competition from the resonant scattering of the molecules with the optical deenhancement from the copper surface.

**Registry No.** *o*-Aminophenol, 95-55-6; 2-hydroxy-1-naphthaldehyde, 708-06-5.

Contribution from the Department of Chemistry, University of California, Davis, California 95616

Novel Oxidation Resulting from the Reaction of Tin(II) Chloride with Ir₂(CO)₂(μ-S)(μ-Ph₂PCH₂PPh₂)₂: Structure of Ir₂(CO)₂(SnCl₃)₂(μ-S)(μ-Ph₂PCH₂PPh₂)₂
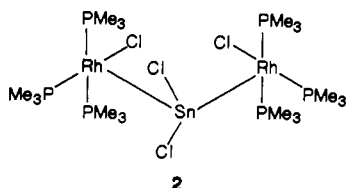
Alan L. Balch,* Krista M. Waggoner, and Marilyn M. Olmstead

Tin(II) chloride is known to interact with complexes of the platinum metals and to enhance their catalytic activity.[1] Frequently this occurs through the insertion into M–Cl bonds to give M–SnCl₃ groups. Recently, however, several new modes of bonding of tin(II) chloride with platinum metal complexes have been found. Reaction 1, which involves a rhodium metallo-


(1)
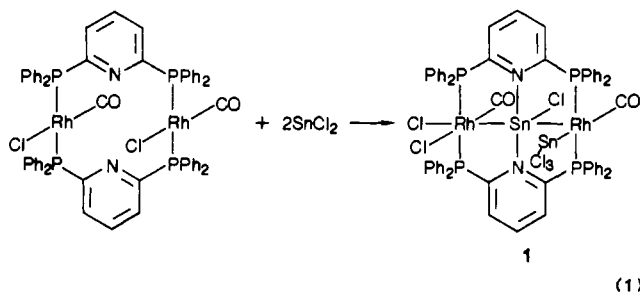
macrocycle, yields **1** in which two modes of interaction are seen. One tin(II) chloride forms a SnCl₃⁻ group in an entirely normal fashion, while another tin(II) chloride has entered the center of the macrocycle and transferred a chloride ligand (via oxidative addition) to the rhodium on the left side.[2] Tin(II) chloride reacts with 2 equiv of Rh(PMe₃)₃Cl to yield the novel unbridged Rh–Sn–Rh chain compound **2**.[3] The metallomacrocycle, Ir₂-

2

(CO)₂Cl₂(μ-Ph₂PCH₂As(Ph)CH₂PPh₂)₂ (**3**), reacts with tin(II) chloride to give the deep blue/green adduct **4** via eq 2.[4,5] Com-


SnCl₃⁻ (2)
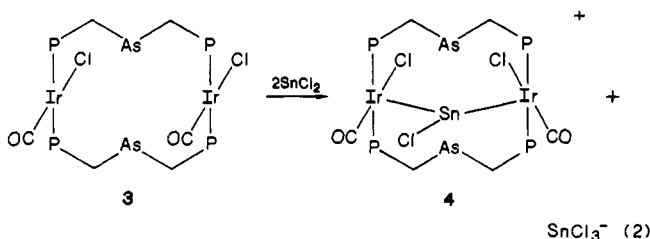
(1) Young, J. F.; Gillard, R. D.; Wilkinson, G. *J. Chem. Soc.* **1964,** 5176. Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983,** *22,* 427, 434. Young, J. F. *Adv. Inorg. Chem. RadioChem.* **1968,** *11,* 91. Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978,** *24,* 251.
(2) Balch, A. L.; Hope, H.; Wood, F. E. *J. Am. Chem. Soc.* **1985,** *107,* 6936.
(3) Chan, D. M. T.; Marder, T. B. *Angew. Chem., Int. Ed. Engl.* **1988,** *27,* 442.
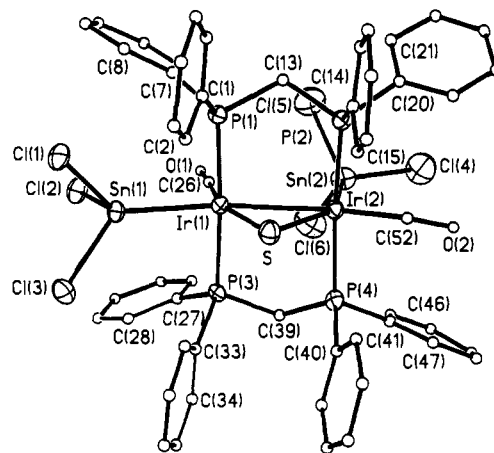
Figure 1. Perspective view of Ir₂(CO)₂(SnCl₃)₂(μ-S)(μ-dpm)₂ showing 50% thermal contours for the heavy atoms and uniform, arbitrarily sized circles for carbon and oxygen.

pound **4** has the tin complexed by the two iridium ions; no Sn–As bonds are present. In order to explore the effects of orientation and separation of the two Ir coordination planes on the ability to bind tin(II) in this fashion, we undertook an examination of the reaction of tin(II) chloride with the A-frame complex Ir₂-(CO)₂Cl₂(μ-S)(μ-dpm)₂[6] (**5**) (dpm is bis(diphenylphosphino)-

5
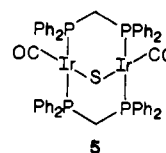
methane). This complex has a much shorter Ir···Ir separation (~3.15 Å estimated from the rhodium analogue[7]) than that in the metallomacrocycle **3** (where a similar estimate is ~5.4 Å[8]) and has the iridium coordination planes inclined at an angle of 75° rather than nearly parallel as in **3**.

Results

Addition of an excess of tin(II) chloride in methanol to a purple solution of Ir₂(CO)₂(μ-S)(μ-dpm)₂ in dichloromethane/methanol immediately produces a yellow solution. When allowed to stand for 24 h, this produces green crystals of Ir₂(CO)₂(SnCl₃)₂(μ-S)(μ-dpm)₂ (**6**) in 81% yield. These have no significant solubility in any common organic solvent, although they do impart a faint greenish color to dimethyl sulfoxide, benzene, and toluene. Because their intense color was somewhat similar to that of **4**, we suspected that they might have a similar structure. The infrared spectrum (Nujol), however, shows carbon monoxide stretching vibrations at 2031 m, 1998 vs and 1978 s cm⁻¹. The increase in these values compared to those of **1** (1918 s, 1902 vs cm⁻¹)[6] suggests that the original complex has undergone oxidation in some fashion.

Crystals of **6**·1.5CH₂Cl₂ suitable for X-ray diffraction were available directly from the original preparation. Atomic positional parameters are given in Table I. Table II contains selected bond distances and angles. Figure 1 shows a perspective view of the molecule.

The complex retains the A-frame structure present in **1** with two trans-dpm bridges and a bridging sulfide. Two SnCl₃⁻ ligands have been added to the molecule (which has undergone a net

(4) Balch, A. L.; Nagle, J. K.; Olmstead, M. M.; Reedy, P. E., Jr. *J. Am. Chem. Soc.* **1987,** *109,* 4123.
(5) Balch, A. L.; Olmstead, M. M.; Reedy, P. E., Jr.; Reimer, S. J., to be submitted for publication.
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Table I. Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) for Ir₂(μ-S)(μ-dpm)₂(CO)₂(SnCl₃)₂

