

Complexation and C-H/C-P Bond Activation of the (PPh₂)C₆₀H Molecule on Triosmium Carbonyl Clusters

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Reaction of $(PPh_2)C_{60}H$ (1) and $Os_3(CO)_{10}(NCMe)_2$ produces $Os_3(CO)_{10}(\mu,\eta^3-(PPh_2)C_{60}H)$ (2), with one edge of the triosmium cluster bridged by the phosphine group and one C=C double bond of 1. Treating compound 1 with $Os_3(CO)_{11}(NCMe)$ affords $Os_3(CO)_{11}((PPh_2)C_{60}H)$ (3), with the phosphine ligand coordinated to one osmium atom. Thermolysis of 2 in refluxing chlorobenzene leads to orthometalation of one phenyl group and C-H/C-P bond activation of the $(PPh_2)C_{60}H$ ligand to afford the phosphido cluster $(\mu-H)_2Os_3(CO)_9(\mu_3,\eta^2-PPh(C_6H_4))$ (4) and C_{60} molecule. Compound 3 undergoes thermal decarbonylation in refluxing toluene to produce 2. The molecular structures of compounds 1-BH₃, 2, and 3 were determined by an X-ray diffraction study.

Introduction

The availability of gram quantities of the fullerene C_{60} has facilitated the study of the reactivity of this intriguing molecule.¹ The first fullerene-transition metal complex was reported by Fagan in the reaction of $[Cp*Ru(NCMe)_3]^+$ and C_{60} .² Because the p-orbitals within a hexagon of the C_{60} framework are tilted away from the center of the ring,³ the C_{60} hexagons behave more like a cyclohexatriene unit, and complexation of transition metals to the fullerene core proceeds similarly to well-established reactions of electrondeficient olefins in a dihapto manner to one or more π -bonds.⁴ The binding of C_{60} to transition metals in a η^2 -fashion becomes clearly evident by the formation of

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various complexes.⁵ Furthermore, coordination to two or three of the double bonds of a hexagon was found in several ruthenium,⁶ osmium,⁷ rhenium,⁸ and iridium⁹ cluster complexes, such that the metals are η^2 -bound to adjacent bonds of a C₆ face. Syntheses of σ -bonded fullerene metal derivatives are usually from reaction of fullerene dianion C₆₀²⁻ with organometal halides,¹⁰ hydrometalation of metal-hydride compounds,¹¹ or metalation of fullerene with metalcentered radicals through photodissociation of dimetallic complexes.¹² Remarkably, pentahaptofullerene metal complexes have been obtained by treating C₆₀HR₅ or C₆₀R₅⁻ (R = alkyl and aryl) with precursory metal complexes or metal salts.¹³

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Article

With the development of an extensive organic chemistry of fullerenes, it is now possible to construct a variety of modified fullerenes that incorporate a metal-binding group into their structure.¹⁴ The syntheses of such fullerene-containing ligands offer the potential to exploit the chemical reactivity, redox and electron-acceptor characteristics, photochemical behavior, electron-withdrawing properties, and novel structural features that a fullerene group provides.¹⁵ For instance, the fullerene-phosphines have been made through addition of phosphide or borane-protected phosphide nucleophiles to C_{60} and subsequent protonation of the resulting anion.¹⁶ Some mononuclear palladium and platinum complexes of the type $(C_{60}$ -phosphine)₂MCl₂ were prepared, which display catalytic activity in Grignard re-agent/styrene cross-coupling reactions.^{16a} As part of our interest in cluster and phosphine chemistry,¹⁷ herein we present the complexation of (PPh2)C60H to triosmium carbonyl clusters and show their thermal reactivity leading to C-H/C-P bond activation of the fullerene-phosphine molecule mediated by the trimetallic framework.

Results and Discussion

Functionalization of fullerene with a protected diphenylphosphenyl group was prepared by treating C_{60} with H_3B -PPh₂⁻ at low temperature, followed by protonation to afford (H₃B-PPh₂)C₆₀H (1-BH₃), according to the method reported by Nakamura and co-workers.¹⁶ The (PPh₂) C_{60} H (1) molecule was generated by removing the BH₃ protecting group with $N(C_2H_4)_3N$ (DABCO)¹⁶ immediately before use. The reaction of 1 and Os₃(CO)₁₀(NCMe)₂ in refluxing toluene results in substitution of the labile acetonitrile ligands by the phosphine group and one C=C double bond of 1 to generate $Os_3(CO)_{10}(\mu, \eta^3 - (PPh_2)C_{60}H)$ (2) in 54% yield after separation by TLC and crystallization from CS₂/MeOH. On the other hand, treating 1 with $Os_3(CO)_{11}(NCMe)$ produces $Os_3(CO)_{11}((PPh_2)C_{60}H)$ (3) in 55% yield, with the acetonitrile ligand being replaced by the phosphine group. The reactions are summarized in Scheme 1.

