Inorg. Chem. 2005, 44, 6425-6430



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

Te-Wei Chiu,^{†,‡} Yen-Hsiang Liu,[†] Kai-Ming Chi,[‡] Yuh-Sheng Wen,[†] and Kuang-Lieh Lu^{*,†}

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan, and Department of Chemistry and Biochemistry, National Chung Cheng University, Chiayi 62, Taiwan

Received March 23, 2005

Three novel triosmium complexes with unusual coordination characteristics are reported. Treatment of the hydridotriosmium cluster $(\mu$ -H)₂Os₃(CO)₁₀ with CNNPPh₃ in CH₂Cl₂ gave complexes $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2$ - η^2 -C(H)-NNPPh₃) (1) and $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2$ - η^1 -CHPPh₃) (2). Complex 1 represents the first example of the existence of a coordinated phosphinazine ligand. An in-situ ¹H NMR study showed that the reaction of $(\mu$ -H)₂Os₃(CO)₁₀ with CNNPPh₃ 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 $(\mu$ -H)₃Os₃(CO)₉ $(\mu_3$ - η^1 -CCO₂CH₂Ph) (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 μ_3 -alkylidyne ligand where the symmetrically triply bridged CCO₂CH₂Ph 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

- Comprehensive Organometallic Chemistry II; Shriver, D. F., Bruce, M. I., Eds.; Elsevier Science Ltd.: Oxford, 1995; Vol. 7, pp 683– 834.
- (2) (a) Franz, J. A.; Kolwaite, D. S.; Linehan, J. C.; Rosenberg, E. Organometallics 1994, 13, 585. (b) Adams, R. D.; Qu, B.; Smith, M. D. Organometallics 1992, 11, 4847. (c) Yeh, W. Y.; Shiue, T. W.; Peng, S. M.; Lee, G. H. Organometallics 1993, 12, 2990. (d) Falloon, S. B.; Szafert, S.; