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# Synthesis, Structure, and Transformation of Novel Osmium Azine and Ylide Complexes

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Three novel triosmium complexes with unusual coordination characteristics are reported. Treatment of the hydridotriosmium cluster $(\mu\text{-H})_2Os_3(CO)_{10}$ with $CNNPPh_3$ in $CH_2Cl_2$ gave complexes $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-C(H)-NNPPh}_3)$ (**1**) and $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-CHPPh}_3)$ (**2**). Complex **1** represents the first example of the existence of a coordinated phosphinazine ligand. An in-situ $^1$H NMR study showed that the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $CNNPPh_3$ produced complex **1** as the initial product in 100% conversion. The latter is not stable in solution and slowly eliminates nitrogen to form an unusual ylide complex **2** in quantitative yield. The thermolysis of **2** in refluxing toluene afforded $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-CCO}_2CH_2Ph)$ (**3**) as a colorless compound. Complexes **1**–**3** were characterized by spectroscopic methods and single-crystal X-ray diffraction analysis. The interesting feature of structure **3** is the presence of a $\mu_3$-alkylidyne ligand where the symmetrically triply bridged $CCO_2CH_2Ph$ fragment lies perpendicular to and above the triosmium triangle.

## Introduction

Trinuclear osmium complexes have been extensively used as model compounds because of their relative stability.[1,2] Many osmium-containing intermediates have been isolated and characterized, thus providing a better understanding of many fundamental reactions involved in organometallic chemistry.[2] *N*-Isocyanoiminetriphenylphosphorane ($CNNPPh_3$) is a versatile ligand, which easily substitutes for a more labile ligand to afford metal *N*-isocyanide complexes and also undergoes nucleophilic or electrophilic reactions.[3] Upon coordination to the metal, the $CNNPPh_3$ moiety has been reported to further undergo Wittig-type reactions with ketones and aldehydes in the presence of a catalytic amount of acid to form *N*-isocyanoimine analogues.[4−7] Although $CNNPPh_3$ has been known for many years, only a few related studies concerning its organometallic chemistry have appeared in the literature.[3−5] In the course of our continuing

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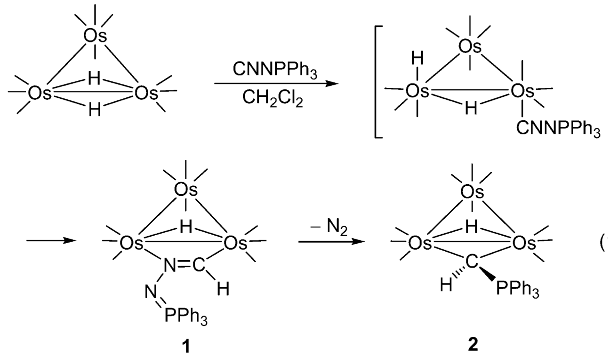
studies on the chemistry of metal isocyanide complexes,[4,8,9] we have been interested in the reactivity of $CNNPPh_3$-containing complexes to try to understand the mediation effect of the metal centers on the property of this coordinated ligand.[5,10] Herein we report on the synthesis and transformation of three unprecedented triosmium complexes containing unusual ligands derived from the reaction of $CNNPPh_3$ with the hydridotriosmium complex $H_2Os_3(CO)_{10}$. Their coordination modes are reported here for the first time.

## Results and Discussion

**Reaction of $H_2Os_3(CO)_{10}$ with $CNNPPh_3$.** The purple hydridotriosmium cluster $H_2Os_3(CO)_{10}$ was prepared by bubbling hydrogen into a solution of $Os_3(CO)_{12}$ in refluxing *n*-octane over a 2 h period.[11] The $H_2Os_3(CO)_{10}$ produced was then dissolved in $CH_2Cl_2$ and treated with $CNNPPh_3$ at room temperature to afford a yellow complex, $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-C(H)NNPPh}_3)$ (**1**), and a small amount of an orange complex, $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-CHPPh}_3)$ (**2**, eq 1).



