

$J = 7.4$ Hz, 2 H, ortho), 7.35 (t, 2 H, meta), 7.28 (t, 1 H, para), 5.13 (mult, 6 H), 4.70 (s, 2 H, PhCH₂), 1.25 (d, $J = 6.2$ Hz, 36 H). ¹³C NMR (THF-*d*₈): δ 155.20 (d of t, $J_{\text{CRh}} = 69.3$ Hz, $J_{\text{CP}} = 21.0$ Hz, RNC), 132.82 (s, ipso Ph), 129.4 (d of d, $^1J_{\text{CH}} = 160.7$ Hz, $^2J_{\text{CH}} = 7.5$ Hz, ortho Ph), 128.55 (d of t, $^1J_{\text{CH}} = 161.2$ Hz, $^2J_{\text{CH}} = 7.1$ Hz, para Ph), 127.31 (d of mult, $^1J_{\text{CH}} = 159.6$, meta Ph), 69.23 (d, $^1J_{\text{CH}} = 146.7$ Hz, CHMe₂), 47.92 (t, $^1J_{\text{CH}} = 143.6$ Hz, PhCH₂), 24.81 (quar of virtual t, $^1J_{\text{CH}} = 125.6$ Hz, $^3J_{\text{CP}} + ^5J_{\text{CP}} = 3.7$ Hz, CH(CH₃)₂). ³¹P{¹H} NMR (THF-*d*₈): 127.7 (d, $J_{\text{PRh}} = 202.1$ Hz). IR (pentane): 2130 cm⁻¹ (ν_{CN}). Anal. Calcd for C₂₆H₄₉ClNO₆P₂Rh: C, 46.5; H, 7.35; N, 2.08; P, 9.22; Cl, 5.28. Found: C, 46.7; H, 7.32; N, 2.12; P, 9.38; Cl, 5.43.

trans-RhClP(O-*i*-Pr)₃(4-ClC₆H₄NC). Preparation was similar to that of the PhCH₂NC analogue; it was isolated in 92% yield as light yellow crystals. ¹H NMR (C₆D₆): δ 6.88 and 6.74 (AA'BB' pattern, $^3J_{\text{AB}} + ^5J_{\text{AB}} = 8.7$ Hz, 4 H), 5.42 (septet of virtual t, $J_{\text{HH}} = 6.2$ Hz, $^3J_{\text{HP}} + ^5J_{\text{HP}} = 9.7$ Hz, 6 H), 1.34 (d, $J_{\text{HH}} = 6.2$ Hz, 36 H). ¹³C{¹H} NMR (C₆D₆): δ 131.88 and 130.40 (ipso and para Ph), 129.41 and

126.54 (ortho and meta Ph), 69.32 (CHMe₂), 24.60 (CH(CH₃)₂); RNC not observed. ³¹P{¹H} NMR (C₆D₆): δ 126.1 (d, $J_{\text{PRh}} = 200.0$ Hz). IR (pentane): 2098 cm⁻¹ (ν_{CN}).

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Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom positions, and isotropic thermal parameters for **2a** (4 pages); a table of observed and calculated structure factors for **2a** (17 pages). Ordering information is given on any current masthead page.

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

Conversion of an Electron-Rich Triple Bond to a Double Bond by Oxidative Addition of Diphenyl Diselenide to Re₂Cl₄(μ -dppm)₂. Preparation and Characterization of Re₂Cl₄(μ -SePh)₂(μ -dppm)₂ (dppm = Bis(diphenylphosphino)methane)

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The dirhenium(II) complex Cl₂Re(μ -dppm)₂ReCl₂ with a $\sigma^2\pi^4\delta^2\delta^{*2}$ triple bond undergoes a clean, facile reaction with PhSeSePh to produce Cl₂Re(μ -SePh)₂(μ -dppm)₂ReCl₂ in high yield. In this reaction, oxidative addition of the Se-Se single bond to the Re=Re triple bond results in a conversion of the d⁵-d⁵ M₂L₈ parent compound to a d⁴-d⁴ M₂L₁₀ species which possesses a formal double bond ($\sigma^2\pi^2\delta^2\delta^{*2}$). The identity of the product has been confirmed by a single-crystal X-ray study, and the structural results are compared with the data previously reported for the analogous doubly bonded Re₂Cl₄(SePh)₂(dppm)₂. Re₂Cl₄(SePh)₂(dppm)₂ crystallizes in the monoclinic space group P2₁/n with $a = 13.115$ (2) Å, $b = 15.463$ (5) Å, $c = 14.309$ (2) Å, $\beta = 102.00$ (1)°, $V = 2838$ (2) Å³, and $Z = 2$. The crystallographic symmetry of the molecule is $\bar{1}$ while the effective molecular symmetry is 2/m (C_{2h}). Important bond distances and angles are Re-Se(av) = 2.462 [1] Å, Re-Cl(av) = 2.45 [1] Å, Re-P(av) = 2.474 [9] Å, \angle Re-Re-Se = 57.33 (4)°, and \angle Re-Re-Cl(av) = 140.4 [1]°. The Re-Re distance in Re₂Cl₄(SePh)₂(dppm)₂ is 2.656 (1) Å, which is 0.04 Å longer than the M-M distance in Re₂Cl₄(dppm)₂. The lengthening of the Re-Re bond is attributed to the difference in size of the bridging groups (SePh vs. Cl). The properties of the title compound were investigated by several other methods, including infrared and UV-visible spectroscopy and electrochemistry. The near-infrared spectrum of Re₂Cl₄(SePh)₂(dppm)₂ exhibits a broad band at 1480 nm ($\epsilon \approx 200$), a feature that is also found in the electronic spectrum of Re₂Cl₄(dppm)₂. A cyclic voltammetric study revealed the presence of four reversible one-electron redox couples; two couples located at $E_{1/2} = +0.95$ and +1.65 V vs. Ag/AgCl correspond to oxidation processes, and two couples at $E_{1/2} = -0.46$ and -1.30 V represent reductions. These metal-based redox properties are very similar to those observed for Re₂Cl₄(dppm)₂, Re₂Cl₄(CO)₂(dppm)₂, and other related dirhenium complexes with an edge-sharing bioctahedral geometry.

Introduction

The cleavage and substitution chemistry of binuclear compounds containing multiple metal-metal bonds is well-documented.¹ A much less developed facet of the reactivity of these complexes is their tendency to oxidatively add a substrate across the unsaturated M-M unit. Current work in these laboratories is directed toward a thorough investigation of the oxidative-addition chemistry of double ($\sigma^2\pi^2$), triple ($\sigma^2\pi^4$ and $\sigma^2\pi^4\delta^2\delta^{*2}$), and quadruple ($\sigma^2\pi^4\delta^2$) bonds. A primary objective in pursuing these studies is the development of high-yield, rational syntheses of edge-sharing bioctahedral complexes. Some results that have appeared in the literature include the reactions of disulfides (RSSR) with the double bond of Ta₂Cl₆(Me₂S)₃² and with the quadruple bond of Mo₂Cl₄(L-L)₂^{3,4} compounds to yield the thiolate-bridged M₂L₁₀

complexes (Me₂S)Cl₃Ta(μ -SEt)₂TaCl₃(Me₂S) and (L-L)-Cl₂Mo(μ -SR)₂MoCl₂(L-L) (R = Et, L-L = 1,2-bis(dimethylphosphino)ethane (dmpe), 4,7-dithiadecane (dtd); R = Ph, L-L = dmpe, dtd, 3,6-dithiooctane (dto)). These interesting compounds possess unusual electronic properties, and a few of them have been subjected to in-depth structural, magnetic, and theoretical studies.

The promising nature of the oxidative-addition reactions involving double, quadruple, and electron-poor triple bonds prompted us to extend our studies by probing the reactivity of the electron-rich triple bond as found in the coordinatively unsaturated dirhenium(II) compounds. Preliminary results from the reactions of Re₂Cl₄(μ -dppm)₂ with halogens, disulfides, and diselenides indicate that a smooth addition occurs which converts the parent Re^{II}Re^{II} complex to a Re^{III}Re^{III} species. The doubly bonded Re₂Cl₄(μ -SePh)₂(μ -dppm)₂ with bridging SePh groups was prepared via reaction of PhSeSePh with Re₂Cl₄(dppm)₂. The structural, spectroscopic, and electrochemical properties of the product are presented in this paper. This result represents the first instance in which a d⁴-d⁴ M₂L₁₀ complex has been prepared from a d⁵-d⁵ M₂L₈ compound. The approach takes advantage of the facile oxidation of the $\sigma^2\pi^4\delta^2\delta^{*2}$ bond, and it is a superior method for the designed synthesis of new edge-sharing bioctahedral

- (1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982, and references therein.
- (2) Campbell, G. C.; Canich, J. M.; Cotton, F. A.; Duraj, S. A.; Haw, J. F. *Inorg. Chem.* **1986**, *25*, 287.
- (3) Cotton, F. A.; Powell, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3371.
- (4) Cotton, F. A.; Diebold, M. P.; O'Connor, C. J.; Powell, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7438.

Table I. Summary of X-ray Crystallographic Parameters for $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$

formula	$\text{Re}_2\text{Cl}_4\text{Se}_2\text{P}_4\text{C}_{62}\text{H}_{54}$
fw	1595.15
space group	$P2_1/n$
systematic absences	$h0l, h + l = 2n; 0k0, k = 2n$
$a, \text{\AA}$	13.115 (2)
$b, \text{\AA}$	15.463 (5)
$c, \text{\AA}$	14.309 (2)
α, deg	90
β, deg	102.00 (1)
γ, deg	90
$V, \text{\AA}^3$	2838 (2)
Z	2
$d_{\text{calcd}}, \text{g/cm}^3$	1.868
cryst size, mm	$0.32 \times 0.12 \times 0.10$
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	59.345
data collec instrument	CAD-4
radiation (monochromated in incident beam)	Mo K α ($\lambda = 0.71073 \text{\AA}$), graphite monochromated
orientation reflcns: no.; range (2θ), deg	25; $20 < 2\theta < 30$
temp, $^\circ\text{C}$	22 ± 2
scan method	ω scans
data collec range, 2θ , deg	$4 \leq 2\theta \leq 47$
no. of unique data, total	3972
no. of data with $F_o^2 > 3\sigma(F_o^2)$	2271
no. of parameters refined	334
transmission factors: max, min	0.9959, 0.8110
R^a	0.0404
R_w^b	0.0442
quality-of-fit indicator ^c	1.15
largest shift/esd, final cycle	0.06
largest peak, $e/\text{\AA}^3$	0.832

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

complexes with a $\sigma^2\pi^2\delta^*2\delta^2$ electronic configuration.

