the other hand, it is obvious to anticipate a higher lability of the internal CO groups toward substitution, since they are bonded to a higher oxidation state metal. The IR spectra of **3** and **4** are consistent with selective replacement of the two CO ligands on the inner Re atoms (see next section).

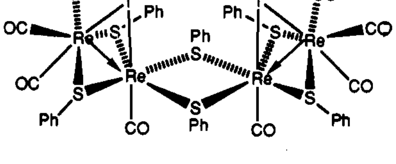
Exchange of the two CO ligands in compound **2** is remarkably difficult considering that they are bonded to Re(III). Days of reflux in toluene are required to drive the substitution reaction to completion. A possible explanation for this unusual inertness is the presence of a high number of donor sulfur atoms around the Re(III) centers, thereby raising the energy of the Re(III) orbitals and strengthening the π component of the Re–CO bond.

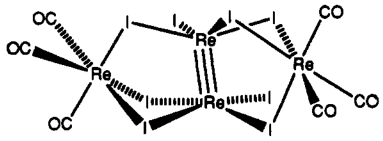
Compound **2** reacts slowly at room temperature in THF solution with CO at atmospheric pressure according to eq 7. This reaction

$$\mathrm{Re_4I_2(SPh)_6(CO)_8 + 10CO \rightarrow}$$
$$\mathrm{Re_2(SPh)_2(CO)_8 + 2ReI(CO)_5 + 2S_2Ph_2} \quad (7)$$

consists of a reductive elimination of S$_2$Ph$_2$ promoted by coordination of CO. No other carbonyl compounds were detected in the final reaction mixture. The identity of the products is consistent with the observation that compound **2** could be formed by the reverse of eq 7 in refluxing toluene.

It is interesting to compare compound **2** with the reported[6] tetranuclear compound Re$_4$I$_8$(CO)$_6$, which is also a mixed-valence compound containing two Re(I) and two Re(III) centers. The two compounds have different structures, illustrated as follows:





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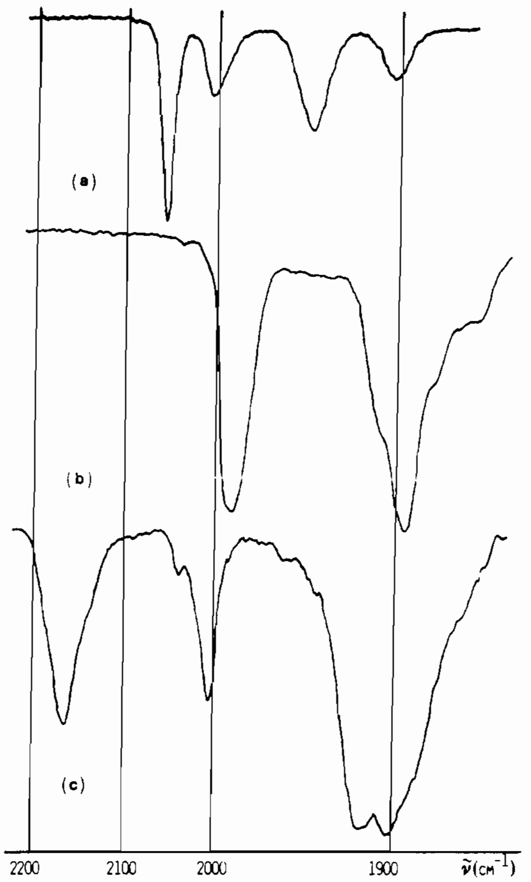

Figure 3. IR spectra of compounds **2** (a), **3** (b), and **4** (c) in the carbonyl stretching region. Solvent = CH_2Cl_2 (**2**) and toluene (**3**, **4**).