Compounds 2 and 3 form an air-stable, black and yellowbrown crystalline solid, respectively, and have been characterized by elemental analysis, mass, IR, and NMR spectroscopy. The molecular ion peak at m/z 1762 (¹⁹²Os) for 2 is the combination of Os₃(CO)₁₀ and one (PPh₂)C₆₀H moiety. On the contrary, the FAB and EI mass spectra of 3 did not give resolvable ion peaks with m/z > 1000, while the MALDI mass spectrum displays the highest ion peak at m/z 1678 (¹⁹²Os), corresponding to the [M⁺-4CO] fragment, and the isotope distribution matches the calculated pattern.



Compound **1-BH**₃ presents the phenyl proton resonances at δ 8.52 (m, 4H) and 7.65 (6H) and the H–C₆₀ proton resonance at δ 6.96 (d, $J_{P-H} = 24$ Hz). In contrast, the ¹H NMR spectrum of **2** shows four multiplet signals at δ 8.91, 8.33, 7.68, and 7.55 in a ratio of 1:2:6:1, likely due to steric constraints of the phenyl groups upon coordination of the phosphorus atom to the Os₃ cluster. Most strikingly, the H–C₆₀ proton resonance shows a substantial upfield shift to δ 6.10 (d, $J_{P-H} = 23$ Hz), which may be attributed to shielding by ring current of the phenyl groups.¹⁸

The ¹H NMR spectrum of **3** at room temperature shows only two broad signals at δ 8.31 (4H) and 7.62 (6H) for the phenyl protons, indicating the molecule is fluxional in solution, likely through Os-P-C(C₆₀) bond rotation or scrambling of the phosphine group in different sites of the cluster. Isomerism of phosphine-substituted triosmium clusters is well documented in the literature.¹⁹ The slow-exchange ¹H NMR spectrum taken at -80 °C reveals the H-C₆₀ proton resonance at δ 6.93 (d, $J_{P-H} = 24$ Hz) and seven multiplet signals in the range δ 8.00-7.09 for the phenyl proton resonances.

The molecular structure of **1-BH**₃ is illustrated in Figure 1. Addition of one PPh₂(BH₃) group and one hydrogen atom to a (6:6)-double bond causes distortion of the C_{60} framework from an idealized I_h symmetry. The P1-C14 length is 1.886(4) Å, and the bond angles imposed on the phosphorus atom, $105.3(2) - 113.0(2)^\circ$, are only slightly deviated from the ideal 109.5°. The distances C14-C38 = 1.58(6) Å, C14-C15 =1.537(6) Å, C14-C18 = 1.537(5) Å, C37-C38 = 1.521(5)Å, and C38-C39 = 1.512(6) Å are typical C-C single-bond lengths, while the remaining C–C lengths are 1.38 Å (av) (6:6-ring junctions) and 1.45 Å (av) (6:5-ring junctions). The C14 and C38 atoms are sp³ hybridized to show a distorted tetrahedral bonding, where the P-C-C and C-C-C angles centered on the C14 atom are in the range $99.9(3) - 116.0(3)^{\circ}$, and the C-C-C angles centered on the C38 atom are 101.5(3)-115.2(4)°. Overall, the fullerene architecture is elongated compared with the unperturbed C₆₀ molecule, such that the angles between the C14-C38 vector and the planes defined by C15-C14-C18 and C37-C38-C39 are