Experimental Section

Starting Materials. The complex $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ was prepared according to the literature procedure.¹ Diphenyl diselenide was purchased from Aldrich Chemicals and was used without further purification. The solvents were dried and freshly distilled under an atmosphere of dinitrogen before use. Dichloromethane that was used in the electrochemical experiments was of the highest purity commercially available and was used as received.

Reaction Procedures. All reactions were carried out under an argon atmosphere by using standard vacuum line techniques. Solid samples were handled in air, however, and the title compound appears to be indefinitely stable in solutions that have been exposed to oxygen.

Preparation of $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$. A solution of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.20 g, 0.156 mmol) and PhSeSePh (0.20 g, 0.641 mmol) in toluene (10 mL) was refluxed for 10 h under an atmosphere of argon. The initial purple solution gradually became red-orange with the precipitation of a rose solid. The entire reaction solution was stripped to dryness, and the residue was washed with copious amounts of diethyl ether to remove the excess PhSeSePh . The resulting crude solid was recrystallized from $\text{CH}_2\text{Cl}_2\text{-MeOH}$ (2:1). Dark red-brown crystals formed over a period of 2 days at 0°C and were filtered off and washed with diethyl ether; yield 0.21 g (87%). Anal. Calcd for $\text{C}_{62}\text{H}_{54}\text{Cl}_4\text{Re}_2\text{P}_4\text{Se}_2$: C, 46.68; H, 3.41. Found: C, 46.24; H, 3.68. IR (Nujol mull, cm^{-1}): 1590 w, 1535 w, 1490 m, 1440 m, 1195 w, 1160 w, 1135 w, 1100 m, 1035 w, 1005 w, 800 sh, 790 m, 745 s, 700 s, 535 s, 520 m, 490 m, 306 m, 285 w.

Preparation of Single Crystals for Structure Determination. Crystals of $\text{Cl}_2\text{Re}(\mu\text{-SePh})_2(\mu\text{-dppm})_2\text{ReCl}_2$ that were suitable for X-ray crystallographic studies were grown by carefully layering methanol over a dichloromethane solution containing the compound. During a period of several days, diffusion occurred slowly enough to permit satisfactory crystal growth. A crop of small red-brown crystals were obtained by this procedure.

X-ray Structure Analysis. (i) **Data Collection and Reduction.** A red crystal of $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ with approximate dimensions $0.32 \times 0.12 \times 0.10$ mm was mounted on the top of a glass fiber and coated with epoxy resin. Geometric and intensity data were collected at room temperature on a Enraf-Nonius CAD-4 diffractometer equipped with Mo K α radiation. The procedures that were used for data collection have been described previously.⁵ The crystal belongs to the uniquely deter-

Table II. Atomic Positional Parameters and Equivalent Isotropic Displacement Parameters (\AA^2) and Their Estimated Standard Deviations for $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2^a$

atom	x	y	z	b
Re(1)	0.08880 (4)	0.04050 (4)	-0.00204 (4)	2.816 (9)
Se(1)	-0.0164 (1)	0.07295 (9)	0.1176 (1)	3.67 (3)
P(1)	0.0092 (3)	0.1432 (2)	-0.1284 (3)	3.03 (8)
P(2)	0.1945 (2)	-0.0537 (2)	0.1217 (3)	2.99 (8)
Cl(1)	0.2342 (2)	0.359 (3)	-0.0845 (2)	4.03 (8)
Cl(2)	0.1967 (3)	0.1606 (2)	0.0764 (3)	4.07 (9)
C(1)	-0.087 (1)	0.184 (1)	0.111 (1)	4.3 (4)
C(2)	-0.029 (1)	0.262 (1)	0.113 (1)	5.6 (4)
C(7)	0.058 (1)	0.2528 (8)	-0.1271 (9)	3.0 (3)
C(13)	0.006 (1)	0.1238 (9)	-0.2550 (9)	3.5 (3)
C(8)	0.162 (1)	0.261 (1)	-0.140 (1)	4.5 (3)
C(6)	-0.194 (1)	0.183 (1)	0.123 (1)	5.9 (4)
C(9)	0.196 (1)	0.345 (1)	-0.161 (1)	5.3 (4)
C(19)	-0.1287 (9)	0.1593 (9)	-0.1255 (9)	3.4 (3)
C(3)	-0.079 (1)	0.338 (1)	0.130 (1)	6.5 (5)
C(4)	-0.183 (1)	0.341 (1)	0.145 (1)	6.5 (5)
C(5)	-0.239 (1)	0.265 (1)	0.138 (1)	6.4 (5)
C(10)	0.129 (1)	0.416 (1)	-0.169 (1)	6.3 (5)
C(11)	0.030 (1)	0.409 (1)	-0.153 (1)	6.3 (5)
C(12)	-0.008 (1)	0.3254 (9)	-0.130 (1)	4.6 (4)
C(14)	0.064 (1)	0.0630 (9)	-0.288 (1)	4.2 (4)
C(15)	0.064 (1)	0.0568 (9)	-0.388 (1)	4.8 (4)
C(16)	0.002 (1)	0.110 (1)	-0.453 (1)	5.7 (4)
C(17)	-0.060 (1)	0.173 (1)	-0.419 (1)	5.3 (4)
C(18)	-0.0571 (1)	0.180 (1)	-0.320 (1)	4.7 (4)
C(20)	0.324 (1)	-0.0853 (9)	0.106 (1)	3.8 (3)
C(21)	0.3998 (9)	-0.020 (1)	0.116 (1)	4.2 (4)
C(22)	0.5032 (9)	-0.040 (1)	0.111 (1)	4.5 (4)
C(23)	0.526 (1)	-0.127 (1)	0.095 (1)	6.6 (5)
C(24)	0.453 (1)	-0.191 (1)	0.089 (2)	8.7 (6)
C(25)	0.348 (1)	-0.169 (1)	0.094 (1)	5.8 (4)
C(26)	0.2287 (9)	-0.025 (1)	0.249 (1)	4.0 (3)
C(27)	0.284 (1)	-0.088 (1)	0.311 (1)	4.5 (4)
C(28)	0.308 (1)	-0.071 (1)	0.410 (1)	4.5 (4)
C(29)	0.282 (1)	0.011 (1)	0.443 (1)	5.4 (4)
C(30)	0.230 (1)	0.073 (1)	0.384 (1)	5.3 (4)
C(31)	0.204 (1)	0.0560 (9)	0.283 (1)	4.2 (4)

^aAnisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

mined $P2_1/n$ space group, and the unit cell parameters and orientation matrix were refined by a least-squares fit to the positions of 25 reflections in the range $20 < 2\theta < 30^\circ$. The lattice dimensions and the b -axis mirror plane were verified by axial photography. The ω -scan technique was used to scan data points in the range $4 < 2\theta < 47^\circ$. Three check reflections monitored throughout data collection displayed no significant gain or loss in intensity. Data reduction was carried out by standard methods using well-established computational procedures.^{6a} The data were corrected for Lorentz and polarization effects, and azimuthal scans (ψ scans) of eight reflections with an Eulerian angle χ near 90° were used as a basis for an empirical absorption correction.^{6b} Pertinent crystallographic parameters are summarized in Table I.

(ii) **Structure Solution and Refinement.** The systematic absences from the data indicated that the crystal belongs to the $P2_1/n$ space group. The position of the unique Re atom was determined from a three-dimensional Patterson map. With the midpoint of the dimeric unit residing on a crystallographic inversion center, the asymmetric unit is defined by half of a molecule of $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$. A series of alternating least-squares refinements and difference Fourier maps led to complete development of the unique atoms in the coordination sphere of the rhenium atom. In the final refinement, 2271 data were used to fit 334 variable parameters (data:parameter ratio of 7), giving convergence with residuals of $R = 0.0404$ and $R_w = 0.0442$. The quality-of-fit index is 1.15, and the final least-squares cycle did not shift any parameter by more than 0.06 times its estimated standard deviation. The largest peak in the last difference Fourier map was $0.832 e/\text{\AA}^3$.

(5) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(6) (a) Data processing was done on a PDP-11/60 computer with PDP-11-simulated VAXSDP and on a VAX-11/780 computer with programs for the package VAXSDP. (b) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

Table III. Selected Bond Distances (Å) and Angles (deg) for $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2^a$

atom 1	atom 2	dist	atom 1	atom 2	dist
Re(1)	Re(1)'	2.656 (1)	P(1)	C(19)	1.834 (12)
Re(1)	Se(1)	2.461 (2)	P(2)	C(19)	1.852 (13)
Re(1)	P(1)	2.468 (4)	P(2)	C(20)	1.822 (13)
Re(1)	P(2)	2.481 (4)	P(2)	C(26)	1.840 (14)
Re(1)	Cl(1)	2.442 (3)	C(1)	C(2)	1.42 (2)
Re(1)	Cl(2)	2.460 (4)	C(1)	C(6)	1.45 (2)
Se(1)	C(1)	1.949 (15)	C(2)	C(3)	1.38 (2)
P(1)	C(7)	1.811 (14)	C(9)	C(10)	1.40 (2)
P(1)	C(13)	1.828 (14)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Re(1)	Re(1)'	Se(1)	57.33 (4)	Se(1)	Re(1)	Se(1)'	114.72 (4)
Re(1)	Re(1)'	P(1)	94.58 (9)	P(1)	Re(1)	P(2)	171.3 (1)
Re(1)	Re(1)'	P(2)	94.02 (8)	Cl(1)	Re(1)	Cl(2)	79.0 (1)
Re(1)	Re(1)'	Cl(1)	140.6 (1)	Re(1)	Se(1)	Re(1)'	65.28 (4)
Re(1)	Re(1)'	Cl(2)	140.36 (9)	Re(1)	Se(1)	C(1)	118.3 (4)

^a Primed atoms are related to unprimed atoms by the inversion center.

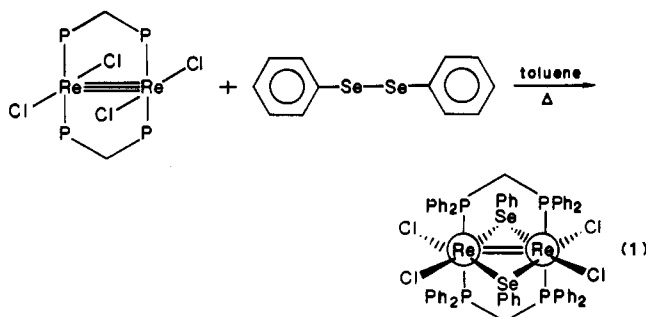
Positional and isotropic thermal parameters for $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ are given in Table II. Selected bond distances and angles are summarized in Table III.