(1)

The FAB mass spectrum of **1** showed a molecular ion peak at *m*/*z* 1161, which corresponds to an adduct of $H_2Os(CO)_{10}$ and $CNNPPh_3$. The $^1H$ NMR spectrum of **1** showed a bridging hydride peak at $\delta$ −15.49 ppm, phenyl proton signals in the $\delta$ 7.47−7.58 ppm region, and another proton signal at $\delta$ 8.82 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, the triphenyl phosphine group gave rise to a singlet at $\delta$ 8.09 ppm, demonstrating that the $CNNPPh_3$ is not coordinated to the osmium cluster in the terminal mode. [cf. the terminal $CNNPPh_3$ ligands in complexes $ReBr(CO)_3(CNPh)(CNNPPh_3)$ and $ReBr(CO)_3(CNPr)(CNNPPh_3)$ resonate at $\delta$ 32.36 and 32.14, respectively].[5] The heteronuclear $^1H-^{13}C$ (HMQC) spectrum showed that the proton at $\delta$ 8.82 was bound to the carbon atom ($\mathit{C}NNPPh_3$) at $\delta$ 155.5 ppm. These findings indicate the reaction involves the insertion of an isocyanide into the metal−hydride bond.[12]

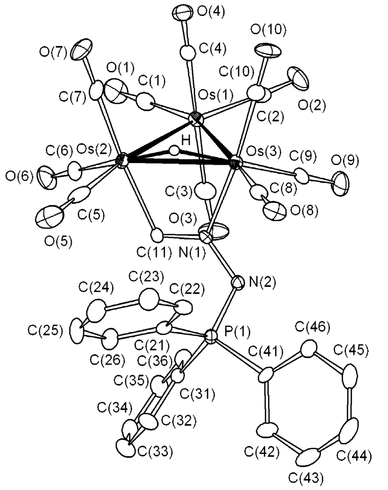


**Figure 1.** ORTEP diagram of $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-C(H)NNPPh}_3)$ (**1**).

An X-ray structure analysis of **1** was undertaken to investigate the exact coordination characteristics of the $CNNPPh_3$ ligand within the cluster. An ORTEP drawing of **1** is shown in Figure 1, and relevant crystallographic data are given in Tables 1 and 2. The three Os atoms define an isosceles triangle with one elongated edge (Os(2)−Os(3) = 2.923(2) Å) and two shorter edges (Os(1)−Os(2) = 2.868(1) Å and Os(1)−Os(3) = 2.873(2) Å). The C(11) and N(1) atoms of the $C(H)NNPPh_3$ moiety coordinate at two axial sites of the Os(2)−Os(3) vector forming a $\mu_2$-$\eta^2$-edge-bridged phosphinazine moiety. The Os(2), Os(3), N(1), and C(11) atoms are nearly coplanar. The plane defined by these four atoms is nearly orthogonal to that defined by the triosmium atoms. The C(11)−N(1) forms a double bond (1.28(1) Å), and N(1)−N(2) forms a single bond (1.42(1) Å).[13] A partial double-bond character exists between N(2)−P(1) with a distance of 1.596(7) Å.[13]

An in-situ $^1H$ NMR study showed that the reaction of $(\mu\text{-H})_2Os_3(CO)_{10}$ with $CNNPPh_3$ produced complex **1** as the initial product in 100% conversion. The proposed pathway for the formation of complex **1** is shown in eq 1. Adams and co-workers observed that the reaction of hydridotriosmium cluster with an isocyanide ligand (CNR) forms adducts of the type $H_2Os_3(CO)_{10}(CNR)$ (R = $C_6H_5$, Me, $Bu^t$).[12a,b] Although we were unable to detect any reaction intermediates, we propose that the hydridotriosmium cluster reacts with $CNNPPh_3$ initially forming $H_2Os_3(CO)_{10}(CNNPPh_3)$, and this reaction is followed by the insertion of isocyanide into the metal hydride to afford complex **1**. Other related triosmium

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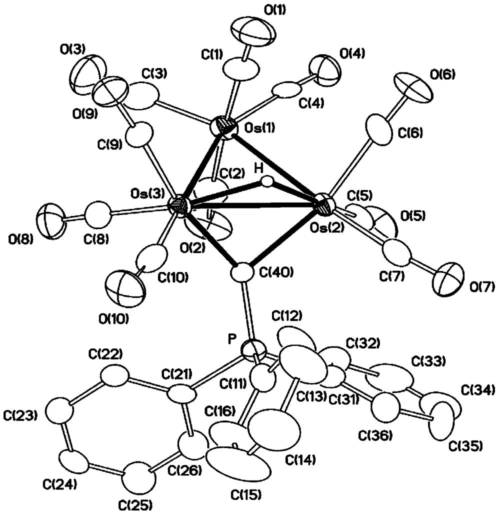

**Figure 2.** ORTEP diagram of ($\mu$-H)$Os_3(CO)_{10}$($\mu_2$-$\eta^1$-$CHPPh_3$) (**2**).

complexes containing a C═N moiety are well-known in the literature, dating as far back as the works of Deeming and Adams in the late 1970s and early 1980s.[14,15] More recently, Rosenberg and co-workers reported the synthesis and transformation of a number of imidoyl-bridged triosmium clusters.[16] In comparison with those triosmium complexes containing the C═N moiety, the coordinated phosphinazine ligand in complex **1** is observed for the first time.