	x	y	z	U
Ir(1)	2232 (1)	5523 (1)	179 (1)	24 (1)[a]
Ir(2)	2288 (1)	4332 (1)	-1087 (1)	22 (1)[a]
Sn(1)	3429 (1)	6381 (1)	1392 (1)	23 (1)[a]
Sn(2)	1137 (1)	4887 (1)	-1498 (1)	35 (1)[a]
Cl(1)	4271 (2)	7314 (3)	1442 (3)	34 (2)[a]
Cl(2)	2767 (2)	7343 (3)	1758 (3)	36 (2)[a]
Cl(3)	4001 (2)	5844 (3)	2647 (2)	38 (2)[a]
Cl(4)	322 (3)	4302 (4)	-2561 (4)	67 (2)[a]
Cl(5)	890 (3)	6340 (3)	-1847 (3)	56 (2)[a]
Cl(6)	513 (4)	4848 (5)	-675 (4)	86 (3)[a]
S	3340 (2)	4508 (3)	-174 (3)	31 (2)[a]
P(1)	3015 (2)	6525 (3)	-622 (2)	23 (2)[a]
P(2)	2534 (2)	5264 (3)	-1954 (2)	23 (2)[a]
P(3)	2518 (2)	4554 (3)	1043 (2)	18 (1)[a]
P(4)	2151 (2)	3267 (3)	-257 (2)	22 (2)[a]
O(1)	1551 (6)	6543 (8)	157 (7)	39 (3)
O(2)	2083 (6)	2918 (8)	-2244 (7)	44 (3)
C(1)	3839 (8)	6594 (9)	-608 (8)	21 (4)
C(2)	4338 (8)	6122 (11)	-106 (10)	33 (4)
C(3)	4935 (9)	6156 (11)	-122 (10)	33 (4)
C(4)	5056 (10)	6677 (12)	-684 (10)	42 (5)
C(5)	4572 (9)	7174 (12)	-1186 (10)	39 (5)
C(6)	3958 (8)	7120 (11)	-1138 (9)	30 (4)
C(7)	2810 (8)	7607 (11)	-465 (10)	32 (4)
C(8)	3280 (10)	8226 (11)	-145 (10)	37 (5)
C(9)	3116 (10)	9048 (12)	80 (10)	41 (5)
C(10)	2495 (10)	9212 (12)	-49 (11)	43 (5)
C(11)	2004 (10)	8643 (12)	-386 (11)	45 (5)
C(12)	2181 (9)	7879 (12)	-603 (10)	40 (5)
C(13)	2551 (8)	6364 (9)	-1650 (8)	20 (4)
C(14)	3285 (7)	5091 (9)	-2128 (8)	20 (4)
C(15)	3701 (9)	4433 (11)	-1779 (10)	35 (4)
C(16)	4273 (9)	4338 (11)	-1931 (10)	32 (4)
C(17)	4426 (9)	4895 (13)	-2437 (10)	34 (4)
C(18)	4000 (8)	5507 (10)	-2801 (9)	28 (4)
C(19)	3423 (9)	5602 (11)	-2666 (10)	32 (4)
C(20)	1958 (8)	5246 (10)	-2949 (9)	27 (4)
C(21)	1567 (9)	5922 (12)	-3262 (11)	41 (5)
C(22)	1094 (10)	5836 (13)	-4026 (11)	50 (5)
C(23)	1055 (9)	5123 (12)	-4423 (11)	47 (5)
C(24)	1463 (9)	4466 (12)	-4143 (10)	38 (5)
C(25)	1915 (9)	4519 (12)	-3397 (10)	39 (5)
C(26)	1995 (9)	6159 (11)	139 (10)	35 (4)
C(27)	2100 (8)	5045 (10)	1647 (9)	26 (4)
C(28)	2455 (8)	5261 (10)	2407 (9)	28 (4)
C(29)	2161 (9)	5714 (11)	2858 (11)	38 (5)
C(30)	1529 (10)	5944 (12)	2555 (11)	45 (5)
C(31)	1194 (11)	5698 (12)	1815 (11)	49 (5)
C(32)	1474 (9)	5257 (11)	1368 (10)	34 (4)
C(33)	3159 (8)	3961 (11)	1737 (9)	31 (4)
C(34)	2999 (9)	3435 (11)	2273 (10)	36 (4)
C(35)	3464 (8)	2978 (11)	2801 (10)	30 (4)
C(36)	4107 (9)	2990 (11)	2804 (11)	40 (5)
C(37)	4224 (9)	3482 (11)	2280 (10)	37 (5)
C(38)	3790 (7)	3970 (9)	1746 (8)	17 (3)
C(39)	1947 (8)	3720 (10)	550 (9)	26 (4)
C(40)	2825 (8)	2533 (10)	140 (9)	23 (4)
C(41)	3274 (8)	2424 (10)	-197 (9)	27 (4)
C(42)	3746 (9)	1813 (11)	86 (10)	39 (5)
C(43)	3777 (10)	1308 (12)	723 (10)	40 (5)
C(44)	3310 (9)	1454 (11)	1067 (10)	34 (4)
C(45)	2845 (8)	2048 (10)	800 (9)	28 (4)
C(46)	1506 (8)	2509 (10)	-697 (9)	25 (4)
C(47)	1654 (10)	1776 (12)	-1008 (10)	43 (5)
C(48)	1154 (10)	1159 (13)	-1369 (11)	48 (5)
C(49)	571 (11)	1311 (14)	-1386 (12)	58 (6)
C(50)	403 (12)	2078 (14)	-1122 (13)	64 (6)
C(51)	896 (10)	2664 (13)	-756 (11)	49 (5)
C(52)	2187 (9)	3486 (11)	-1816 (10)	36 (4)
Cl(7)	5057 (4)	4413 (4)	4419 (4)	77 (2)
Cl(8)	872 (5)	3369 (6)	1502 (6)	125 (3)
Cl(9)	-143 (5)	2167 (7)	707 (6)	138 (4)
C(53)	4617 (20)	5303 (26)	4628 (23)	49 (11)
C(54)	418 (17)	2560 (23)	1568 (19)	125 (12)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

two-electron oxidation) in an unsymmetrical fashion. Overall, the structure of **6** resembles two other binuclear dpm-bridged complexes, Ir₂(CO)₂Cl₂(μ-EtO₂CC≡CCO₂Et)(μ-dpma)₂ (Ir–Ir

Table II. Selected Bond Distances (Å) and Angles (deg) for Ir₂(CO)₂(SnCl₃)₂(μ-S)(μ-dpm)₂·1.5CH₂Cl₂

Bond Distances			
Ir(1)–S	2.326 (5)	Ir(2)–S	2.392 (4)
Ir(1)–Sn(1)	2.611 (1)	Ir(2)–Sn(2)	2.575 (1)
Ir(1)–C(26)	1.91 (2)	Ir(2)–C(52)	1.84 (2)
Ir(1)–P(1)	2.379 (5)	Ir(2)–P(2)	2.358 (5)
Ir(1)–P(3)	2.359 (4)	Ir(1)–P(4)	2.348 (5)
Ir(1)–Ir(2)	2.878 (1)		
Sn(1)–Cl(1)	2.361 (5)	Sn(2)–Cl(4)	2.353 (5)
Sn(1)–Cl(2)	2.366 (5)	Sn(2)–Cl(5)	2.381 (5)
Sn(1)–Cl(3)	2.372 (4)	Sn(2)–Cl(6)	2.378 (9)
C(26)–O(1)	1.17 (2)	C(52)–O(2)	1.16 (2)

Bond Angles			
P(1)–Ir(1)–P(3)	176.0 (1)	P(2)–Ir(2)–P(4)	171.6 (2)
Ir(2)–Ir(1)–Sn(1)	164.2 (1)	Ir(1)–Ir(2)–C(52)	167.3 (6)
Ir(2)–Ir(1)–C(26)	104.7 (5)	Ir(1)–Ir(2)–Sn(2)	92.9 (1)
Ir(2)–Ir(1)–S	53.5 (1)	Ir(1)–Ir(2)–S	51.4 (1)
Sn(1)–Ir(1)–C(26)	91.1 (5)	Sn(2)–Ir(2)–C(52)	99.8 (6)
Sn(1)–Ir(1)–S	110.7 (1)	S–Ir(2)–C(52)	116.0 (6)
S–Ir(1)–C(26)	158.2 (5)	Sn(2)–Ir(2)–S	144.3 (1)
P(1)–Ir(1)–Ir(2)	91.3 (1)	P(2)–Ir(2)–Ir(1)	92.5 (1)
P(1)–Ir(1)–Sn(1)	88.7 (1)	P(2)–Ir(2)–Sn(2)	91.9 (1)
P(1)–Ir(1)–S	88.7 (2)	P(2)–Ir(2)–S	90.0 (2)
P(1)–Ir(1)–C(26)	92.2 (6)	P(2)–Ir(2)–C(52)	87.6 (6)
P(3)–Ir(1)–Ir(2)	91.6 (1)	P(4)–Ir(2)–Ir(1)	91.5 (1)
P(3)–Ir(1)–Sn(1)	87.8 (1)	P(4)–Ir(2)–Sn(2)	95.3 (1)
P(3)–Ir(1)–S	90.9 (2)	P(4)–Ir(2)–S	86.8 (1)
P(3)–Ir(1)–C(26)	89.6 (6)	P(4)–Ir(2)–C(52)	86.9 (6)
Ir(1)–C(26)–O(1)	176.4 (15)	Ir(2)–C(52)–O(2)	173.3 (18)
Ir(1)–Sn(1)–Cl(1)	126.1 (1)	Ir(2)–Sn(2)–Cl(4)	121.6 (2)
Ir(1)–Sn(1)–Cl(2)	108.7 (1)	Ir(2)–Sn(2)–Cl(5)	121.3 (2)
Ir(1)–Sn(1)–Cl(3)	127.5 (1)	Ir(2)–Sn(2)–Cl(6)	123.4 (2)
Cl(1)–Sn(1)–Cl(2)	99.3 (2)	Cl(4)–Sn(2)–Cl(5)	96.3 (2)
Cl(1)–Sn(1)–Cl(3)	91.4 (2)	Cl(4)–Sn(2)–Cl(6)	93.4 (2)
Cl(2)–Sn(1)–Cl(3)	97.7 (2)	Cl(5)–Sn(2)–Cl(6)	93.6 (2)
Ir(1)–S–Ir(2)	75.2 (1)		