Physical Measurements. Electronic spectra were measured on dichloromethane solutions with a Cary 17D spectrophotometer. Electrochemical measurements were done by using a Bioanalytical Systems, Inc., Model BAS100 electrochemical analyzer in conjunction with a Bausch and Lomb, Houston Instruments Model DMP 40 digital plotter. Experiments were carried out in dichloromethane containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as a supporting electrolyte. A three-electrode cell configuration was used, with a platinum disk, model BAS MF 2032, and a platinum wire as a working and auxiliary electrode, respectively. A BAS MF 2020 Ag/AgCl cell was used as a reference electrode (against which ferrocene is oxidized at $E_{1/2} = +0.42$ V). All potentials were referenced to the Ag/AgCl electrode at 22 ± 2 °C with a full positive feedback resistance compensation and are uncorrected for junction potentials. $E_{1/2}$ values are determined as $(E_{p,a} + E_{p,c})/2$. Infrared spectra were recorded on a Perkin-Elmer 785 spectrophotometer. Microanalyses were performed by Galbraith Laboratories of Knoxville, TN.

Results and Discussion

(a) Preparation. The reaction of excess diphenyl diselenide, PhSeSePh, with $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ in refluxing toluene gives, in high yield, the red crystalline compound $\text{Cl}_2\text{Re}(\mu\text{-SePh})_2(\mu\text{-dppm})_2\text{ReCl}_2$. The product is easily separated from unreacted PhSeSePh, and recrystallization from $\text{CH}_2\text{Cl}_2\text{-MeOH}$ affords an analytically pure sample. This new compound has been characterized by X-ray crystallography, elemental analysis, IR and UV-visible spectroscopy, and cyclic voltammetry. The new compound is air-stable both in the solid state and in solution and is quite soluble in dichloromethane and chloroform and moderately soluble in common organic solvents such as toluene.

The reaction reported here is the addition of one molecule of PhSeSePh to $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with concomitant oxidation from Re_2^{4+} to a product that is a derivative of the Re_2^{6+} core, a process that corresponds to a decrease in bond order from 3 to 2 (eq 1).



The synthetic strategy employed in eq 1 is capable of being generalized and will provide a useful method for the preparation of new doubly bonded M_2L_{10} compounds from readily available starting materials. In the present case, the approach has permitted the isolation of an unusual species with SePh groups spanning the

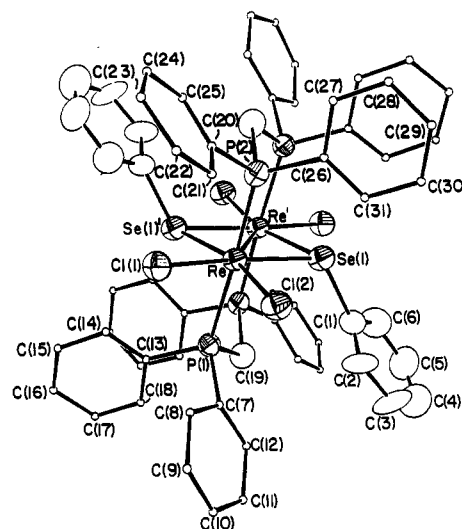


Figure 1. ORTEP drawing of a single molecule of $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$, showing the atom-labeling scheme. Phenyl-group carbon atoms in the dppm ligands are represented as small circles for clarity. All other atoms are represented by their 50% probability ellipsoids.

dimetal unit. To our knowledge, this is the first example of a multiply bonded compound possessing SeR ligands, although there are several examples of dimolybdenum and ditantalum complexes with thiolato groups.²⁻⁴

A reaction similar to eq 1 has also been observed to occur when a solution of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ is heated in the presence of diphenyl disulfide (PhSSPh) or halogens. These products are believed to be structurally analogous to $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$ but with bridging thiolate or halide ligands in place of the SePh moieties. We are currently investigating the exact nature of these products.

(b) Molecular Structure. The structure of the $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ molecule is shown in Figure 1, where the atom-labeling scheme is also given. Important distances and angles within the molecule are listed in Table III. As can be seen from the ORTEP drawing in Figure 1, the dimeric unit is centrosymmetric. The effective molecular symmetry is D_{2h} if one includes only the skeletal atoms that comprise the immediate coordination sphere of the Re atoms, whereas the point group is lowered to C_{2h} ($2/m$) when all atoms are taken into consideration (see Figure 1). The geometry of the molecule is that of an edge-sharing bioctahedron with the six positions in the equatorial plane being occupied by four terminal chlorine atoms and two bridging SePh groups. Apical positions, above and below the equatorial plane, are filled by the four phosphorus atoms of the two trans dppm ligands. The conformation of the Re-P-C-P-Re five-membered rings is that of a half-chair with the two methylene carbon atoms in anti positions with respect to the plane containing the rhenium and phosphorus atoms. In a similar fashion, the phenyl groups

on the Se atoms are anti with respect to the equatorial plane containing the rhenium, selenium, and chlorine atoms. These conformational preferences allow for a strictly centrosymmetric molecule, and as can be clearly seen in the ORTEP drawing, the result is a molecule that quite easily accommodates the sterically demanding phenyl groups.

With the X-ray results previously reported⁷ for $\text{Re}_2\text{Cl}_4(\mu\text{-Cl})_2(\mu\text{-dppm})_2$ serving as a convenient backdrop, we now turn to a discussion of the structural details of the new compound. The bond angles around the rhenium atoms are distorted in a familiar way, viz., opening of the $(\mu\text{-Se})\text{-Re}\text{-}(\mu\text{-Se})'$ angle (114.72°), due to the presence of metal-metal bonding. The corresponding angle in $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ is slightly less, $(\mu\text{-Cl})\text{-Re}\text{-}(\mu\text{-Cl})' = 113.67^\circ$, owing to the smaller size of chlorine vs. that of selenium atoms. The terminal chlorine ligands in $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ are swept back from the center of the molecule with an average $\text{Re}\text{-Re}\text{-Cl}_t$ angle of $140.4 [1]^\circ$, which is not unlike the values found for $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ ($138.7 [5]^\circ$),⁷ $\text{Re}_2\text{Cl}_5(\text{OC}_2\text{H}_5)(\text{dppm})_2$ ($138 [5]^\circ$),⁷ and similar binuclear compounds. Other angles of importance such as $\text{Re}\text{-Se}\text{-Re}'$ ($65.28 (4)^\circ$) and $\text{Re}\text{-Re}\text{-P}_{av}$ ($94.3 [3]^\circ$) are within expected ranges. All bond distances within the molecule are quite normal, and a list of the important ones can be found in Table III.

A major point of discussion concerning the structure of a binuclear compound is the magnitude of the M-M separation. As there are still relatively few examples of nonorganometallic doubly bonded compounds, it is important to determine the structures of new species exhibiting this type of bonding. A compilation of structural data from related compounds can lead to the establishment of trends that lend insight into the factors that influence the nature and extent of M-M bonding.⁹ The results of these studies are not particularly meaningful, however, unless the compounds vary in a systematic manner. In M_2L_{10} compounds the three basic factors that may be varied are the identity of the metal, the identities of the terminal ligands (two types), and the identity of the bridging group. If only one of these factors at a time is made to vary, then the structural comparisons between different compounds are quite meaningful. An example of a homologous series of M_2L_{10} compounds is $\text{M}_2\text{Cl}_6(\text{R}_2\text{PCH}_2\text{PR}_2)_2$ ($\text{M} = \text{Nb, Ta, Mo, Re, Ru}$; $\text{R} = \text{Me, Ph}$), which we studied in order to infer, from the trend in M-M distances, the order of the MO's responsible for M-M bonding.¹⁰ The results are in accord with theoretical predictions concerning the relative energies of the δ and δ^* orbitals.^{10,11}

In the present case, the new compound $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$ differs from the previously reported complex $\text{Re}_2\text{Cl}_4(\mu\text{-Cl})_2(\mu\text{-dppm})_2$ only in the nature of the bridging group (SePh vs. Cl). The Re-Re distance in $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ is $2.656 (1) \text{ \AA}$, whereas it is $2.616 (1) \text{ \AA}$ for $\text{Re}_2\text{Cl}_6(\text{dppm})_2$.⁷ This is most likely a consequence of the larger size of the bridging Se atoms, a type of influence that has been documented in other systems.^{7,9} The nature of the terminal ligands has also been observed to play a significant role in the Re=Re bonding as evidenced by the lengthening of the Re-Re bond from $2.616 (1) \text{ \AA}$ in $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ to $2.667 (1) \text{ \AA}$ in $\text{Re}_2\text{Cl}_5(\text{OEt})(\text{dppm})_2$ upon substitution of one equatorial chloride by an ethoxide ligand.

(c) **UV-Visible Spectroscopy and Electrochemistry.** The electronic spectrum of $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$ was recorded in dichloromethane solution and is shown in Figure 2. The molecule exhibits bands at $\lambda_{\text{max}} = 430$ (sh), 468 ($\epsilon \approx 4100$), and 770 nm ($\epsilon \approx 330$) in the visible region and an additional absorption in the near-infrared region at 1480 nm ($\epsilon \approx 200$). The last feature was also observed in the corresponding spectra of $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ ($\lambda_{\text{max}} = 1435 \text{ nm}$) and $\text{Re}_2\text{Cl}_6(\text{Ph}_2\text{Ppy})_2$ ($\lambda_{\text{max}} =$

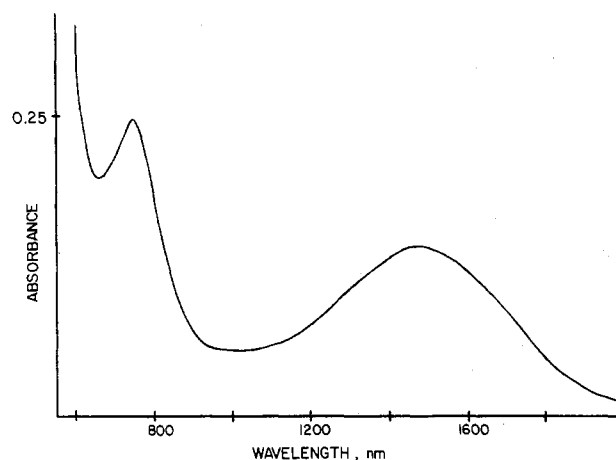


Figure 2. Near-infrared and visible absorption spectrum of $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$ in dichloromethane solution.

