Table III. Crystallographic Data for $Ir_2(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2\cdot 1.5CH_2Cl_2$

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 $Ir_2(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2\cdot 1.5CH_2Cl_2$ 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).

Acknowledgment. We thank the National Science Foundation (Grant CHE 8519557) for support and Johnson Matthey Inc. for a loan of iridium.

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; $Ir_2(CO)_2(SnCl_3)_2(\mu\text{-}S)(\mu\text{-dpm})_2\cdot 1.5CH_2Cl_2$, 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.

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(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.

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

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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

$$2Os(TTP)(py)_2 \rightarrow [Os(TTP)]_2 + 4py \tag{1}$$

$$2Mo(OEP)(H_5C_6C{\equiv}CC_6H_5) \rightarrow [Mo(OEP)]_2 + 2H_5C_6C{\equiv}CC_6H_5 \tag{2}$$

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 ^1H 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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2% methanolic solution, and after evaporation of the solvent it was redissolved in the minimum amount of CH_2Cl_2 and treated with Me_3SiCl (0.5 mL). The solution turned dark red. Five volumes of hexanes were layered over the top of this solution, and the product was crystallized by cooling (−20 °C). The lustrous green crystals were collected by filtration, washed with hexanes, and dried under vacuum. Yield: 507 mg (38%). Anal. Calcd for $C_{48}H_{36}ClN_4ORe$: C, 63.59; H, 4.01; N, 6.18. Found: C, 64.45; H, 4.20; N, 5.35; ^1H NMR ($CDCl_3$, ppm): H_β, 9.39 (s, 8 H); H_o, 8.12 (m, 8 H); H_m, 7.61 (m, 8 H); tolyl CH_3, 2.72 (s, 12 H). UV-vis (CH_2Cl_2) λ_{max}, nm (log ε): 335 (4.83), 376 sh (4.68), 522 (4.62), 650 (3.88). LSIMS (tetraglyme/HCl): M^+, *m/e* 906, cluster; $M^+ - Cl$, *m/e* 871, cluster.

Re(OEP)(PMe$_3$)$_2$. A 1:1 volume solution of trimethylphosphine/toluene (9 mL total) was vacuum-transferred into a 25-mL conical Schlenk flask containing Re(OEP)(O)(Cl) (200 mg, 0.260 mmol) and a boiling stone. The mixture was freeze-pump-thawed three times (10^{-2} Torr vacuum). Protected with a blast shield and a hood sash, the mixture was heated to 110 °C for 24 h.

Caution! Although no accidents have occurred by utilizing this procedure, there exists a possibility of explosion so these safety precautions must be performed. The solution volume must be less than half the flask volume so the vapor from the refluxing solution has room to expand.

The mixture became homogeneous and the solution color changed from green to orange. After it was cooled, the phosphine solution was vacuum-transferred into another flask and the residue was heated at 80 °C under 10^{-2} Torr vacuum for 6 h. In a glovebox, the toluene-soluble portion was flash chromatographed (SiO_2, 2 × 9 cm) with toluene as eluent. The first orange band was evaporated and the solid crystallized from toluene. Yield: 169 mg (75%). Anal. Calcd for $C_{42}H_{62}N_4P_2Re$: C, 57.91; H, 7.17; N, 6.43. Found: C, 58.11; H, 7.22; N, 6.36. ^1H NMR (C_6D_6, ppm): H_{meso}, 11.6 (very broad); $-CH_2CH_3$, 5.55 (broad, s, 16 H); $-CH_2CH_3$, 3.74 (broad, s, 24 H); PMe_3, −14.9 (broad, 18 H). UV-vis (toluene) λ_{max}, nm (log ε): 325 (4.59), 395 (4.85), 466 sh (3.88), 496 (4.24), 546 sh (3.13), 670 (2.64), 717 (3.07). μ_{eff} (benzene) = 1.5 μ_B. LSIMS+ (tetraglyme): M^+, *m/e* 871, cluster; $M^+ - PMe_3$, *m/e* 794, cluster; $M^+ - 2PMe_3$, *m/e* 719, cluster.

Re(TTP)(PMe$_3$)$_2$·C$_6$H$_5$CH$_3$. This complex was prepared exactly as described above. Yield: 168 mg (69%). Anal. Calcd for $C_{54}H_{54}N_4P_2Re{\cdot}C_7H_8$: C, 66.65; H, 5.68; N, 5.10. Found: C, 66.56; H, 5.74; N, 5.51. ^1H NMR (C_6D_6, ppm): H_β, not observed; H_o, 11.08 (very broad, 8 H); H_m, 7.83 (broad, s, 8 H); tolyl CH_3, 2.67 (s, 12 H); PMe_3, −14.8 (very broad, 18 H); toluene-CH_3, 2.14 (s, 3 H). UV-vis (toluene): 328 (4.64), 4.09 (4.95), 472 (4.12), 4.82 sh (4.11), 622 (3.05), 781 (2.64). μ_{eff} (benzene) = 1.6 μ_B. LSIMS+ (tetraglyme): M^+, *m/e* 1007, cluster; $M^+ - PMe_3$, *m/e* 931, cluster; $M^+ - 2PMe_3$, *m/e* 855, cluster.

Re(OEP)(PEt$_3$)$_2$. Re(OEP)(O)(Cl) (400 mg, 0.519 mmol) and PEt_3 (20 gm) were refluxed under argon for 36 h. The green suspension became homogeneous and orange in color. The solution was cooled and the excess phosphine vacuum transferred into another flask. The product was isolated as described for the PMe_3 complexes and crystallized from hexanes as black blades (340 mg, 69%). Anal. Calcd for $C_{48}H_{74}N_4P_2Re$: C, 60.34; H, 7.82; N, 5.87. Found: C, 60.54; H, 7.81; N, 5.93. ^1H NMR (C_6D_6, ppm): H_{meso}, not observed; $-CH_2CH_3$, 5.62 (broad s, 16 H); $-CH_2CH_3$, 3.81 (broad s, 24 H); P-CH_2CH_3, −15.1 (very broad s); P–CH_2CH_3, −5.43 (broad s, 18 H). UV-vis (toluene) λ_{max}, nm (log ε): 329 (4.63), 396 (4.86), 464 (4.00), 496 (4.18), 546 sh (3.33), 668 (2.71), 730 (3.04); μ_{eff} (benzene) = 1.6 μ_B. FABMS (sulfolane): M^+, *m/e* 955, cluster; $M^+ - PEt_3$, *m/e* 837, cluster; $M^+ - 2PEt_3$, *m/e* 719, cluster.

Table I. Crystallographic Data for Re(TTP)(PMe$_3$)$_2$·C$_6$H$_5$CH$_3$

formula	$C_{54}H_{54}N_4P_2$-Re·C_7H_8	*Z*	1
		temp, °C	−50[a]
fw	1099.3	*d*(calcd), g/cm^3	1.367
space group	C_i^1–$P\bar{1}$	radiation	graphite-monochromated Mo Kα (λ(Kα_1) = 0.7093 Å)
a, Å	10.358 (3)		
b, Å	12.192 (4)	linear abs coeff, cm^{-1}	24.03
c, Å	12.905 (4)		
α, deg	63.01 (1)	transmissn factors	0.650–0.749
β, deg	67.52 (1)	$R(F^2)$	0.094
γ, deg	84.67 (1)	$R_w(F^2)$	0.107
vol, Å^3	1336	$R(F)$ ($F_o^2 > 3\sigma(F_o^2)$)	0.057

[a] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974.

Table II. Positional and Equivalent Isotropic Thermal Parameters, B_{eq}, for Re(TTP)(PMe$_3$)$_2$·C$_6$H$_5$CH$_3$

atom	*x*	*y*	*z*	B_{eq}, Å^2
Re	0	0	0	2.84 (2)
P	−0.18011 (21)	0.12744 (18)	0.05373 (18)	4.08 (9)
N(1)	0.10802 (55)	0.15215 (45)	−0.16711 (45)	3.3 (2)
N(2)	0.10773 (52)	0.03604 (45)	0.08773 (47)	3.1 (2)
C(1)	0.09273 (69)	0.19346 (58)	−0.27963 (57)	3.3 (3)
C(2)	0.18957 (75)	0.30110 (59)	−0.37140 (58)	3.8 (3)
C(3)	0.26069 (74)	0.32398 (58)	−0.31449 (63)	4.1 (3)
C(4)	0.21390 (68)	0.23231 (56)	−0.18528 (61)	3.3 (3)
C(5)	0.25853 (69)	0.22332 (60)	−0.09408 (62)	3.6 (3)
C(6)	0.21265 (67)	0.13270 (61)	0.03133 (62)	3.5 (3)
C(7)	0.26861 (73)	0.11810 (66)	0.12132 (67)	4.2 (3)
C(8)	0.20119 (74)	0.01466 (65)	0.22994 (65)	4.2 (3)
C(9)	0.09756 (69)	−0.03698 (59)	0.21167 (60)	3.3 (3)
C(10)	0.00529 (71)	−0.14264 (57)	0.29864 (58)	3.4 (3)
C(11)	0.36763 (73)	0.32232 (62)	−0.13291 (60)	3.7 (3)
C(12)	0.33270 (73)	0.40827 (68)	−0.08605 (67)	4.6 (3)
C(13)	0.43201 (91)	0.49997 (71)	−0.12060 (75)	5.5 (4)
C(14)	0.56688 (89)	0.50896 (73)	−0.20048 (72)	5.1 (4)
C(15)	0.60076 (84)	0.42525 (87)	−0.24717 (75)	6.2 (4)
C(16)	0.50392 (84)	0.33103 (77)	−0.21276 (74)	5.6 (4)
C(17)	0.67682 (96)	0.60715 (85)	−0.23656 (86)	7.9 (5)
C(18)	0.01479 (70)	−0.20742 (58)	0.42483 (59)	3.5 (3)
C(19)	−0.01864 (71)	−0.15507 (55)	0.50635 (62)	3.5 (3)
C(20)	−0.00165 (79)	−0.21501 (66)	0.61949 (63)	4.3 (3)
C(21)	0.04682 (85)	−0.32804 (73)	0.65688 (68)	4.8 (4)
C(22)	0.0793 (10)	−0.38198 (69)	0.57802 (85)	6.7 (5)
C(23)	0.06244 (92)	−0.32302 (68)	0.46330 (72)	5.5 (4)
C(24)	0.0680 (11)	−0.39451 (79)	0.77992 (78)	7.8 (5)
C(25)	−0.1424 (15)	0.28805 (92)	−0.05140 (98)	16.0 (7)
C(26)	−0.2090 (12)	0.1280 (11)	0.1978 (10)	10.6 (7)
C(27)	−0.3501 (11)	0.0892 (13)	0.0737 (16)	15 (1)
C1(S)	0.5711 (33)	−0.1097 (30)	−0.4745 (14)	15 (1)
C2(S)	0.4578 (31)	−0.0944 (26)	−0.5122 (19)	13 (1)
C3(S)	0.3926 (22)	0.0174 (34)	−0.5381 (17)	14 (1)
C4(S)	0.4246 (30)	−0.1865 (27)	−0.5231 (28)	14 (2)

Re(TTP)(PEt$_3$)$_2$. This compound was prepared by the same procedure described above, starting with Re(TTP)(O)(Cl) (200 mg, 0.221 mmol). The product crystallized from toluene as lustrous dark blue crystals (205 mg, 85%). Anal. Calcd for $C_{60}H_{66}N_4P_2Re$: C, 66.02; H, 6.11; N, 5.13. Found: C, 66.42; H, 6.10; N, 5.07. ^1H NMR (C_6D_6, ppm); H_β, not observed; H_o, 11.25 (very broad s, 8 H); H_m, 7.86 (broad s, 8 H); tolyl CH_3, 2.64 (s, 12 H); P–CH_2CH_3, −14.7 (very broad s), P–CH_2CH_3, −5.12 (broad s, 18 H). UV-vis (toluene) λ_{max}, nm (log ε): 330 (4.66), 411 (4.99), 475 (4.20), 488 sh (4.13), 628 (3.18), 790 (2.93). μ_{eff} (benzene) = 1.6 μ_B. FABMS (sulfolane): M^+, *m/e* 1091, cluster; $M_+ - PEt_3$, *m/e* 973, cluster; $M^+ - 2PEt_3$, *m/e* 855, cluster.

X-ray Crystallographic Study of Re(TTP)(PMe$_3$)$_2$·C$_6$H$_5$CH$_3$. Preliminary examination of an air-stable crystal of the complex on an Enraf-Nonius CAD4 diffractometer established that the crystal belongs to the triclinic system. Intensity data were collected at −50 °C on a Picker FACS-1 diffractometer as earlier we found that crystals break when cooled below −100 °C. Crystal data and details of data collection are given in Tables I and SI.[10] Six standard reflections, measured every 100 reflection interval, showed no systematic variations in their intensities. Procedures and programs standard in the laboratory at Northwestern were used to solve and refine this structure.[11] The centrosymmetric space group $P\bar{1}$ was assumed and proved to be correct as the structure

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(1) Collman, J. P.; Barnes, C. E.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3500.

(2) Collman, J. P.; Barnes, C. A.; Woo, L. K. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 7684.

(3) Collman, J. P.; Garner, J. M.; Woo, L. K., to be submitted for publication.

(4) Abbreviations: TPP, 5,10,15,20-tetraphenylporphyrinato dianion; TTP, 5,10,15,20-tetra-*p*-tolylporphyrinato dianion; TMP, 5,10,15,20-tetramesitylporphyrinato dianion; OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; py, pyridine.

(5) Buchler, J. W.; Puppe, L.; Rohbock, K.; Schneehage, H. H. *Chem. Ber.* **1973**, *106*, 2710.

(6) Collman, J. P.; Garner, J. M., to be submitted for publication.

(7) (a) Baker, M. V.; Field, L. D.; Hambley, T. N. *Inorg. Chem.* **1988**, *16*, 2874. (b) Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1980**, *19*, 1095. (c) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 371.

(8) Fuhrhop, J. H.; Smith, K. M. *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed., Elsevier: Amsterdam, **1975**; p 769.

(9) Melaven, A. D.; Fowle, J. N.; Brickell, W.; Hiskey, C. F. *Inorg. Synth.* **1950**, *3*, 188.

(10) Supplementary material.

(11) For example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273.

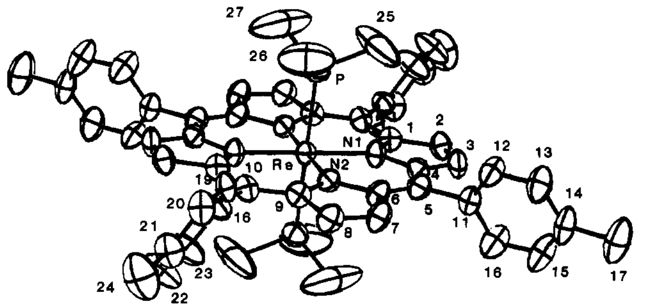

Figure 1. Drawing of the Re(TTP)$(PMe_3)_2$ molecule. The thermal ellipsoids are drawn at their 50% probability values.

refined satisfactorily by full-matrix least-squares methods. A disordered toluene molecule was located from a difference electron density map. All non-hydrogen atoms were refined anisotropically. All H atoms, except those for the toluene molecule, were idealized and included as fixed contributions. The final cycle of the refinement was carried out on F_o^2 with all the data. Details on refinement, including agreement indices, are summarized in Table I. Final positional and equivalent isotropic parameters are given in Table II. Table SII[10] lists the anisotropic thermal parameters and the H atom parameters. The final values of $10|F_o|$ vs $10|F_c|$ are given in Table SIII.[10]

Results and Discussion

Under forcing conditions, rhenium(II) porphyrin complexes have been prepared in good yields by treating rhenium(V) complexes with excess phosphines as diagrammed in eq 3. The

$$\text{Re(Por)(O)(Cl)} + \tfrac{7}{2}\text{PR}_3 \rightarrow \text{Re(Por)(PR}_3)_2 + \text{R}_3\text{PO} + \tfrac{1}{2}\text{R}_3\text{PCl}_2 \quad (3)$$

phosphine oxide and phosphonium chloride products were detected as white solids that sublimed from the reaction residues. Magnetic measurements and crystallographic results show that these are low-spin complexes with trans axial phosphine ligands. The ^1H resonances for Re(OEP)$(PMe_3)_2$ in toluene show a Curie law dependence over the temperature range of −70 to +100 °C. A six-line ESR spectrum (Re, 100%, $I = {}^5/_2$, $g = 2.33$) with no resolved hyperfine splitting from the P or N nuclei was obtained at 298 and 77 K from a powder sample of Re(TTP)$(PMe_3)_2$. The solids are air stable, but the solutions oxidize slowly (>1 week). Vacuum pyrolysis (300 °C, 10^{-6} Torr) of both Re(TTP)$(PMe_3)_2$ and Re(TTP)$(PEt_3)_2$ affords the desired dimer $[Re(TTP)]_2$. Pyrolysis (210 °C, 10^{-6} Torr) of Re(OEP)$(PEt_3)_2$ similarly affords $[Re(OEP)]_2$, but under these same conditions Re(OEP)$(PMe_3)_2$ sublimes unchanged.[6] Recently, Sishta et al.[12] reported that vacuum pyrolysis of the ruthenium complexes Ru(por)$(PR_3)_2$ (por = OEP or TMP, PR_3 = *n*-Bu_3P or PPh_3) yields five-coordinate Ru(por)(PR_3) species.

Structure of Re(TTP)$(PMe_3)_2$·$C_6H_5CH_3$. The molecular geometry and labeling scheme for this complex are shown in Figure 1. Selected bond distances and angles are listed in Table III; a more complete tabulation is given in Table SIV.[10] The complex has crystallographically imposed C_i symmetry with the Re atom at the inversion center. The metal atom is thus constrained to be in the plane of the four nitrogen atoms. The coordination geometry around the metal is an axially elongated octahedron; the bond distances Re–P, Re–N(1), and Re–N(2) are 2.414 (2), 2.062 (5), and 2.056 (5) Å, respectively. The Re–P distance (2.414 (2) Å) is shorter than those of other mononuclear Re(II) bis(phosphine) complexes reported in the literature: 2.470 (4) Å for *all-trans*-Re$(CO)_2Cl_2(PEt_3)_2$[13] and 2.454 (2) and 2.445 (2) Å for *all-trans*-$[Re(CN\text{-}t\text{-}Bu)_2(NCCH_3)_2(PPh_3)_2][BF_4]_2$.[14]

The P–C bond distances are nonrepresentative owing to the high thermal motion of the methyl groups. The bond parameters of the porphyrin ring are typical for a metalloporphyrin.[15] The porphyrin ring is essentially planar, the average deviation from the mean plane being 0.031 Å. The deviation of the atoms from the 24-atom least-squares plane of the porphyrin is given in Table SV.[10] As is normal for metalloporphyrin complexes,[15] the tolyl rings are rotated considerably out of the plane of the macrocycle (dihedral angles between the tolyl groups and the mean porphyrin plane are 70.5 and 66.1°). Structures of the out-of-plane rhenium(I) porphyrin complexes $[Re(CO)_3]_2$(TPP) and $[Re(CO)_3]_2$(TPP)·$SbCl_6$ are known where two metal ions are bonded to the porphyrin, one above and one below the plane of the macrocycle.[16]

Table III. Bond Distances (Å) and Bond Angles (deg) for Re(TTP)$(PMe_3)_2$·$C_6H_5CH_3$

Distances			
Re–P	2.414 (2)	C(1)–C(2)	1.434 (8)
Re–N(1)	2.062 (5)	C(3)–C(4)	1.434 (8)
Re–N(2)	2.056 (5)	C(6)–C(7)	1.423 (9)
av Re–N	2.059 (5)	C(8)–C(9)	1.435 (9)
N(1)–C(1)	1.373 (7)	av C_a–C_b	1.432 (9)
N(1)–C(4)	1.417 (7)	C(2)–C(3)	1.341 (9)
N(2)–C(6)	1.398 (7)	C(7)–C(8)	1.361 (9)
N(2)–C(9)	1.399 (7)	av C_b–C_b	1.351 (10)
av N–C_a	1.397 (16)	C(5)–C(11)	1.502 (9)
C(1)–C(10)′[a]	1.386 (8)	C(10)–C(18)	1.492 (8)
C(4)–C(5)	1.379 (8)	av C_m–C_{ph}	1.497 (9)
C(9)–C(10)	1.389 (8)		
C(5)–C(6)	1.397 (8)		
av C_a–C_m	1.388 (8)		
P–C(25)	1.776 (10)		
P–C(26)	1.770 (10)		
P–C(27)	1.755 (10)		
av P–C	1.767 (10)		
Angles			
N(1)–Re–N(2)	90.7 (2)	Re–P–C(25)	115.1 (4)
N(1)–Re–P	89.6 (2)	Re–P–C(26)	113.8 (3)
N(2)–Re–P	91.2 (1)	Re–P–C(27)	117.4 (4)
av N–Re–P	90.4 (11)	av Re–P–C	115.4 (15)
Re–N(1)–C(1)	127.1 (4)	N(1)–C(1)–C(2)	108.6 (6)
Re–N(1)–C(4)	125.0 (4)	N(1)–C(4)–C(3)	106.3 (6)
Re–N(2)–C(6)	126.1 (4)	N(2)–C(6)–C(7)	108.2 (6)
Re–N(2)–C(9)	126.3 (4)	N(2)–C(9)–C(8)	107.9 (6)
av Re–N–C_a	126.1 (7)	av N–C_a–C_b	107.8 (9)
C(6)–N(2)–C(9)	107.4 (5)	N(1)–C(1)–C(10)′	125.2 (6)
C(1)–N(1)–C(4)	107.9 (5)	N(1)–C(4)–C(5)	125.7 (6)
av C_a–N–C_a	107.7 (5)	N(2)–C(6)–C(5)	125.2 (6)
C(1)–C(2)–C(3)	107.8 (6)	N(2)–C(9)–C(10)	125.0 (6)
C(2)–C(3)–C(4)	109.4 (6)	av N–C_a–C_m	125.3 (6)
C(6)–C(7)–C(8)	108.5 (6)	C(2)–C(1)–C(10)′	126.1 (6)
C(7)–C(8)–C(9)	108.0 (6)	C(3)–C(4)–C(5)	127.9 (6)
av C_a–C_b–C_b	108.4 (6)	C(5)–C(6)–C(7)	126.5 (6)
C(4)–C(5)–C(11)	116.7 (6)	C(8)–C(9)–C(10)	127.0 (6)
C(6)–C(5)–C(11)	116.1 (6)	av C_b–C_a–C_m	126.9 (7)
C(9)–C(10)–C(18)	115.8 (6)	C(4)–C(5)–C(6)	127.2 (6)
C(1)′–C(10)–C(18)	117.4 (6)	C(9)–C(10)–C(1)′	126.8 (6)
av C_a–C_m–C_{ph}	116.5 (6)	av C_a–C_m–Ca_a	127.0 (6)

[a] Primed and unprimed atoms with the same label are related by the crystallographic inversion center.

Now that the structure of Re(TTP)$(PMe_3)_2$ has been determined, the compound will serve as a calibration standard for planned EXAFS determinations of the Re–Re and Re–N bond lengths in $[Re(TTP)]_2$ and $[Re(OEP)]_2$.

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Registry No. PEt_3, 554-70-1; PMe_3, 594-09-2; Re(OEP)(O)(Cl), 117201-90-8; Re(TPP)(O)(Cl), 117201-86-2; $Re(OEP)(PMe_3)_2$, 117201-87-3; $Re(TPP)(PMe_3)_2{\cdot}C_6H_5CH_3$, 117201-89-5; $Re(OEP)(PEt_3)_2$, 117201-91-9; $Re(TPP)(PEt_3)_2$, 117201-92-0.

Supplementary Material Available: Table SI (crystallographic details), Table SII (anisotropic thermal parameters and hydrogen atom parameters), Table SIV (bond distances and angles), Table SV (least-squares planes and dihedral angles between the least-squares planes) (9 pages); Table SIII (observed and calculated structure amplitudes) (21 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of the Cluster Cation $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-}Ph_2PCH_2PPh_2)_3]^+$, Containing both PtAu and PtAg Bonds

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The chemistry of complexes containing either Pt–Au or Pt–Ag bonds is a rapidly growing area of research.[2-10] The compounds are of interest because of their new and interesting structures and bonding modes and as models for the heterobimetallic metal catalysts. For example, gold leads to significant changes in the catalytic activity and selectivity of platinum catalysts.[11]

