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Summary: Reaction of $o-C_{c}H_{d}(PPhH)(SH)$ (3) with $Mn(CO)_5Br$ and $Re(CO)_5Br$ in chloroform provided sulfido-bridged binuclear complexes { $fac-[o-C_6H_4PPhCl)$ - $(\mu_2-S) Mn(CO)_3 \}_2$ (4) and $[o-C_6H_4(PPhH)(\mu_2-S)](\mu_2-Br) Re_2(CO)_7(5)$, respectively. Both complexes 4 and 5 were characterized by spectral and crystal structural analyses. The hydrogen atom of the secondary phosphine moiety (P-H) of **3** was replaced by a chlorine atom in dimanganese complex 4 to form P-Cl but was retained in rhenium complex 5. Methanolysis of 4 gave methoxylsubstituted product $\{fac-[o-C_6H_4(PPh(OCH_3))(\mu_2-S)]Mn (CO)_{3}_{2}$.

Introduction

Bridging phosphido- and sulfidometal complexes have received much attention due to their uncommon coordination modes and properties,¹⁻⁴ and few metal complexes containing both functionalities in the same molecule, such as 1 and 2, are known.⁵⁻⁸ Synthesis of



a mixed thiolato- and phosphidodiiron species 1 was reported by Evertz and Huttner and its reactivity was investigated by Seyferth and co-workers. These works were mainly devoted to iron carbonyl complexes. Here, we present work on selective formation of sulfidometal complexes from the reaction of mixed donor ligand 3 with $BrMn(CO)_5$ and $BrRe(CO)_5$.



Figure 1. ORTEP plot of manganese(I) complex 4.

Results and Discussion

Reaction of 3^9 with two equimolar quantities of Mn(CO)₅Br in refluxing chloroform overnight provided crude product 4 (Scheme 1). Upon recrystallization from a mixture of tetrahydrofuran and ether, binuclear manganese complex 4 was obtained as a yellow-orange crystalline solid in 53% yield. Spectral data of complex 4 include three absorptions $(2024, 1963, 1931 \text{ cm}^{-1})$ for carbonyl ligands in the infrared spectrum, a singlet at 173 ppm in the ³¹P NMR spectrum, and a multiplet absorption in the range 7.94-7.71 ppm for aromatic protons in the ¹H NMR spectrum, but these spectral data are insufficient to determine the exact structure of 4. X-ray crystal structural analysis confirms the formulations of 4 (Figure 1) that clearly indicates the complex to be a sulfido-bridged binuclear species.

Atomic coordinates and selected bond lengths and angles of complex 4 are given in Tables 1 and 2, respectively. Complex 4 possesses a crystallographic center of symmetry. Both manganese atoms are in identical octahedral environments constituted by three facially coordinated carbonyl ligands, one phosphorus, and two sulfur donors. These sulfur donors act as bridges between two metal ions to form a four-membered core; the Mn-Mn distance at 3.598(2) Å indicates