Compound **2** has two additional CO ligands with respect to $Re_4I_8(CO)_6$. The former can be described as the formal union of two $Re(CO)_3{}^+$ moieties with an edge-sharing bioctahedral $[Re_2(\mu\text{-}SPh)_2I_2(SPh)_4(CO)_2]^{2-}$ core, whereas the latter is the formal union of two $Re(CO)_3{}^+$ moieties with a staggered, triply bonded $[Re_2I_8]^{2-}$ core.[6] We have tried to decarbonylate compound **2** to see if an hypothetical $Re_4I_2(SPh)_6(CO)_6$ molecule analogous to $Re_4I_8(CO)_6$ could be formed. Compound **2** was recovered unchanged after prolonged UV irradiation in refluxing toluene. It may be argued that, since the synthetic methodology for the formation of $Re_4I_8(CO)_6$ (oxidation of $ReI(CO)_3(THF)_2$ with I_2) is similar to the reaction that led to the formation of compound **2**, the first steps of the two syntheses are identical and $Re_4I_8(CO)_6$ could be obtained via a $Re_4I_8(CO)_8$ intermediate with a structure analogous to that of compound **2**, which readily decarbonylates. The higher resistance of compound **2** toward decarbonylation could be ascribed to the stronger Re(III)–CO bond when the better donor SPh ligands are present. We attempted to prepare a tetranuclear rhenium compound with a SPh/I ratio intermediate between those of compound **2** and $Re_4I_8(CO)_6$. By reacting $Re_2(SPh)_2(CO)_8$ with the equimolar amount of I_2 in refluxing toluene, we hoped to eventually form a compound of stoichiometry $Re_4I_4(SPh)_4(CO)_n$ (n = 6 or 8). We found, instead, that this reaction produces compound **2** and $Re_2I_2(CO)_8$, presumably according to the stoichiometry shown in eq 8.

$$3Re_2(SPh)_2(CO)_8 + 2I_2 \rightarrow Re_4I_2(SPh)_6(CO)_8 + Re_2I_2(CO)_8 + 8CO \quad (8)$$

(d) IR Spectroscopic Properties. The solution IR spectrum in the carbonyl stretching region agrees with the solid-state structure and the oxidation state assignment given above. The compound shows four broad stretching vibrations in CH_2Cl_2 solution (see Figure 3a). According to the overall symmetry of the molecule (ideally C_{2v}), seven bands ($3A_1 + 3B_1 + B_2$) would be expected. However, the eight carbonyl ligands can ideally be divided into two sets of oscillators: the six ones bonded to the external Re atoms and the two ones bonded to the internal Re atoms. Assuming, to a first approximation, that the interaction between the two sets of oscillators is small, we would expect the first set to give rise to a spectrum due to the isolated $Re(CO)_3$ system (the two $Re(CO)_3$ moieties are far from each other and should interact only to a negligible extent), while the second set should show two ($A_1 + B_1$) bands. Since all the known compounds containing a $Re(CO)_3$ frame show two main bands with the one at lowest frequency being possibly split for lower symmetry complexes, four or five bands are effectively expected for the structure shown in Figure 1. The two bands due to the inner $Re_2(CO)_2$ oscillator are expected to appear at higher frequency than those due to the two $Re(CO)_3$ moieties because of the higher oxidation state. The observed IR pattern shown in Figure 3a is consistent with the above considerations. The two bands at 2004 and 1903 cm^{-1} agree in relative intensity and wavenumber values with the pattern generally observed for Re(I) compounds of type $ReX(CO)_3L_2$ (symmetric, A_1, and asymmetric, E, for the local C_{3v} symmetry of the $Re(CO)_3$ moiety).[17] The other two bands at 2052 and 1948 cm^{-1} are assigned to symmetric and asymmetric vibrations, respectively, of the $Re_2(CO)_2$ oscillator. The higher intensity for the band at higher wavenumber (A_1) is in agreement with the relative syn configuration of the two CO ligands. The band at 1948 cm^{-1} would in fact be expected to be very weak or absent for an antisymmetric vibration of two perfectly parallel CO ligands. However, coupling with the same symmetry (B_1) stretching modes of the two lateral $Re(CO)_3$ moieties is anticipated to transfer intensity to this mode.

The replacement of two CO ligands with two PPh_3 ligands results in compound **3**, whose IR spectrum is shown in Figure 3b. According to the above interpretation, it is logical to assign the band at 1995 cm^{-1} and the broader feature at 1896 cm^{-1} to the $Re(CO)_3$ moieties. The shift to lower frequencies upon CO replacement with PPh_3 is consistent with the better donor capability of the phosphine ligands, which is transmitted through the Re(I)$\rightarrow$Re(III) dative bonds to the Re(I) centers. The bands of compound **2** at 2052 and 1948 cm^{-1} have no counterparts in compound **3**, in agreement with replacement of the CO ligands bound to the inner Re(III) centers. If CO substitution had occurred on the two lateral $Re(CO)_3$ moieties, a much more complex IR spectrum would be expected for compound **3**. The other possibility that CO replacement has occurred at the inner positions but the product has undergone a charge redistribution to a Re(II)–Re(II)–Re(II)–Re(II) valence state is also unlikely, because in that case the stretching frequencies of the two $Re(CO)_3$ groups would be expected to increase, contrary to what is observed. Thus, IR evidence points to the formulation of **3** as a mixed-valence compound with a structure identical with that of the parent compound **2**.