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Figure 1. Molecular structure of 1-BH₃. The phenyl hydrogens have been artificially omitted. Selected bond distances (Å): P1-C14 = 1.886(4), P1-C1 = 1.802(5), P1-C7 = 1.819(4), P1-B1 = 1.913(5), C14-C15 = 1.537(6), C14-C18 = 1.537(5), C14-C15 = 1.537(6), C14-C38 = 1.586(6), C15-C41 = 1.373(6), C15-C16 = 1.428(6), C37-C38 = 1.521(5), C38-C39 = 1.512(6), C39-C40 = 1.363(6), C40-C41 = 1.474(6), C37-C48 = 1.435(6), C47-C48 = 1.446(6), C39-C47 = 1.442(6). Selected bond angles (deg): C1-P1-C7 = 109.9(2), C1-P1-B1 = 113.0(2), C1-P1-C14 = 105.3(2), C7-P1-B1 = 112.3(2), C7-P1-C14 = 108.0(2), B1-P1-C14 = 108.0(2), P1-C14-C15 = 116.0(3), P1-C14-C18 = 106.0(3), P1-C14-C38 = 113.9(4), C15-C14-C18 = 99.9(3), C15-C14-C38 = 113.9(4), C18-C14-C38 = 114.3(3), C14-C15-C16 = 109.9(4), C15-C16-C17 = 108.7(4), C14-C18-C17 = 110.1(3), C14-C38-C37 = 114.9(3), C14-C38-C39 = 115.2(4), C37-C38-C39 = 101.5(3).



Figure 2. Molecular structure of 3. The phenyl hydrogens have been artificially omitted. Selected bond distances (Å): P1-C24 = 1.95(2), P1-C12 = 1.84(1), P1-C18 = 1.81(2), P1-Os1 = 2.362(4), Os1-Os2 = 2.887(1), Os1-Os3 = 2.9139(9), Os2-Os3 = 2.885(1), C24-C25 = 1.54(2), C24-C29 = 1.58(2), C24-C33 = 1.54(2), C28-C29 = 1.51(2), C29-C30 = 1.53(2). Selected bond angles (deg): Os1-Os2-Os3 = 60.65(2), Os1-Os3-Os2 = 59.71(2), Os2-Os1-Os3 = 59.64(3), Os1-P1-C24 = 118.1(5), Os1-P1-C12 = 109.9(6), Os1-P1-C18 = 121.0(5), C12-P1-C18 = 103.1(7), C12-P1-C24 = 105.2(6), C18-P1-C24 = 97.6(7), P1-C24-C25 = 106.7(9), P1-C24-C29 = 111.1(9), P1-C24-C33 = 112(1), C24-C29-C28 = 116(1), C24-C29-C30 = 116(1), C28-C29-C30 = 101(1), C25-C24-C29 = 113(1), C25-C24-C33 = 101(1), C29-C24-C33 = 113(1).

57.8° and 55.1°, respectively, while such angles are 31° in free C_{60} .

The molecular structure of 3, shown in Figure 2, is derived from the mother molecule $Os_3(CO)_{12}$ by replacing

an equatorial carbonyl group with a phosphine ligand. The Os1-P1 bond is slightly tilted from the trimetallic plane by 4.4°. The Os_3 unit forms an isosceles triangle with the Os1-Os3 distance (2.9139(9) Å) being slightly longer



Figure 3. Molecular structure of 2. The phenyl hydrogens have been artificially omitted. Selected bond distances (Å): P1-C23 = 1.93(1), P1-C11 = 1.81(1), P1-C17 = 1.80(1), P1-Os1 = 2.380(3), Os1-Os2 = 2.9360(8), Os1-Os3 = 2.8607(8), Os2-Os3 = 2.8866(8), Os2-C29 = 2.20(1), Os2-C30 = 2.25(1), C23-C24 = 1.52(2), C23-C28 = 1.50(2), C23-C42 = 1.52(2), C24-C25 = 1.50(2), C24-C39 = 1.51(2), C28-C29 = 1.51(2), C29-C30 = 1.43(2), C29-C43 = 1.48(2), C42-C43 = 1.43(2), C43-C44 = 1.38(2), C44-C45 = 1.40(2), C45-C46 = 1.34(2). Selected bond angles (deg): Os1-Os2-Os3 = 58.85(2), Os1-Os3-Os2 = 61.44(2), Os2-Os1-Os3 = 59.72(2), Os1-P1-C23 = 116.0(4), Os1-P1-C11 = 110.2(5), Os1-P1-C17 = 117.7(4), C11-P1-C17 = 103.1(6), C11-P1-C23 = 106.3(6), C17-P1-C23 = 102.2(5), P1-C23-C24 = 116.4(8), P1-C23-C28 = 108.2(8), P1-C23-C42 = 103.5(7), C24-C23-C28 = 114(1), C24-C23-C42 = 114(1), C28-C23-C42 = 98.9(9), C23-C24-C25 = 117(1), C23-C24-C39 = 117(1), C25-C24-C39 = 100(1).

(ca. 0.03 Å) than the other two Os–Os bonds. The average Os–Os distance for 3 (2.895(1) Å) is ca. 0.02 Å longer than that determined for $Os_3(CO)_{11}(\eta^2-C_{60})^{7a}$ and may be attributed to the stronger net donor but weaker acceptor capability of phosphine compared with olefin. The P1-C24 bond (1.95(2) Å) is ca. 0.06 Å longer than that in 1-BH₃, and the Os1-P1-C24 angle (118.1(5)°) increases by 10° compared with the B1-P1-C14 angle $(108.0(2)^\circ)$ in 1-BH₃, consistent with steric repulsions between the bulky Os₃ cluster and C₆₀ moiety. Conversely, the C-P1-C angles are compressed, ranging from 97.6(7)° to 105.2(6)°. The dihedral angle between the Os1-P1-C24 plane and the Os3 triangle is 32.9(5)°. The Os1, Os2, and Os3 atoms are each linked to three, four, and four terminal carbonyl groups. Individual Os–CO distances range from 1.87(2) to 2.00(2)Å, C–O distances range from 1.08(2) to 1.17(2) Å, and the Os-C-O angles are in the range $172(2)-177(2)^{\circ}$. The axial carbonyls are roughly orthogonal to the Os₃ surface (85.6(5)-92.8(9)°) and eclipsed to each other $(1.05 - 4.87^{\circ}).$

The ORTEP diagram of **2** is presented in Figure 3, where the (PPh₂)C₆₀H unit is coordinated to two equatorial sites of the Os₃ cluster through the phosphine group and one C=C double bond in a μ , η^3 -bonding feature. The bond lengths Os1-P1 = 2.380(3) Å and P1-C23 = 1.93(1) Å and the angle Os1-P1-C23 = 116.0(4)° are compatible with those in **3**. The C₆₀ moiety is bound to the Os2 atom in an η^2 fashion through a 6:6-ring junction, as found in other η^2 -C₆₀ transition metal complexes.⁵ The Os-C₆₀ distances are Os2-C29 = 2.20(1) Å and Os2-C30 = 2.25(1) Å, which are comparable to the values found in $Os_3(CO)_{11}(\eta^2 - C_{60})$ and related complexes.7 The dihedral angle between the C29-Os2-C30 and Os₃ planes is 10.8(8)°. The distance C29-C30 = 1.43(2) Å is elongated (ca. 0.05 Å) in comparison with other unperturbed (6:6)-double bonds and may be attributed to π -back-donation from the Os2 atom. On the other hand, the C29 and C30 atoms are pulled away from the fullerene surface, such that the angles between the C29-C30 edge and the C28-C29-C43 and C31-C30-C46 planes are 45.2° and 47.9°, respectively, while the corresponding angles for the C35-C36 edge of 3 are 32.3° and 39.0°. The trimetallic parts are based on a triangular array of osmium atoms in which the Os1-Os2 distance of 2.9360(8) A is significantly longer than the other two intermetallic distances, Os1-Os3 = 2.8607(8) Å and Os2-Os3 = 2.8866(8) Å. The Os1, Os2, and Os3 atoms are each associated with three, three, and four terminal carbonyl ligands. Individual Os-CO distances range from 1.90(2) Å (for Os1-C1) to 2.08(2) Å (for Os3-C7), C-O distances range from 1.05(2) Å (for C7–O7) to 1.15(2) Å (for C3–O3), and the Os–C–O angles are in the range $173(2)-179(2)^{\circ}$. Coordination of the bulky $(PPh_2)C_{60}H$ species in a μ,η^3 -fashion causes substantial distortions for the carbonyl arrangements on the Os₃ triangle (Figure 4). For instance, the axial carbonyl groups are not perpendicular to the Os₃ plane with the Os-Os-CO angles ranging from 79.9(4)° (Os1-Os2-C4) to 96.5(4)°



Figure 4. View of 2 and 3, showing the distorted C_{60} framework and the arrangement of carbonyl ligands on triosmium clusters.



(Os1-Os2-C5) and are staggered with the C-Os-Os-C torsional angles in the range $16.1-22.9^{\circ}$.