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Table 1.	Atomic	Coordinates and	Thermal Para	meters of 4	
	x	у	z	$B_{\rm iso},{\rm \AA}^2$	
Mn	0.12326(5)	0.52913(3)	0.98610(11)	2.73(3)	
S -	-0.01342(9)	0.47796(6)	0.77501(18)	2.77(6)	
Р	0.18839(10)) 0.43758(6)	1.06479(20)	2.97(6)	
C1	0.17512(11) 0.39987 (7)	1.33580(21)	4.85(8)	
01	0.0563(3)	0.65309(17)	0.8666(6)	4.78(21)	
O2	0.2932(3)	0.58421(19)	1.2743(6)	5.58(22)	
03	0.2358(3)	0.53258(19)	0.6580(5)	5.10(22)	
C1	0.0754(4)	0.6045(3)	0.9085(7)	3.2(3)	
C2	0.2257(4)	0.56270(24)	1.1651(8)	3.5(3)	
C3	0.1917(4)	0.53059(23)	0.7871(8)	3.31(24)	
C4	0.3242(4)	0.42724(22)	1.0757(8)	3.4(3)	
C5	0.3937(4)	0.4381(3)	1.2527(9)	5.0(3)	
C6	0.4969(5)	0.4337(3)	1.2526(12)	6.5(4)	
C7	0.5276(5)	0.4197(3)	1.0784(14)	6.9(5)	
C8	0.4595(5)	0.4098(3)	0.9029(11)	6.2(4)	
C9	0.3577(4)	0.4138(3)	0.9009(9)	4.5(3)	
C10	0.1238(4)	0.38465(22)	0.8836(7)	2.99(24)	
C11	0.1552(4)	0.32531(24)	0.8724(8)	3.8(3)	
C12	0.0966(5)	0.28583(24)	0.7390(9)	4.3(3)	
C13	0.0076(4)	0.3053(3)	0.6171(8)	4.2(3)	
C14 -	-0.0244(4)	0.36343(24)	0.6272(7)	3.45(25)	
C15	0.0322(3)	0.40356(21)	0.7605(7)	2.73(23)	
A1	0.5743(24)	0.7557(17)	0.248(20)	47.0(54)	
A2	0.572(3)	0.7688(22)	-0.006(18)	55.5(52)	
A3	0.706(3)	0.250(3)	0.16(3)	45.8(101)	
A4	0.697(3)	0.237(4)	-0.10(3)	63.7(85)	
Table 2. Selected Bond Lengths (Å) and Angles (deg)					
Mn-S	2	.368(2) S-N	Mn-S _a	82.24(6)	
Mn-S _a	2	.408(2) S-N	vín-P	85.30(6)	
Mn-P	2	.242(2) S-N	Mn-C1	95.1(2)	
Mn-C	1 1	.839(6) S-N	Mn-C2	174.4(2)	
Mn-C	2 1	.795(6) S-N	Mn-C3	90.7(2)	
Mn-C	3 1	.780(6) $S_a -$	Mn-P	92.57(5)	
S-C15	5 1	.780(5) P-N	Mn-Cl	176.0(2)	
P-C10) 1	.789(5) P-M	Mn-C2	90.8(2)	
P-Cl	2	.055(2) P-N	Mn-C3	87.6(2)	
C1-01	i 1	.135(7) Mn-	-S-Mn _a	97.76(6)	
C2-02	2 1	.147(7) Mn-	-P-C1	118.81(8)	
C3-O3	3 1	.152(7)			

no metal-metal bond. The metal-carbon bond *trans* to the phosphorus donor (Mn-C1) is longer than those *trans* to the sulfur ones due to the *trans* influence. A chlorine atom, instead of the expected hydrogen atom, is identified as a substituent on the phosphorus atom consistent with the absence of P-H coupling in the NMR spectrum.

Reaction of **3** with Re(CO)₅Br under similar conditions provided a sulfido complex **5**. The ³¹P NMR spectrum of **5** in CDCl₃ shows a singlet at δ 26.7 ppm, and the ¹H NMR spectrum shows, besides the signal due to aromatic protons, a doublet at 7.44 ($J_{P-H} = 373$ Hz) ppm for the shift of P-H. Both spectral data clearly indicate the coordination of a secondary phosphine to the metal ion. Unlike the manganese complex **3**, the P-H moiety in complex **5** was not replaced by a chlorine atom to form P-Cl. The structure of this complex is confirmed by

	x	у	z	B iso, Å ²
Re1	0.62462(9)	0.83726(5)	0.11278(7)	2.73(4)
Re2	0.40797(9)	0.66407(6)	0.07815(7)	3.43(5)
Br	0.44577(25)	0.77640(15)	-0.04839(18)	4.21(13)
S	0.6100(6)	0.7150(3)	0.2027(4)	3.1(3)
Р	0.7795(6)	0.7694(3)	0.0313(4)	2.8(3)
Cl	0.4914(22)	0.8799(12)	0.1787(15)	3.9(12)
01	0.4121(15)	0.9082(9)	0.2202(12)	5.2(10)
C2	0.6383(23)	0.9255(13)	0.0285(17)	4.2(13)
O2	0.6459(16)	0.9778(9)	-0.0233(13)	6.0(11)
C3	0.7554(19)	0.8774(1)	0.2280(16)	2.9(11)
O3	0.8316(15)	0.8999(9)	0.3009(11)	5.5(9)
C4	0.9224(20)	0.8119(11)	0.0018(15)	2.9(10)
C5	0.9770(20)	0.8746(13)	0.0549(16)	4.1(14)
C6	1.0840(24)	0.9077(13)	0.0279(20)	5.3(16)
C7	1.1416(22)	0.8794(12)	-0.0538(18)	4.4(13)
C8	1.0857(23)	0.8155(14)	-0.1087(17)	5.0(14)
C9	0.9780(22)	0.7809(12)	-0.0824(17)	3.9(12)
C10	0.8292(21)	0.6850(11)	0.1097(14)	3.4(12)
C11	0.9307(22)	0.6423(12)	0.0947(170	4.3(12)
C12	0.948(3)	0.5717(13)	0.1492(20)	5.8(15)
C13	0.865(3)	0.5470(14)	0.2149(18)	5.5(16)
C14	0.7679(24)	0.5926(13)	0.2327(16)	4.5(14)
C15	0.7438(19)	0.6611(13)	0.1773(14)	3.3(11)
C16	0.518(3)	0.5991(12)	0.0042(19)	5.0(16)
016	0.5845(16)	0.5633(9)	-0.0388(12)	5.5(9)
C17	0.3853(20)	0.5898(13)	0.1767(18)	4.2(13)
017	0.3746(18)	0.5454(9)	0.2430(14)	7.0(11)
C18	0.2546(23)	0.6327(12)	-0.0189(21)	5.2(15)
O18	0.1624(18)	0.6123(10)	-0.0855(15)	7.8(12)
C19	0.2976(22)	0.7290(12)	0.1464(16)	3.8(12)
O19	0.2350(15)	0.7652(9)	0.1903(11)	4.8(9)
Table 4. Selected Bond Distances (Å) and Bond Angles (deg) of 5				

Re1-Br	2.661(3)	Re2-Br	2.633(3)
Re1-S	2.479(6)	Re2-S	2.510(6)
Re1-P	2.414(6)	Re2-C16	2.00(2)
Re1-C1	1.92(2)	Re2-C17	1.85(2)
Re1-C2	1.92(2)	Re2-C18	1.88(3)
Re1-C3	1.90(2)	Re2-C19	1.96(2)
Br-Dal-S	82 6(2)	Br-Bat-S	P2 6(1)
BI Kel-3	82.0(2)	BI-Rez-S	02.0(1)
Br-Re1-P	84.8(2)	Br-Re2-C16	90.0(6)
Br-Re1-C1	91.2(6)	Br-Re2-C17	175.5(7)
Br-Re1-C2	93.1(7)	Br-Re2-C18	93.8(7)
Br-Re1-C3	178.0(6)	Br-Re2-C19	88.7(5)
S-Re1-P	81.5(2)	S-Re2-C16	89.9(7)
S-Re1-C1	92.4(6)	S-Re2-C17	93.9(7)
S-Re1-C2	173.4(6)	S-Re2-C18	176.0(7)
S-Re1-C3	95.9(6)	S-Re2-C19	91.0(7)
P-Re1-C1	173.1(7)	Re1-Br-Re2	92.32(8)
P-Re1-C2	93.2(6)	Re1-Br-Re2	99.9(2)
P-Re1-C3	93.6(6)		

X-ray structural analysis. Atomic coordinates and selected bond distances and angles are listed in Tables 3 and 4, respectively. As the ORTEP plot of 5 (Figure 2) shows, both rhenium fragments are bridged unsymmetrically by bromide and thiolato ligands. The large distance of Re-Re [3.819(2) Å] indicates no bonding



Figure 2. ORTEP plot of rhenium complex 5.