Compound **4** is obtained from **2** by substitution of two CO ligands with CyNC (eq 6). The IR spectrum is shown in Figure 3c and is consistent with a structure and oxidation state assignments identical with those of compounds **2** and **3**. The bands of the external $Re(CO)_3$ moieties are found at 2013, 1917, and 1903 cm^{-1}. These bands are similar to those assigned to the same vibrations in compound **2**. The shift to lower frequencies observed for compound **3** is not observed here, in agreement with the lower σ basicity and/or higher π acidity of the CyNC ligands with respect to PPh_3. There are two additional bands at 2172 and 2047 cm^{-1}, the second being much weaker than the first. These are consistent with the CN stretching vibrations (symmetric and antisymmetric, respectively) of the two syn isonitriles. Stretching vibrations of isonitrile groups bonded to Re(III) are found[18] in the wide 2300–2000-cm^{-1} range.

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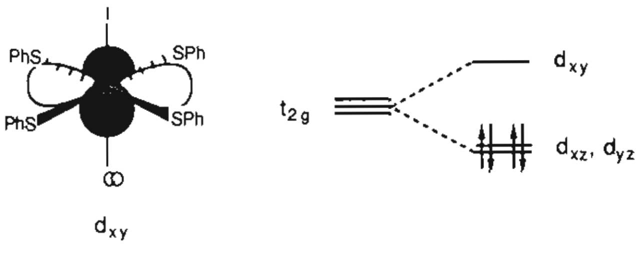
Discussion

Compound **2** was prepared by four different routes: (a) from $Re_2I_2(CO)_8$ and S_2Ph_2 (eq 4), (b) from $Re_2I_2(CO)_6(S_2Ph_2)$ and S_2Ph_2 (eq 5), (c) from $ReI(CO)_5$, $Re_2(SPh)_2(CO)_8$, and S_2Ph_2 (reverse of eq 7), and (d) from $Re_2(SPh)_2(CO)_8$ and I_2 (eq 8). It is noteworthy that, in the routes described by eqs 4 and 5, reductive elimination of I_2 is promoted by the oxidative addition of the less oxidizing S_2Ph_2, a possible contribution to the driving force of the reaction being the formation of the tetranuclear species and CO release. The lack of formation of a similar tetranuclear product when $Re_2Br_2(CO)_8$ is used in place of the iodide analogue could be ascribed to the reduced tendency of Br_2 to reductively eliminate. On the other hand, the use of Se_2Ph_2 or Te_2Ph_2 in conjunction with the iodide system also failed to lead to tetranuclear analogues of **2** because, presumably, these two dichalcogenides are not strong enough as oxidizing agents. The formation of **2** by oxidative addition of S_2Ph_2 to rhenium(I) carbonyl precursors resembles the formation of $W_3(SPh)_4(CO)_{10}$ and $Fe_3(SPh)_6(CO)_6$ from $W(CO)_6$ and $Fe(CO)_5$, respectively.[4g,19]

As mentioned under Results, the crystallographic data are best consistent with the assignment of the +I oxidation state to the lateral Re atoms and the +III oxidation state to the inner ones. The pattern of the metal–metal distances was interpreted as due to the presence of Re(I)→Re(III) dative bonds. Dative bonds between metal atoms are common in the literature,[20] although no example appears to have been previously reported where both the donor and acceptor metal atoms are rhenium atoms. An example for iridium is the Ir^IIr^{III} system $(COD)Ir(\mu\text{-}p\text{-}CH_3C_6H_4NCHNC_6H_4\text{-}p\text{-}CH_3)_2Ir(OCOCF_3)_2L$ (L = H_2O, py, Me_2SO, MeCN).[21] It is worth pointing out that both the mixed- and the homogeneous-valence formulations would result in a spin-paired ground-state configuration. As expected, compound **2** is diamagnetic in the solid state.