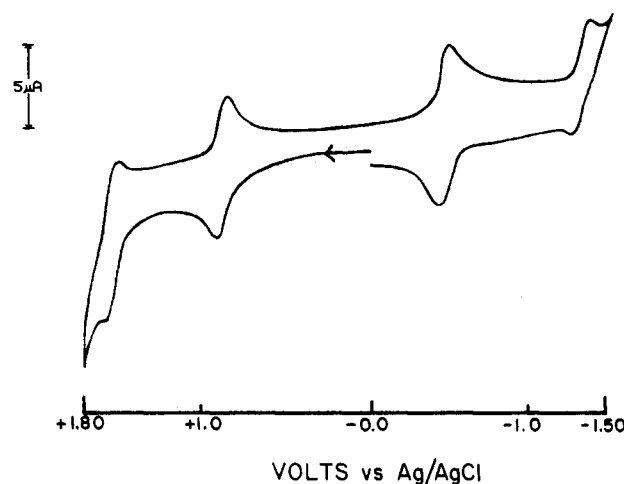


Figure 3. Cyclic voltammogram of $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$ in 0.2 M TBAH-dichloromethane at 200 mV/s at a Pt-disk electrode.

1525 nm). The band appears to be a characteristic electronic transition for M_2L_{10} dirhenium(III) complexes although the assignment still remains unclear. One possible explanation for the presence of the low-energy transition is that the Re_2^{6+} compounds are contaminated by a trace amount of a compound derived from the Re_2^{5+} core. These paramagnetic $\text{Re}^{\text{II}}\text{Re}^{\text{III}}$ species are known to exhibit a band in the near-infrared region. This has been ruled out, however, both in the earlier study⁷ and in this case by careful investigations of the purity of the complexes. The sample of $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ that was used for the spectroscopic studies was examined by cyclic voltammetry procedures and analyzed for percent C and H. The results were quite good, and we are confident that the sample was free of impurities.

The new compound exhibits a rich electrochemistry as evidenced by the presence of four reversible couples between $+2.0$ and -2.0 V in the cyclic voltammogram. This extensive redox behavior is diagnostic of Re_2^{6+} complexes, and it resembles that which was reported for $\text{Re}_2\text{Cl}_6(\text{dppm})_2$,⁷ $\text{Re}_2\text{Cl}_6(\text{Ph}_2\text{Ppy})_2$,⁷ and $\text{Re}_2\text{Cl}_4(\text{CO})_2(\text{dppm})_2$ (whose structural and electrochemical properties strongly favor assignment as an Re_2^{6+} core by regarding the bridging CO group as divalent).¹² $\text{Re}_2\text{Cl}_4(\text{SePh})_2(\text{dppm})_2$ possesses two one-electron oxidations at $E_{1/2} = +0.95$ and $+1.65 \text{ V}$ vs. Ag/AgCl and two one-electron reduction processes at potentials of -0.460 and -1.30 V vs. Ag/AgCl . The range of oxidation states traversed in these processes in $\text{Re}_2^{4+} \rightarrow \text{Re}_2^{8+}$, which is a remarkable net four-electron change (eq 2).

Concluding Remarks. The new compound $\text{Re}_2\text{Cl}_4(\mu\text{-SePh})_2(\mu\text{-dppm})_2$ possesses an edge-sharing bioctahedral geometry, and

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

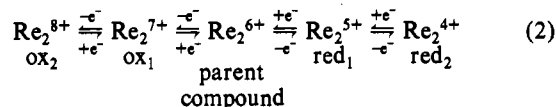
(8) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

(9) Cotton, F. A., submitted for publication in *Polyhedron*.

(10) Chakravorty, A. R.; Cotton, F. A.; Diebold, M. P.; Lewis, D. B.; Roth, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 971.

(11) Shaik, S.; Hoffmann, R.; Fisel, C. R.; Summerville, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4555.

(12) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 3524.



its properties, both structural and spectroscopic, are very similar to those previously reported for $\text{Re}_2\text{Cl}_6(\text{dppm})_2$.⁷ These compounds contain $\text{Re}=\text{Re}$ double bonds with the electronic configuration being $\sigma^2\pi^2\delta^*\delta^2$ as predicted by Shaik and Hoffmann.¹¹ Indeed, experimental evidence obtained from our recent study of a series of $\text{M}_2\text{Cl}_6(\text{L-L})_2$ compounds supports the molecular orbital ordering that places the δ^* orbital lower in energy than the δ orbital.¹⁰ The factors that influence the relative energies of these orbitals are not well-understood, however, and we are interested in preparing compounds that vary in a systematic manner, thereby allowing new trends to be established. Until recently, our efforts to "construct" homologous series have been thwarted by a general

lack of synthetic methods for the purposeful design of M_2L_{10} compounds. The present study documents the existence of a facile oxidative-addition chemistry for the electron-rich triple bond of dirhenium as found in $\text{Re}_2\text{X}_4(\text{L-L})_2$ compounds. This result is important because it provides the basis for a useful, predictable strategy for the preparation of new M_2L_{10} compounds with M-M double bonds. This approach, which is also applicable to triple and quadruple bonds, is sure to figure prominently in our future research involving the synthesis of new edge-sharing bioctahedral complexes.