interaction between them. Inspection of the core of the four-membered ring [torsional angles: S-Re1-Br-Re2 11.7(1)°; Re1-Br-Re2-S -11.5(1)°; Br-Re2-S-Re1 12.6(1)°; Re2-S-Re1-Br -12.4(1)°] reveals that one atom in the ring is bent from the plane of the other three by about 12°. The coordination spheres of both Re1 and Re2 are roughly octahedral with three carbonyl ligands occupying a *facial* arrangement around Re1 and substituted donors (thiolato and bromide) in a *cis* relationship around the other rhenium atom (Re2). The bond distances of rhenium to carbonyl ligands (Re-C) decrease according to the order of *trans* ligands of phosphine, thiolate, and bromide (Table 4), which is a consequence of the *trans* influence, as previously seen in the manganese complex 4.



From these results, it appears that the reaction of **3** with $Mn(CO)_5Br$ or $Re(CO)_5Br$ tends to form a sulfidobridged complex instead of a phosphido complex, but the formation of dinuclear cores differs for the two metal complexes because the bromide ligand is retained by the rhenium complex, whereas the manganese complex loses its bromide ligand, allowing two sulfur donors to form the dinuclear species. As expected, the phosphorus-chloride bond readily underwent methanolysis to give methoxyl-substituted product **6**. The P-Cl bond in **4** is similarly reactive to those in (μ -chlorophosphido) species.^{6,7}

Experimental Section

¹H and ³¹P NMR spectra were determined on a Bruker AC-E 200 or a Bruker AM-300WB spectrometer. Chemical shifts

Table 5. Crystal Data for Complexes 4 and 5

compd	4 -4/5(ether)	5
formula	C15H9ClMnPSO3	C19H10BrPSO7Re2
	4/5[(CH3CH2)O]	
fw	450.07	865.67
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
temp, K	298	298
a, Å	13.431(8)	10.478(4)
b, Å	22.319(5)	17.946(14)
<i>c</i> , Å	6.751(1)	12.361(4)
β , deg	102.08(3)	102.31(3)
$V, Å^3$	1979(1)	2271(2)
<i>F</i> (000)	918.4	1584
Ζ	4	4
$D_{\rm cald},{\rm gcm^{-3}}$	1.510	2.532
2θ range, deg	19.18-24.28	18.44-22.56
μ , mm ⁻¹	0.99	5.58
scan type	$\omega - 2\theta$	$\omega - 2\theta$
radiation	Μο Κα	Μο Κα
cryst dimens, mm ³	$0.30\times0.30\times0.30$	$0.35 \times 0.35 \times 0.40$
scan width, deg	$0.80 \pm 0.35 \tan \theta$	$0.75 \pm 0.35 \tan \theta$
transm range	0.87, 1.00	0.23, 1.00
2θ max, deg	45.0	45.0
reflns, measd	2588	2963
no. of unique refln	2587	2963
no. of refln obsd ^a	2072	2051
computation	NRCSDP-VAX ^b	NRCSDP-VAX
soln method	heavy atom	heavy atom
no of params	236	280
R ^c	0.037	0.054
R_w^c	0.039	0.057
S^c	2.81	4.33

^a I > $2\sigma(I)$. ^b Reference 11. ^c $R = \sum |F_o - F_c|/\sum(F_o)$; $R_w = [\sum w(F_o - F_c)^2/\sum(wF_o)^2]^{1/2}$; $S = [\sum w(F_o - F_c)^2/(\text{no. of reflns } - \text{ no. of params})]$.

are given in parts per million relative to 85% H₃PO₄ for ³¹P NMR spectra in CDCl₃, unless otherwise noted. Infrared spectra were recorded on a Bio-Rad FTS-40 instrument. Elemental analyses were made on a Perkin-Elmer 240C instrument. All reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen atmosphere. Ligand **3** was prepared according to the previously reported method.⁹ Chloroform was filtered through alumina and distilled over phosphorus pentoxide under nitrogen.