Gold has a strong tendency to form Au–Au bonds or bridged AuM_2 or AuM_3 units and most Pt–Au-bonded complexes fall into one of these categories.[2-5] There are well-characterized compounds with simple Au–Pt bonds, but they are ligand bridged.[6] A common synthetic method for introduction of gold–metal bonds is to treat a metal hydride with an LAu^+ derivative, leading to isolobal substitution of LAu^+ for H^+ and hence formation of an Au–M bond. Braunstein synthesized the first PtAu cluster in this way by treating $[PtHCl(PEt_3)_2]$ with 2 equiv of Ph_3PAu^+ to give the cluster cation $[PtCl(AuPPh_3)_2(PEt_3)_2]^+$, but the introduction of only one LAu^+ unit was not achieved.[3]

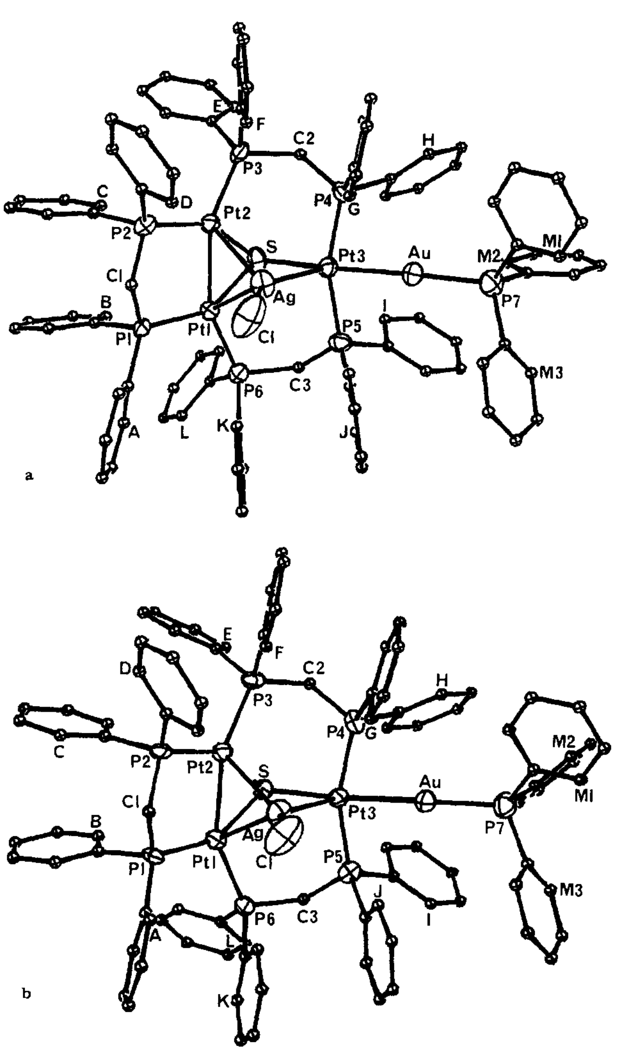

Figure 1. Views of (a) cation A and (b) cation B showing the numbering of the atoms. The carbon atoms of rings A to M3 are numbered cyclically from n = 1 to 6, starting with the atom attached to phosphorus. The ring label is placed adjacent to the n = 2 atom of each ring. The 50% probability ellipsoids are shown for Au, Pt, Ag, Cl, S, and P atoms. Carbon atoms are represented by spheres of arbitrary size.

As part of our studies of Pt–Au-bonded compounds,[12] reactions of $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]^+$ ($\mathbf{1}^+$) (dppm = $Ph_2PCH_2PPh_2$)[13] with Ph_3PAu^+ were carried out with the aim of substituting the hydride ligand by the Ph_3PAu unit. The target molecules could not be prepared, but the title complex, containing the Pt_3AuAg core, was isolated instead. This paper reports the synthesis, structure, and spectroscopic properties of this complex.

Results and Discussion

A solution containing $[Au(NO_3)(PPh_3)]$ and a suspension of AgCl was prepared by mixing approximately equimolar amounts of $[AuCl(PPh_3)]$ and $AgNO_3$ in dichloromethane/methanol. Addition of this mixture to $[Pt_3H(\mu_3\text{-}S)(\mu\text{-dppm})_3]PF_6$ (**1**) in dichloromethane caused an immediate color change from yellow to red, and the product $[Pt_3(\mu_3\text{-}S)(AuPPh_3)(\mu_3\text{-}AgCl)(\mu\text{-dppm})_3]PF_6$ (**2**) was isolated in good yield. If the AgCl precipitate

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