**Table 1.** Crystal Data and Refinement of ($\mu$-H)$Os_3(CO)_{10}$($\mu_2$-$\eta^2$-C(H)$NNPPh_3$) (**1**), ($\mu$-H)$Os_3(CO)_{10}$($\mu_2$-$\eta^1$-$CHPPh_3$) (**2**), and ($\mu$-H)$_3Os_3(CO)_9$($\mu_3$-$\eta^1$-$CCO_2CH_2Ph$) (**3**)

| | $C_{29}H_{17}N_2O_{10}Os_3P$ | $C_{29}H_{17}O_{10}Os_3P$ | $C_{36}H_{20}O_{22}Os_6$ |
|---|---|---|---|
| fw | 1155.00 | 1127.00 | 1945.67 |
| *T*, K | 293(2) | 293(2) | 293(2) |
| wavelength, Å | 0.71073 | 0.71073 | 0. 71073 |
| cryst syst | monoclinic | triclinic | triclinic |
| space group | *C*2/*c* | $P\bar{1}$ | $P\bar{1}$ |
| *a*, Å | 32.61(2) | 9.174(2) | 8.287(2) |
| *b*, Å | 13.157(2) | 11.905(2) | 14.998(3) |
| *c*, Å | 17.719(9) | 15.000(5) | 18.674(4) |
| α, deg | 90 | 84.56(2) | 90.10(2) |
| *β*, deg | 121.83(3) | 91.84(2) | 96.73(2) |
| *γ*, deg | 90 | 107.60(1) | 98.32(2) |
| *V*, $Å^3$ | 6458(5) | 1554.6(6) | 2280.3(9) |
| Z | 8 | 2 | 2 |
| $D_{calcd}$, g $cm^{-3}$ | 2.372 | 2.408 | 2.825 |
| $\mu$(Mo Kα), $mm^{-1}$ | 11.882 | 12.335 | 16.729 |
| *F*(000) | 4208 | 1028 | 1724 |
| cryst size, mm | 0.24, 0.21, 0.14 | 0.26, 0.22, 0.14 | 0.19, 0.38, 0.41 |
| no. measured reflns | 5686 | 5837 | 8621 |
| no. unique reflns | 5686 | 5461 | 8013 |
| no. obsd reflns | 4150 | 3766 | 5735 |
| R1[a] [$I > 2\sigma(I)$] | 0.0361 | 0.0419 | 0.0551 |
| wR2[a] [all data] | 0.0861 | 0.1217 | 0.1694 |
| GOF | 1.055 | 1.047 | 1.013 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma|F_o|[w(F_o^2)^2]\}^{1/2}$.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for ($\mu$-H)$Os_3(CO)_{10}$($\mu_2$-$\eta^2$-C(H)$NNPPh_3$) (**1**)

| Bond Distances | | | |
|---|---|---|---|
| Os1−Os2 | 2.868(1) | Os3−N1 | 2.098(6) |
| Os1−Os3 | 2.873(2) | Os3−C8 | 1.93(1) |
| Os1−C1 | 1.92(1) | Os3−C9 | 1.90(1) |
| Os1−C2 | 1.91(1) | Os3−C10 | 1.90(1) |
| Os1−C3 | 1.94(1) | P1−N2 | 1.596(7) |
| Os1−C4 | 1.93(1) | P1−C21 | 1.818(9) |
| Os2−Os3 | 2.923(2) | P1−C31 | 1.812(9) |
| Os2−C5 | 1.87(1) | P1−C41 | 1.800(9) |
| Os2−C6 | 1.88(1) | N1−N2 | 1.417(9) |
| Os2−C7 | 1.95(1) | N1−C11 | 1.28(1) |
| Os2−C11 | 2.097(9) | | |

| Bond Angles | | | |
|---|---|---|---|
| Os2−Os1−Os3 | 61.20(3) | Os2−C11−N1 | 114.0(6) |
| Os1−Os2−Os3 | 59.47(4) | Os2−Os3−C10 | 107.6(3) |
| Os1−Os2−C5 | 173.2(3) | N1−Os3−C8 | 87.5(3) |
| Os1−Os2−C11 | 88.5(2) | N1−Os3−C9 | 92.5(3) |
| Os3−Os2−C11 | 66.4(2) | N1−Os3−C10 | 174.1(4) |
| C5−Os2−C11 | 84.9(4) | Os3−N1−N2 | 120.7(5) |
| C6−Os2−C11 | 92.8(4) | Os3−N1−C11 | 112.0(6) |
| C7−Os2−C11 | 171.8(4) | N2−N1−C11 | 127.2(7) |
| Os1−Os3−Os2 | 59.33(4) | P1−N2−N1 | 118.2(5) |
| Os1−Os3−N1 | 90.8(2) | N2−P1−C21 | 114.1(4) |
| Os2−Os3−N1 | 67.3(2) | | |

**Spectroscopic Characterization and Crystal Structure of Complex 2.** The FAB mass spectrum of **2** showed a molecular ion peak at *m*/*z* 1133, with 28 fewer mass units compared to that of complex **1**. Hence, complex **1** was converted into complex **2** by the elimination of either a CO ligand or a $N_2$ molecule. The $^1H$ NMR spectrum of complex **2** showed a bridging hydride as a double-doublet centered at $\delta$ −16.67 ppm, another double-doublet resonance at $\delta$ 4.70 ppm integrating as one proton, and phenyl protons at $\delta$ 7.44−7.64. The triphenylphosphine group gives rise to a resonance at 47.77 ppm in the $^{31}P$ spectrum. A single crystal of **2** was obtained by recrystallization from chloroform. An ORTEP drawing from the X-ray analysis of complex **2** is shown in Figure 2, and the derived bond distances and angles are summarized in Table 3. The structure of **2** consists of a triangle of osmium atoms with one shorter edge (Os(2)−Os(3) = 2.811(1) Å) and two longer edges (Os(1)−Os(2) = 2.868(1) Å and Os(1)−Os(3) = 2.871(1) Å). An unidentified bridging atom, either a carbon or a nitrogen, is coordinated to two axial sites of the Os(2)−Os(3) vector. The X-ray structure could not fully differentiate whether this unidentified atom is a carbon or a nitrogen atom. However, an elemental analysis of complex **2** showed the conspicuous absence of nitrogen. The $^{13}C$ NMR spectrum of **2** is consistent with this unidentified bridging atom being a carbon, the chemical shift of which is $\delta$ −1.20 ppm, with a coupling constant of $J_{CP}$ = 25.2 Hz, indicating that carbon was bound to a $PPh_3$ group. The $^1H-^{13}C$ (HMQC) spectrum also indicated that this carbon was also bound to a proton, which resonated at $\delta$ 4.70 ppm. The $^1H$ NMR spectrum further confirmed the existence of this C−H bond, since this proton signal appeared as a double-doublet as the result of coupling with both the $PPh_3$ group ($J_{HP}$ = 6.9 Hz) and the bridging hydride ($J_{HH}$ = 4.2 Hz). This conclusion was confirmed by the heteronuclear $^1H-^{15}N$ (HMQC) spectrum, which shows no cross signals. These results indicate that complex **2** contains a unique phosphine-stabilized $\mu_2$-alkylidyne C(H)($PPh_3$) moiety, which is zwitterionic in

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**Table 3.** Selected Bond Distances (Å) and Angles (deg) for $(\mu\text{-H})Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-}CHPPh_3)$ (**2**)

Bond Distances

| | | | |
|---|---|---|---|
| Os1−Os2 | 2.868(1) | Os1−C1 | 1.93(2) |
| Os2−Os3 | 2.811(1) | Os1−C2 | 1.94(2) |
| Os3−Os1 | 2.871(1) | Os1−C3 | 1.88(2) |
| Os2−C40 | 2.17(1) | Os1−C4 | 1.89(2) |
| Os3−C40 | 2.15(1) | C5−O5 | 1.15(2) |
| Os2−C5 | 1.87(1) | C6−O6 | 1.11(2) |
| Os2−C6 | 1.95(2) | C7−O7 | 1.12(2) |
| Os2−C7 | 1.89(2) | C9−O9 | 1.13(2) |
| Os3−C8 | 1.86(2) | C10−O10 | 1.14(2) |
| Os3−C9 | 1.91(1) | C40−P | 1.75(1) |
| Os3−C10 | 1.91(2) | | |