Synthesis of {fac-[$o-C_{6}H_{4}(PPhCl)(\mu_{2}-S)$]Mn(CO)₃}₂ (4). A mixture of Mn(CO)₅Br (348.8 mg, 1.27 mmol) and ligand **3** (138.2 mg, 0.63 mmol) in chloroform (14 mL) was heated to reflux for 3 h. Concentration of the reaction mixture yielded the crude product, which was recrystallized from ether and tetrahydrofuran to give **4** as an orange-yellow crystalline solid (202.5 mg, 52%): mp 218-222 °C dec; IR (CH₂Cl₂) $\nu_{CO} = 2024$, 1963, 1931 cm⁻¹; ¹H NMR δ 7.94-7.71 (m); ³¹P NMR (CDCl₃) δ 173. Anal. Calcd for C₃₀H₁₈Cl₂O₆P₂S₂Mn₂: C, 46.12; H, 2.32. Found: C, 46.15; H, 2.31.

Synthesis of $[o-C_6H_4(PPhH)(\mu_2-S)](\mu_2-Br)Re_2(CO)_7$ (5). A mixture of $Re(CO)_5Br$ (370 mg, 0.91 mmol) and 3 (100 mg, 0.458 mmol) in chloroform (7 mL) was heated to reflux for 16 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel eluted with chloroform and hexane. A yellow band fraction was collected and concentrated to give the desired product as a light yellow solid (187 mg, 47%): mp 156-158 °C dec; IR (KBr) $\nu_{CO} = 2109, 2038, 2005, 1958, 1944, 1898 cm^{-1}; {}^{1}H NMR \delta 7.8-7.2 (m, 9 H), 7.44 (d, <math>J_{P-H} = 373$ Hz, 1 H); ${}^{31}P$ NMR δ 26.9. Anal. Calcd for $C_{19}H_{10}BrO_7PSRe_2$: C, 26.36; H, 1.16. Found: C, 26.57; H, 1.29.

Synthesis of {fac-[$o-C_6H_4(PPh(OCH_3))(\mu_2-S)$]Mn(CO)₃}₂ (6). A solution of 4 (57.2 mg, 0.073 mmol) in methanol was heated to reflux for 1 h. Upon concentration of the reaction mixture, the residue was filtered through silica gel to give the desired product 6 as a yellow solid (48.0 mg, 85%): IR (KBr) 2015, 1951, 1921 cm⁻¹; ¹H NMR δ 7.8–7.2 (m, 18 H), 3.93 (br, singlet, 6 H); ³¹P NMR δ 179.6. Anal. Calcd for C₃₂H₂₄O₈P₂S₂-Mn₂: C, 49.76; H, 3.13. Found: C, 49.50; H, 3.50.

Crystallography. Suitable single crystals of complexes 4 and 5 for X-ray analysis were obtained by recrystallization from ether and tetrahydrofuran at about -20 °C. Data were measured and collected on an Enraf-Nonius CAD-4 diffractometer. The heavy-atom method was used and least-squares refinement was undertaken with all non-hydrogen atoms anisotropic. Atomic scattering factors were taken from ref 10. The computing program was the NRCC SDP VAX package.¹¹ Refinement details follow: F_{o} and F_{c} are the observed and calculated structure factor amplitudes, respectively; the function minimized was $\sum w(F_{o} - F_{c})^{2}$, with $w^{-1} = \sigma^{2}(F_{o})$, $\sigma(F_{o})$ from counting statistics; $R_{F} = \sum |F_{o} - F_{c}| / \sum (F_{o})$; $R_{w} = [\sum w(F_{o} - F_{c})^{2} / \sum (F_{o}) / \sum (F_{o})]$ $\sum w(F_{o})^{2}]^{1/2}$; S = $[\sum (w(F_{o} - F_{c})^{2})/(\text{no. of reflections} - \text{no. of }$ params)]^{1/2}. Molecules of complex 4 are aligned along the axis

perpendicular to the plane defined by Mn-S-Mn_a-S_a, and solvent molecules are disorderly distributed between the stack of the complex molecules. The computation of solvent molecules was treated as atoms A1-A4 using the atomic scattering factor of an oxygen atom.

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Supplementary Material Available: Lists of thermal parameters and complete bond distances and bond angles of both complexes 4 and 5 (4 pages). Ordering information is given on any current masthead page.

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