Compound **2** remains intact in refluxing toluene (110 °C) over 3 days. Activation of the H–C₆₀ bond of **2** by the Os₃ cluster is accessible in refluxing chlorobenzene (132 °C). However, this thermal reaction is also concomitant with orthometalation of one phenyl group and cleavage of the P–C₆₀ bond to release C₆₀ and generate the known phosphido cluster complex (μ -H)₂Os₃(CO)₉(μ_3 , η^2 -PPh(C₆H₄))²⁰ (**4**) in 58% yield. In contrast, heating **3** in refluxing toluene

for 2 h produces 2 in 72% yield. A proposed mechanism is illustrated in Scheme 2. Apparently, decomplexation of the fullerene C=C double bond at elevated temperature generates a vacant coordination site suitable to undergo *ortho*-H-C(Ph) bond metalation, and the resulting intermediate might place the H-C₆₀ bond in proximity to one osmium atom that facilitates the second C-H bond activation; subsequent cleavage of the P-C₆₀ bond to release steric crowding would produce 4 and C₆₀. Another possibility involves the initial loss of CO from the Os(CO)₄ moiety, followed by ligand activation. On the other hand, thermolysis of 3 results in decarbonylation to create a vacant site, followed by complexation of the fullerene moiety to give 2.

Experimental Section

General Methods. All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. $(H_3B-PPh_2)C_{60}H (1-BH_3)$, ¹⁶ $(PPh_2)C_{60}H (1)$, ¹⁶ Os₃-(CO)₁₀(NCMe)₂,²¹ and Os₃(CO)₁₁(NCMe)²² were prepared as described in the literature. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded on a Jasco FT/IR-4100 IR spectrometer. ¹H spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 MHz. Fastatom-bombardment (FAB) and matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a JEOL JMS-SX102A and Bruker Microflex-LT mass spectrometer, respectively. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Chen-Kung University, Tainan, Taiwan.

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Table 1. Crystallographic Data for 1-BH₃, 2, and 3

	1-BH ₃	2	3
chem formula	$C_{72}H_{14}BP$	C ₈₂ H ₁₁ O ₁₀ Os ₃ P	C ₈₃ H ₁₁ O ₁₁ Os ₃ P
cryst solvent	CS_2	0.5 CS ₂	CS_2
cryst syst	monoclinic	tetragonal	triclinic
fw	996.74	1795.55	1861.62
<i>T</i> , K	200(2)	200(2)	293(2)
space group	$P2_{1}/c$	P4/n	$P\overline{1}$
a, Å	12.8935(3)	29.0200(4)	13.5272(2)
b, Å	32.524(1)	29.0200(4)	14.7670(3)
<i>c</i> , Å	9.9545(3)	14.4970(2)	15.3027(4)
α, deg			100.780(1)
β , deg	106.646(2)		99.911(1)
γ , deg			107.088(1)
$V, Å^3$	3999.5(2)	12208.8(3)	2785.1(1)
Ζ	4	8	2
$D_{\rm calc}, {\rm g} {\rm cm}^{-3}$	1.655	1.954	2.220
μ , mm ⁻¹	0.233	6.358	7.009
R_1/wR_2	0.0575/0.1336	0.0614/0.1724	0.0689/0.1545
GOF on F^2	0.788	1.062	1.060

Synthesis of 2. Compound 1 (50 mg, 0.055 mmol) and Os₃-(CO)₁₀(NCMe)₂ (51 mg, 0.055 mmol) were placed in an ovendried 50 mL Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. Toluene (30 mL) was introduced into the flask via a syringe, and the solution was first stirred at room temperature for 5 h and then heated to reflux for 1 h. The volatile materials were removed under vacuum, and the residue was subjected to TLC, eluting with carbon disulfide. Isolation of the material forming the second dark brown band gave black crystals of Os₃(CO)₁₀(μ , η^3 -(PPh₂)C₆₀H) (2; 52 mg, 0.029 mmol, 54%) after crystallization from CS₂/MeOH. MS (FAB): *m/z* 1762 (M⁺, ¹⁹²Os). Anal. Calcd for C₈₂H₁₁O₁₀Os₃P: C, 56.03; H, 0.63. Found: C, 56.35; H, 0.77. IR (*n*-hexane, *v*CO): 2106 (s), 2069 (vw), 2055 (w), 2039 (m), 2026 (vs), 2007 (w), 1994 (w), 1983 (w), 1975 (w), 1965 (vw) cm⁻¹. ¹H NMR (CS₂+CDCl₃, 23 °C): δ 8.91 (m, 1H, Ph), 8.33 (m, 2H, Ph), 7.68 (m, 6H, Ph), 7.55 (m, 1H, Ph), 6.10 (d, 1H, *J*_{P-H} = 23 Hz, C₆₀H). ³¹P{¹H} NMR (CS₂+CDCl₃, 23 °C): δ 38.0 (s).