Bond Angles

| | | | |
|---|---|---|---|
| Os(2)−C(40)−Os(3) | 80.8(5) | Os(2)−Os(1)−Os(3) | 58.64(2) |
| Os(2)−C(40)−P | 123.2(8) | C(9)−Os(3)−C(40) | 168.9(5) |
| Os(3)−C(40)−P | 129.3(9) | C(6)−Os(2)−C(40) | 165.5(5) |
| Os(1)−Os(2)−C(40) | 84.6(3) | Os(1)−Os(2)−C(7) | 175.9(4) |
| Os(1)−Os(3)−C(40) | 85.0(3) | Os(1)−Os(3)−C(10) | 176.6(4) |

nature. The P−C(40) distance (1.75(1) Å) is shorter than the lengths of the P−$CH_3$ single bond (1.83(3) and 1.84(2) Å) in two ylide complexes.[13,17,18] There are many phosphine-stabilized zwitterionic hydrocarbyl ligands in the literature.[19,20] The structure of **2** resembles that of the methylene cluster $(\mu\text{-H})(\mu\text{-CH}_2)Os_3(CO)_{10}$.[21]

The conversion of **1** to **2** occurred when a $CDCl_3$ solution of **1** was allowed to stand at room temperature, indicating that complex **1** is a reaction intermediate (eq 1). When complex **1** was heated in $CDCl_3$ at 40 °C and the progress of the reaction monitored by $^1H$ NMR spectroscopy,[22] complex **1** was converted to **2** in quantitative yield. The rate of this transformation obeys the first-order rate law, and the linear least-squares fits of log[**1**] versus time were used to obtain the rate constants at three different temperatures (40−55 °C). The first-order rate constants in $CDCl_3$ at 40, 50, and 55 °C are $3.95 \times 10^{-5}$, $1.74 \times 10^{-4}$, and $3.09 \times 10^{-4}$ $s^{-1}$, respectively. The activation energy, $E_a$, calculated from the Arrhenius plot is 28.1 kcal/mol. The key step of this transformation appears to involve the elimination of nitrogen to form the highly stabilized coordinated ylide moiety.

**Reactivity of Complex 2.** The thermolysis of **2** was carried out in refluxing toluene under nitrogen for 12 h. The $^1H$ NMR spectrum of the crude products indicated the presence of a number of species with hydride peaks at $\delta$ −12.07, −12.58, −12.72, −13.73, −14.96, −15.15, −19.37, −19.42 (major), and −19.83 ppm, demonstrating the complexity of the reaction. Chromatographic workup of the product permitted the isolation of a low yield of a colorless compound $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO_2CH_2Ph)$ (**3**) and some other unidentified byproducts (eq 2). The IR spectrum of **3** showed only two peaks in the C≡O stretching region indicating that the structure of this compound most likely is highly symmetrical.

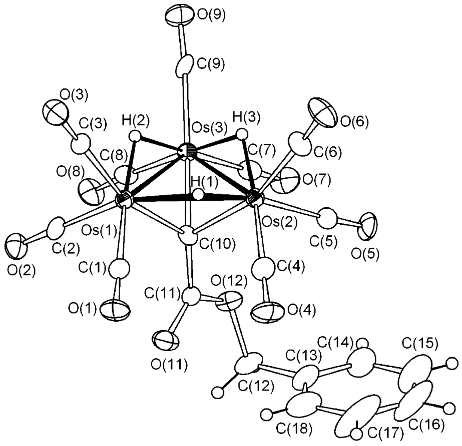


**Figure 3.** ORTEP diagram of $(\mu\text{-H})_3Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO_2CH_2Ph)$ (**3**).

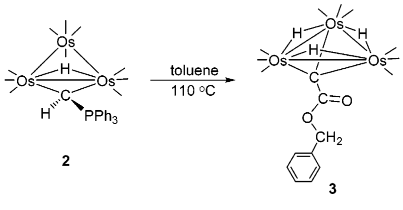
**Table 4.** Selected Bond Distances (Å) and Angles (deg) of $(\mu\text{-H})_3Os_3(CO)_{10}(\mu\text{-}CCO_2CH_2Ph)$ (**3**)