distance, 2.7793 (3) Å)[9] and Ir₂(CO)₂Cl₂(μ-CO)(μ-dpm)₂ (Ir–Ir distance, 2.779 (1) Å),[10] which have, in addition to the bridging groups, four other ligands binding in the plane perpendicular to the Ir₂(dpm)₂ core. The Ir–Ir distance (2.878 (1) Å) in **6** is consistent with the presence of a single bond between these atoms. This distance is considerably shorter than the nonbonded Rh···Rh distance (3.154 (2) Å) in Rh₂(CO)₂(μ-S)(μ-dpm)₂[7] (the rhodium analogue of **1**), but slightly longer than the Ir–Ir distance (2.843 (2) Å) in Ir₂(CO)₂(μ-CO)(μ-S)(μ-dpm)₂.

The Ir–Sn distances in **6** are slightly different with the Ir-(1)–Sn(1) distance being 0.036 Å longer than the Ir(2)–Sn(2) distance. This slight elongation probably is caused by the high trans effect of the Ir–Ir bond. Both Ir–Sn distances are similar to those in (COD)₂IrSnCl₃ (2.642 Å).[11] The Ir–S distances, 2.326 (5) and 2.392 (4) Å, show some asymmetry, but are comparable to the Ir–S bond distance in Ir₂(μ-CO)(CO)₂(μ-S)(μ-dpm)₂ (2.463 (3) Å)[7] and the Rh–S bond distance (2.367 (3) Å)[6] in Rh₂-(CO)₂(μ-S)(dpm)₂.

We view **6** as a complex containing two Ir(II) centers and two SnCl₃⁻ ligands. Thus **6** is oxidized relative to **1**, but we have not been able to identify the oxidizing agent. Generally, toward the platinum metals, tin(II) chloride acts as a reducing agent.[1] In the present case, disproportionation to Sn(IV) and Sn(0) with Sn(IV) acting as the oxidant toward **1** is a possibility, but we have not seen evidence for the formation of tin metal in the reaction. It is also known that chlorocarbons undergo oxidative addition with low-valent metal complexes and it is entirely possible that the SnCl₃⁻ groups in **2** come from subsequent insertion of tin(II) chloride into Ir–Cl bonds. However, **5** is stable in dichloromethane in the absence of tin(II) chloride. Dudis and Fackler[12] have noted a related phenomenon. The gold(II) ylide complex [Ph₂P-

(9) Sutherland, B. R.; Cowie, M. *Organometallics* **1984**, *3*, 1869.
(10) Sutherland, R. B.; Cowie, M. *Inorg. Chem.* **1984**, *23*, 2324.
(11) Porta, P.; Powell, M. H.; Mawby, R. J.; Venanzi, L. M. *J. Chem. Soc.* **1967**, 1935.
(12) Dudis, D. S.; Fackler, J. P., Jr. *Inorg. Chem.* **1985**, *24*, 3758.