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Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic equivalent displacement parameters (4 pages); a listing of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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Higher Oxidation State Chemistry of Osmocene: Dimeric Nature of the Osmocenium Ion

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A study of the oxidation chemistry of osmocene has led to the discovery of the metal-metal-bonded osmocenium dimer $[(\text{Cp}_2\text{Os})_2]^{2+}$. This complex has been characterized both in solution and in the solid state by determining the structure of the PF_6^- salt by X-ray diffraction. It is composed of two osmocenium cations joined by an Os-Os bond, with the rings tilted back away from the metal-metal bond and each half rotated by 90° with respect to the other. The complex serves as a key synthetic precursor to a variety of higher oxidation state Os(IV) metallocenes. The reaction chemistry of the dimer has been briefly surveyed, and the observed reaction pathways that result in new complexes include radical, disproportionation, and substitution routes. The isolation and characterization of new Os(IV) complexes include a structure determination by X-ray diffraction of the doubly metalated $[\{\text{Cp}(\text{C}_5\text{H}_4)\text{Os}\}_2][\text{PF}_6]_2$.

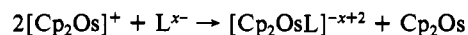
Introduction

In this report are described new higher oxidation state derivatives of osmocene. This chemistry stems in large part from discovery of the key precursor, $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$, which contains the metal-metal-bonded dimer of the osmocenium cation. A number of reactions of this dimer have been elucidated, and these provide routes to a variety of Os(IV) osmocene complexes. The synthesis, characterization, and some reactions of these new derivatives are described here.

Our interest in complexes of this type arose in part from the perception that the Os(IV)/Os(II) couples may be useful experimental probes of two-electron-transfer reactions. It should be recognized that many of the features that qualify pentaammineruthenium complexes as experimental probes of one-electron-transfer reactions are also present in osmium (and ruthenium) metallocenes. It is possible to prepare discrete molecular metallocene complexes that can be systematically modified, that are robust in solution, and that have appropriate oxidation states. We have already shown how simple haloruthenium(IV) and -osmium(IV) metallocenes, $[\text{Cp}_2\text{MX}]^+$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), participate with osmocene in a two-electron-transfer reaction that is facilitated by halide atom transfer,¹ and there is interest in extending this work to potential multiatom bridges and possibly binuclear complexes.

Since the descriptive chemistry of these metallocenes is limited primarily to the halometallocene complexes,² we sought routes

by which ligands other than halide could be coordinated to the metal. One approach that we explored was formation of the osmocenium cation. This species is a desirable starting material for synthetic reactions since it is expected to react with donor ligands in a disproportionation reaction yielding osmium(IV) derivatives and osmocene:



The existing literature on osmocene,³ including that on the chemical and electrochemical oxidation, leads to no clear consensus on the accessibility of the osmocenium cation. We find that when osmocene reacts with cerium(IV), the metal-metal-bonded osmocenium dimer is formed instead of the expected osmocenium cation. This dimer then participates in a number of new reactions, including some that result in coordination of ligands other than halide to Os(IV).

Experimental Section

Materials. Osmocene was obtained from Strem Chemicals, Inc., and used as received. Reagent grade thiourea was recrystallized from hot water, vacuum-dried at 80°C , and stored under argon. Bis(triphenylphosphoranylidene)ammonium azide $[(\text{PNP})\text{N}_3]$ was prepared by metathesis of NaN_3 with $(\text{PNP})\text{Cl}$ in water. The resulting solid was collected, vacuum-dried at 80°C , and recrystallized by vapor diffusion of diethyl ether into a concentrated acetone solution of the salt under argon. The preparation of $[(\text{Cp}_2\text{Os})_2][\text{PF}_6]_2$ and $[\text{Cp}_2\text{OsNO}_3][\text{PF}_6]$ was performed under normal atmospheric conditions with use of standard

(1) Smith, T. P.; Inverson, D. J.; Droege, M. W.; Kwan, K. S.; Taube, H., submitted for publication in *Inorg. Chem.*

(2) Ru: Bennett, M. A.; Bruce, M. I.; Matheson, T. W. *Comprehensive Organometallic Chemistry*; Vol. 4; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 4, pp 762-764. Os: Adams, R. D.; Selegue, J. P. *Comprehensive Organometallic Chemistry*; Vol. 4; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 4, pp 1018-1020.

(3) (a) Fischer, E. O.; Grubert, H. *Chem. Ber.* **1959**, *92*, 2302-2309. (b) Gubin, S. P.; Smirnova, S. A.; Denisovich, L. I.; Lubovich, A. A. *J. Organomet. Chem.* **1971**, *30*, 243-255. (c) Denisovich, L. I.; Zakurin, N. V.; Bezrukova, A. A.; Gubin, S. P. *J. Organomet. Chem.* **1974**, *81*, 207-216. (d) Tirouflet, J.; Laviron, E.; Dabard, R.; Komenda, J. *Bull. Soc. Chim. Fr.* **1963**, *30*, 857-862. (e) Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811-5817. (f) Bohling, D. A. Ph.D. Thesis, University of Minnesota, 1984; pp 74-94.