Bond Distances

| | | | |
|---|---|---|---|
| Os(1)−Os(2) | 2.876(1) | Os(1)−C(1) | 1.92(2) |
| Os(2)−Os(3) | 2.874(1) | Os(1)−C(2) | 1.91(2) |
| Os(3)−Os(1) | 2.890(1) | Os(1)−C(3) | 1.98(2) |
| Os(1)−C(10) | 2.07(2) | Os(2)−C(4) | 1.91(2) |
| Os(2)−C(10) | 2.09(2) | Os(2)−C(5) | 1.94(2) |
| Os(3)−C(10) | 2.10(2) | C(6)−O(6) | 1.11(2) |
| C(10)−C(11) | 1.44(2) | C(1)−O(1) | 1.13(2) |
| C(11)−O(11) | 1.22(2) | C(2)−O(2) | 1.14(2) |
| C(11)−O(12) | 1.36(2) | C(3)−O(3) | 1.12(2) |
| C(12)−O(12) | 1.48(2) | C(12)−C(13) | 1.46(3) |

Bond Angles

| | | | |
|---|---|---|---|
| Os(1)−Os(2)−Os(3) | 60.33(3) | Os(2)−Os(1)−Os(3) | 59.80(3) |
| Os(1)−Os(3)−Os(2) | 59.87(3) | Os(1)−C(10)−Os(3) | 87.7(7) |
| Os(1)−C(10)−Os(2) | 87.5(6) | Os(1)−C(10)−C(11) | 129(1) |
| C(10)−C(11)−O(11) | 126(2) | C(11)−O(12)−C(12) | 117(2) |



(2)

Although the $^{31}P$ NMR spectrum of **3** showed no resonance signals, surprisingly, its $^1H$ NMR spectrum showed aromatic protons at $\delta$ 7.43−7.24 ppm. The molecular structure of this compound was verified by an X-ray crystallographic method. An ORTEP diagram of **3** is shown in Figure 3, and the derived bond distances and angles are summarized in Table 4. The striking feature of the structure is the presence of a $\mu_3$-alkylidyne ligand where the symmetrically triply bridged $CCO_2CH_2Ph$ fragment is lying perpendicular to and above the triosmium triangle. The Os−C distances are as follows:

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Os(1)−C(10) = 2.07(2) Å, Os(2)−C(10) = 2.09(2) Å, and Os(3)−C(10) = 2.10(2) Å. On the basis of IR, $^1$H NMR, and mass analysis, there are three bridging hydrides appearing in the structure.

The FAB mass spectrum of **3** showed a molecular ion peak at *m*/*z* 974 and additional peaks at *m*/*z* 867, 838, 810, and 783 corresponding to the subsequent loss of one $PhCH_2O$ fragment and three CO ligands. In solution, the free rotation of C(10)−C(11) bond allows molecule **3** to attain a $C_{3v}$ symmetry, which explains the IR spectrum of **3**, which contains only two peaks in the CO stretching region. Shapley and Geoffroy reported that the thermally induced loss of carbon monoxide from $Os_3(CO)_{10}(\mu\text{-}CO)(\mu\text{-}CH_2)$ occurs, resulting in the formation of $(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}1,2\text{-}\eta^2\text{-}CCO)$.[23] These two species might be the reaction intermediates when complex **2** eliminated a $PPh_3$ group under refluxing conditions in toluene. The structure of compound **3** shows that two oxygen atoms are present in the triply bridged ligand $C{-}C(O)OCH_2Ph$. This suggests that when one of the carbonyls of **2** is bent and then reacts further, the reaction might eventually lead to the formation of compound **3** with the triply bridged ligand $C{-}C(O)OCH_2Ph$. However, the origin of the second oxygen remains unclear. Presumably, the formation of **3** requires a trace of water or $O_2$, since either of these could serve as the source of the second oxygen. At this stage we are not able to provide details of the reaction pathway. However, this reaction does produce an unprecedented complex with unusual coordination characteristics.

In summary, three novel triosmium complexes derived directly or indirectly from the reaction of $(\mu\text{-}H)_2Os_3(CO)_{10}$ with $CNNPPh_3$ were obtained. The products include the first example of a coordinated phosphinazine ligand (in **1**), a phosphine-stabilized $\mu_2$-alkylidyne (**2**), and a $\mu_3$-alkylidyne (**3**) formed via CO insertion, C−C coupling, and hydrogen migration.