Synthesis of 3. Compound 1 (20 mg, 0.022 mmol) and Os₃- $(CO)_{11}(NCMe)$ (20 mg, 0.022 mmol) were placed in an ovendried 50 mL Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. Dichloromethane (30 mL) was introduced into the flask via a syringe, and the solution was stirred at room temperature for 2 h. The volatile materials were removed on a rotary evaporator, and the residue was subjected to TLC, eluting with carbon disulfide. Isolation of the material forming the second brown band afforded yellow-brown crystals of Os₃-(CO)₁₁((PPh₂)C₆₀H) (**3**; 21 mg, 0.012 mmol, 55%) after crystallization from CS₂/MeOH. MS (MALDI): m/z 1678 (M⁺-4CO, ¹⁹²Os). Anal. Calcd for C₈₄H₁₁O₁₁Os₃PS₂: C, 54.19; H, 0.60. Found: C, 54.24; H, 0.60. IR (CH₂Cl₂, vCO): 2110 (m), 2059 (s), 2036 (s), 2021 (vs), 1991 (m), 1980 (sh) cm⁻¹. ¹H NMR (CS₂+CD₂Cl₂, 25 °C): δ 8.31 (br, 4H, Ph), 7.62 (br, 6H, Ph). ¹H NMR (CS₂+CD₂Cl₂, -80 °C): δ 8.00 (m, 1H, Ph), 7.76 (m, 2H, Ph), 7.71 (m, 1H, Ph), 7.63 (m, 1H, Ph), 7.45 (m, 2H, Ph), 7.32 (m, 2H, Ph), 7.09 (m, 1H, Ph), 6.93 (d, 1H, $J_{P-H} = 24$ Hz, C_{60} H). ³¹P{¹H} NMR (CS₂+C₆D₆, 25 °C): δ 34.1 (br).

Thermolysis of 2. Compound **2** (9 mg, 0.0051 mmol) and chlorobenzene (10 mL) were placed in an oven-dried 50 mL Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. The solution was heated to reflux for 12 h until no IR absorptions due to the starting compound were present. The solution was cooled to room temperature, and the solvent was removed under vacuum. The residue was subjected to TLC, eluting with carbon disulfide. The first purple band gave C_{60} (3 mg, 82%), and the second pale yellow band gave the known phosphido cluster complex (μ -H)₂Os₃(CO)₉(μ_3, η^2 -PPh(C₆H₄)) (**4**; 3 mg, 58%). MS (FAB): m/z 1014 (M⁺, ¹⁹²Os). ¹H NMR (CDCl₃, 23 °C): δ 7.79 (m, 1H, C₆H₄), 7.60–7.52 (m, 5H, Ph), 6.88 (m, 1H, C₆H₄), 6.71 (m, 1H, C₆H₄), 6.22 (m, 1H, C₆H₄), -17.10 (br, 2H, μ -H). ³¹P{¹H} NMR (CDCl₃, 23 °C): δ 41.62 (s). IR (*n*-hexane, ν CO): 2108 (m), 2078 (s), 2051 (s), 2039 (m), 2028 (m), 2011 (s), 1999 (m), 1981 (m) cm⁻¹.

Thermolysis of 3. Compound **3** (10 mg, 0.0055 mmol) and toluene (5 mL) were placed in an oven-dried 25 mL Schlenk flask, equipped with a condenser, under a dinitrogen atmosphere. The solution was heated to reflux for 2 h and cooled to room temperature, and the solvent was removed under vacuum. The residue was separated by TLC with carbon disulfide as eluant to obtain **2** (7 mg, 72%).

Structure Determination for 1-BH₃, 2, and 3. The crystals of 1-BH₃, 2, and 3 found suitable for X-ray analysis, grown from CS₂/MeOH at room temperature, were each mounted in a thinwalled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.65-25.09° for 1-BH₃, 2.11-25.04° for 2, and 2.27-24.99° for 3. Of the 23 595, 71 893, and 24 107 reflections collected, 7054, 10808, and 9756 reflections were independent for 1-BH₃, 2, and 3, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by leastsquares cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package.23 The data collection and refinement parameters are presented in Table 1.

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Supporting Information Available: X-ray crystal files in CIF format for **1-BH₃**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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