A feature of the structure that must be explained is the unfolding distortion from the ideal face-sharing/edge-sharing/face-sharing tetraoctahedral arrangement toward a linear arrangement of the four metal atoms, which imposes severe distortions on the coordination octahedra, especially on the shared vertices occupied by the bridging iodide ligands. The dative bonds involve overlap between one of the metal orbitals of the Re(I) pseudo-t_{2g} manifold and an empty orbital of the Re(III) pseudo-t_{2g} manifold. The disposition of the ligands around the Re(III) centers is such that the Re(III) t_{2g} set will be split. If we identify the axis that joins the CO ligand, through the Re(III) center, to the iodide ligand as the z axis, the d_{xz} and d_{yz} orbitals are involved in Re–CO π back-bonding and are therefore stabilized relative to the d_{xy} orbital. The latter may, in addition, be destabilized by π donation from the four equatorial SPh groups, shown as follows:



The result of this qualitative argument is that the four d electrons of the Re(III) center are anticipated to be located in the d_{xz} and d_{yz} orbitals and leave the d_{xy} orbital available to engage in the dative bond with the Re(I) center. The overlap with the Re(I) donor orbital of appropriate symmetry is maximal when the Re(I) center is located in the equatorial plane of the edge-sharing bioctahedral $Re_2(SPh)_6I_2(CO)_2$ core, and this may be the reason for the observed structural distortion.

As mentioned under Results, compound **2** and $Re_4I_8(CO)_6$ have identical nuclearity and distribution of oxidation states but different structure. Both structures can be ideally thought of as deriving from capping a central Re_2^{6+} core ($[Re_2I_2(SPh)_6(CO)_2]^{2-}$ in one case; $[Re_2I_8]^{2-}$ in the other case) with two $Re(CO)_3^+$ units, and their difference can thus be understood in terms of differences in the central Re_2^{6+} core. Both structural types for these two central units are known for Re(III). $[Re_2I_8]^{2-}$ is stable as such.[22] On the other hand, the isolated ion $[Re_2I_2(SPh)_6(CO)_2]^{2-}$ is not a known species, but isostructural neutral molecules with bridging chlorides,[23] selenolates,[24] or thiolates[15] are known. The problem of whether Re_2^{6+} complexes prefer a quadruply bonded Re_2L_8 or an edge-sharing bioctahedral $Re_2L_8(\mu\text{-}L)_2$ is a long-standing one,[25] and a clear rationale does not appear to be available to date. For instance, whereas $Re_2Cl_8^{2-}$ and the phosphine-substituted $Re_2Cl_6(PEt_3)_2$ are compounds with Re–Re quadruple bonds,[26] the diphosphine-substituted complexes $Re_2Cl_6(L\text{-}L)_2$ (L-L = dppm, dmpm, dppe) have edge-sharing bioctahedral structures.[23] There are no examples of a quadruply bonded structure with thiolate ligands. On the basis of the data available so far, it seems that edge-sharing bioctahedral structures are preferred when the donor power of the ligands around the Re(III) centers increases. Although each inner Re(III) center in compound **2** has a CO ligand, the high substitution with the good donor PhS ligands may be responsible for the structural difference between compounds **2** and $Re_4I_8(CO)_6$. The relatively low stretching frequency and substitution inertness of the Re(III)-bonded CO ligands is consistent with basic Re(III) centers.

Another interesting question concerns the ability of the two Re(III) ions in an edge-sharing bioctahedral structure to bind to each other through an electron-rich double bond.[27] For instance, the two metals are bonded in compounds $Re_2(SEt)_2Cl_4(dto)_2$,[15] $Re_2(SePh)_2Cl_4(dppm)$,[24] and $Re_2Cl_6(L\text{-}L)_2$ (L-L = dppm,[23a] dmpm[23b]) but nonbonded in compound $Re_2Cl_6(dppe)_2$.[23c] Our compound **2** adds to the picture in that there is no bond between the two Re(III) centers and the system is therefore at variance with the $(SEt)_2$-bridged system reported by Powell.[15] In our case, the Re(I)→Re(III) dative bonds satisfy the electronic requirements at the inner Re(III) centers, which then do not need to worry about whether to form or not to form a direct interaction with each other.

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Supplementary Material Available: Full tables of bond distances and angles, thermal parameters, and hydrogen atom coordinates for compound **2** (4 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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