## Experimental Section

**General Data.** The ligand $CNNPPh_3$ was prepared by a previously reported method.[3] Other reagents were purchased from commercial sources and were used as received. All manipulations were performed with standard Schlenk techniques. Solvents were dried by stirring over Na/benzophenone (*n*-octane) or $CaH_2$ (hexane, $CH_2Cl_2$, $CHCl_3$) and were freshly distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer PARAGON 1000 FT-IR spectrometer. NMR spectra were obtained on a Bruker ACP-300 or an AMX-500 FT-NMR spectrometer. Elemental analyses were performed by means of a Perkin-Elmer 2400 CHN elemental analyzer.

**Reaction of $H_2Os_3(CO)_{10}$ with $CNNPPh_3$.** Bubbling hydrogen through a refluxing solution of $Os_3(CO)_{12}$ (100.3 mg, 0.110 mmol) in *n*-octane (100 mL) resulted in a color change from yellow to deep red in 2 h. The solvent was removed under vacuum, and the residue was dissolved in $CH_2Cl_2$ (80 mL) and treated with a solution of $CNNPPh_3$ (36.3 mg 0.120 mmol) in $CH_2Cl_2$ (20 mL) at room temperature. The reaction was complete within seconds, and the color of the solution became yellow. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate. Elution with $CH_2Cl_2$/hexane (50:50) afforded a yellow compound $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}C(H)NNPPh_3)$ (**1**) in 59% yield (75.4 mg, 0.065 mmol) and a small amount of an orange complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CHPPh_3)$ (**2**) in 6% yield (7.2 mg, 6.4 μmol). Anal. Calcd for $C_{27}H_{17}N_2O_{10}POs_3$ (**1**): C, 30.16; H, 1.48; N, 2.43. Found: C, 29.95; H, 1.82; N, 2.31. IR ($CH_2Cl_2$): $\nu_{(CO)}$ 2101 (w), 2059 (s), 2048 (m), 2013 (vs), 1986 (m) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 8.82 (s, 1 H, CH), 7.50 (m, 15 H, Ph), −15.49 (s, 1 H, Os−H−Os) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ 184.58, 183.98, 179.08, 178.34, 175.94, 175.47 (2 CO), 175.01, 174.74, 174.39 (CO), 155.5 (d, $J_{CP}$ = 17.1 Hz, μ-CH═N), 132.8 (Ph), 132.6 (d, $J_{CP}$ = 10.5 Hz, Ph), 128.7 (d, $J_{CP}$ = 11.5 Hz, Ph), 126.9 (d, $J_{CP}$ = 93.5 Hz, Cipso, Ph) ppm. $^{31}$P NMR ($CDCl_3$): $\delta$ 8.09 ppm. Mass (FAB, Os$^{192}$): *m*/*z* 1161 ($M^+$), 1133 ($M^+ - CO$), 1105 ($M^+ - 2CO$), 1077 ($M^+ - 3CO$), 1049 ($M^+ - 4CO$), 1021 ($M^+ - 5CO$), 993 ($M^+ - 6CO$), 965 ($M^+ - 7CO$).

**Preparation of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-}CHPPh_3)$ (2).** Hydrogen was bubbled through a refluxing solution of $Os_3(CO)_{12}$ (150.6 mg, 0.166 mmol) in octane (130 mL) resulting in a color change from yellow to deep red in 2 h. The solvent was removed under vacuum, and the residue was dissolved in $CHCl_3$ (80 mL), treated with $CNNPPh_3$ (50.4 mg 0.167 mmol) in $CHCl_3$ (20 mL), and again refluxed. The reaction was stopped when the IR pattern changed in 2 h. The solvent was removed under vacuum, and the residue was chromatographed on a silica gel TLC plate. Elution with $CH_2Cl_2$/hexane (50:50) afforded an orange complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^1\text{-}CHPPh_3)$ (**2**) in 55% yield (102.9 mg, 0.091 mmol). For **2**: Calcd for $C_{29}H_{17}O_{10}Os_3P$: C, 30.91; H, 1.52. Found: C, 30.88; H, 1.61. IR ($CH_2Cl_2$): $\nu_{(CO)}$ 2089 (m), 2042 (vs), 2031 (m), 2003 (s), 1993 (s), 1956 (s) cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 7.44−7.64 (m, 15 H, Ph), 4.70 (dd, 1 H, CH, $J_{HP}$ = 6.9 Hz, $J_{HH}$ = 4.2 Hz), −16.67 (dd, 1 H, Os−H−Os, $J_{HH}$ = 4.2 Hz, $J_{HP}$ = 1.0 Hz) ppm. $^{13}$C NMR ($CDCl_3$): $\delta$ 189.2, 183.5, 177.8, 177.7, 177.3 (2CO), 176.6 (2CO), 173.9 (2CO), 134.0, 133.8, 133.1, 132.8, 129.6, 129.1, 129.0 (Ph), −1.20 (d, $J_{CP}$ = 25.2 Hz, μ-CHP) ppm. $^{31}$P NMR ($CDCl_3$): $\delta$ 47.77 ppm. Mass (FAB, Os$^{192}$): *m*/*z* 1133 ($M^+$), 1105 ($M^+ - CO$), 1077 ($M^+ - 2CO$), 1049 ($M^+ - 3CO$), 1021 ($M^+ - 4CO$).