Table III. Crystallographic Data for
$Ir_2(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2\cdot1.5CH_2Cl_2$

formula	$C_{53.5}H_{47}O_2Sn_2Cl_9SP_6Ir_2$
fw	1880.77
space group	$P2_1/c$ (No. 14)
a, Å	22.357 (6)
b, Å	15.695 (8)
c, Å	18.320 (7)
β, deg	109.97 (2)
V, Å^{-3}	6048 (4)
T, K	130
Z	4
d_{calcd}, g cm^{-3}	2.07
radiation	Mo Kα (λ = 0.71069 Å)
μ(Mo Kα), cm^{-1}	60.5
range of transmissn factors	0.37–0.54
$R(F)$	0.062
$R_w(F)$	0.068 $[w = 1/(\sigma^2)(F_o)]$

$(CH_2)_2]_2Au_2Cl_2$ undergoes oxidation to the gold(III) dimer $[Ph_2P(CH_2)_2]_2Au_2Cl_4$ in deuteriochloroform/dichloromethane solution when tin(II) chloride is added. They suggest that the role of the tin(II) is to act as a Lewis acid catalyst that removes a coordinated halide to initiate oxidation. A similar function to open an Ir–S bond, thereby activating the freed iridium, may be operational here.

Experimental Section

$Ir_2(CO)_2Cl_2(\mu\text{-}S)(\mu\text{-dpm})_2$ was prepared as described previously.[6] All manipulations were carried out under a purified dinitrogen atmosphere in dioxygen-free solvents.

$Ir_2(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2$. A solution of 1.8 mg (0.081 mmol) of tin(II) chloride dihydrate in 1 mL of methanol was added to a solution of 10.0 mg (0.0081 mmol) of $Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-dpm})_2$ in 2 mL of dichloromethane/methanol (1:1 v/v). The solution rapidly turned from purple to yellow. When the mixture was allowed to stand at 23 °C for 24 h, a precipitate of bright green crystals formed. These were collected by decanting the solution and washing with methanol. Yield: 12.3 mg, 81%.

X-ray Structure Determination and Refinement. Crystals of Ir_2-$(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2\cdot1.5CH_2Cl_2$ were obtained as well-formed plates, directly from the reaction medium. A suitable crystal was mounted on a glass fiber with silicone grease and positioned in the cold stream of the X-ray diffractometer. No decay in the intensities of two standard reflections was observed during the course of data collection. Crystal data are given in Table III.

The usual corrections for Lorentz and polarization effects were applied to the data. Crystallographic programs used were those of SHELXTL, version 5, installed on a Data General Eclipse computer. Scattering factors and corrections for anomalous dispersion were from ref 13.

Solution of the structure was accomplished by direct methods. An absorption correction was applied.[14] Hydrogen atoms were included by using a riding model with C–H of 0.96 Å and $U_H = 1.2U_{iso}$ of the bonded carbon. One of the dichloromethanes lies near a center of symmetry. The complete molecule can be constructed with Cl(7)′–C(53)–Cl(7) or Cl(7)′–C(53)′–Cl(7). Thus C(53) is assigned an occupancy of one-half. The hydrogen on this carbon was not included. In the final cycles of refinement, Ir, Sn, Cl, P, and S atoms were assigned anisotropic thermal parameters. The mean shift/esd was 0.009; the maximum was 0.037 for x of P(4). In the final difference map the largest feature was 3.3 e Å^{-3} in height, 0.88 Å from Ir(1).

Registry No. $Ir_2(CO)_2(\mu\text{-}S)(\mu\text{-dpm})_2$, 73972-13-1; $Ir_2(CO)_2$-$(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2$, 117308-34-6; $Ir_2(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2\cdot$1.5$CH_2Cl_2$, 117405-98-8; Sn, 7440-31-5; Ir, 7439-88-5.

Supplementary Material Available: Tables of all bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates, and crystal data (7 pages); a table of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, p 149–156, 99–101.
(14) XABS produces an absorption tensor from an expression relating F_o and F_c: Moezzi, B. Ph.D. Thesis, University of California, Davis, 1988.
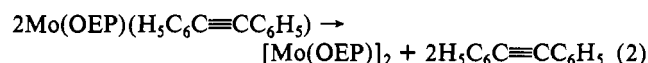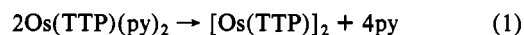
Contribution from the Departments of Chemistry,
Stanford University, Stanford, California 94305,
and Northwestern University, Evanston, Illinois 60208

**Synthesis of Rhenium(II) Porphyrin Complexes
and Crystal Structure of
Bis(trimethylphosphine)(tetra-*p*-tolylporphyrinato)rhenium-
(II)–Toluene**

James P. Collman,*[†] James M. Garner,[†] Kimoon Kim,[‡]
and James A. Ibers*[‡]

Our success in the synthesis of metalloporphyrin dimers containing metal–metal multiple bonds of ruthenium,[1] osmium,[2] molybdenum,[2] and tungsten[3] led us to explore synthetic routes to the analogous rhenium porphyrin complexes. A general route to this class of dimers involves the solid-state pyrolysis of various monomeric metal(II) porphyrin complexes having neutral axial ligands. Examples of such reactions involving osmium and molybdenum porphyrins are illustrated in eq 1 and 2.[4] The neutral

$$2Os(TTP)(py)_2 \rightarrow [Os(TTP)]_2 + 4py \qquad (1)$$

$$2Mo(OEP)(H_5C_6C\equiv CC_6H_5) \rightarrow$$
$$[Mo(OEP)]_2 + 2H_5C_6C\equiv CC_6H_5 \quad (2)$$

axial ligands dissociate from the metal at high temperatures and are removed under high vacuum. The analytically pure dimeric products are then isolated in virtually quantitative yield. This reaction is generally successful because of the thermal stability of the tetradentate porphyrin ligand and low volatility of the monomeric and dimeric metalloporphyrin complexes.

Since rhenium porphyrin precursors suitable for such a vacuum pyrolysis reaction had not been reported, we developed the coordination chemistry of rhenium porphyrins in low oxidation states. This was accomplished by reducing a pentavalent complex first reported by Buchler and co-workers.[5] Herein, we report the synthesis and structural characterization of new rhenium(II) porphyrin complexes with axial trimethyl- and triethylphosphine ligands. These complexes are precursors to the rhenium porphyrin dimers.[6]

Experimental Section

Electronic absorption spectra were obtained with a Cary 219 recording spectrophotometer (300–825 nm), and ^{1}H NMR spectra were recorded on a 300-MHz Nicolet NMC-300 spectrometer with chemical shifts reported relative to tetramethylsilane. Mass spectra were obtained by the LSI or FAB ionization techniques, and calculated isotope intensities matched well with the observed molecular or fragment ion isotope clusters. All manipulations of oxygen- or water-sensitive materials were either performed in a Vacuum/Atmospheres Co. nitrogen atmosphere glovebox ($O_2 < 2$ ppm), on a vacuum line, or in Schlenkware consisting of a thick-walled conical reaction flask (Pyrex) with an E. J. Young valve and O-ring vacuum adapter. Magnetic susceptibility measurements were performed at 22 °C according to the Evans procedure[7] and are corrected for ligand diamagnetism.

Toluene, hexanes, and benzene-d_6 were distilled from their respective purple or blue sodium benzophenone ketyl solutions and stored in a glovebox. Chromatographic silica for purification of the rhenium(II) complexes was predried at 300 °C overnight, then further dried and degassed at 300 °C under 10^{-2} Torr vacuum for 24 h, and stored in the glovebox. Phenol, chlorotrimethylsilane, H_2OEP (Aldrich), triethylphosphine (Strem), and trimethylphosphine (Strem) were used as received. H_2TTP,[8] Re_2O_7,[9] and $Re(OEP)(O)(Cl)$[5] were prepared by the literature procedures.

Re(TTP)(O)(Cl). This complex was prepared in a manner similar to that for the OEP analogue.[5] H_2TTP (1.00 g, 1.49 mmol), Re_2O_7 (0.400 g, 0.83 mmol), and phenol (7.00 g) were heated in a test tube (1.75 × 30 cm) at 210 °C for 12 h. The excess phenol was then distilled under vacuum and the residue dissolved in CH_2Cl_2 and filtered through a Celite pad. The filtrate was concentrated and then chromatographed (SiO_2, 4.5 × 12 cm) with CH_2Cl_2 as the eluent. A dark green band was eluted with

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