**In-Situ $^1$H NMR Study on the Transformation of 1 to 2.** A solution of $(\mu\text{-}H)_2Os_3(CO)_{10}$ (25 mg, 0.029 mmol) in $CDCl_3$ (0.4 mL) in an NMR tube was treated with $CNNPPh_3$ (8.8 mg, 0.029 mmol) in $CDCl_3$ (0.2 mL). The reaction was monitored by $^1$H NMR spectroscopy at 313, 323, and 328 K. The spectral data showed that the complex $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}C(H)NNPPh_3)$ (**1**) was produced as the initial product, and then was slowly converted to $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}CHPPh_3)$ (**2**) in quantitative yield.

**Thermolysis of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}CHPPh_3)$ (2).** A solution of $(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}\eta^2\text{-}CHPPh_3)$ (**2**) (100 mg, 0.0887 mmol) in toluene (80 mL) was refluxed for 12 h, at which time the IR spectrum showed the disappearance of the characteristic bands of the precursor. The reaction was stopped, and the solvent was removed under vacuum. The $^1$H NMR spectrum of the crude products indicated the presence of a number of species with hydride peaks at $\delta$ −12.07, −12.58, −12.72, −13.73, −14.96, −15.15, −19.37, −19.42 (major), and −19.83 ppm, demonstrating the complexity of the reaction. The residue was chromatographed on a silica gel TLC plate. Elution with $CH_2Cl_2$/hexane (50:50) afforded colorless compound $(\mu\text{-}H)_3Os_3(CO)_9(\mu_3\text{-}\eta^1\text{-}CCO_2CH_2Ph)$ (**3**) in 9.3% yield (8 mg, 8.21 μmol). Several unidentified species (−12.58, −12.72, −14.96, −19.37 ppm) are eluted very close to compound **3**. Special care was thus taken to isolate the band corresponding to complex **3**. We were not able to assign the other peaks because of

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serious overlapping and the complexity of the spectrum. IR ($CH_2Cl_2$): $\nu_{(CO)}$ 2087 (s), 2026 (vs), 1668 (s, ester) $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.43−7.24 (m, 5H, Ph), 5.27 (s, 2H, OC*H*$_2$Ph), −19.42 (s, 3H, Os−H−Os) ppm. Mass (FAB, $Os^{192}$): *m*/*z* 978 ($M^+$), 871 ($M^+ - OCH_2Ph$), 843 ($M^+ - OCH_2Ph - CO$), 815 ($M^+ - OCH_2Ph - 2CO$), 787 ($M^+ - OCH_2Ph - 3CO$).

**Crystallographic Analysis.** Crystals of ($\mu$-H)$Os_3(CO)_{10}$($\mu_2$-$\eta^2$-CHNNPPh$_3$) (**1**) and ($\mu$-H)$Os_3(CO)_{10}$($\mu_2$-$\eta^1$-CHPPh$_3$) (**2**) were grown from a mixture of $CH_2Cl_2$ and hexane solutions at −20 °C. Specimens of suitable quality were mounted in a thin-walled glass capillary and used for measurement of precise cell constants and intensity data collection. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) with $\omega - 2\theta$ scan mode. Unit cells were determined and refined using 25 randomly selected reflections obtained using the CAD-4 automatic search, center, index, and least-squares routines. Lorentz/polarization (LP) and empirical absorption corrections were applied the data for these structures. The structures of **1**, **2**, and **3** were solved by direct methods and refined against $F^2$ by the full-matrix least-squares technique, using the WINGX[24] and SHELX[25] software packages.

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**Supporting Information Available:** Crystallographic files for compounds **1**−**3** in CIF format. $^1H$ NMR spectra showing the transformation of **1** into **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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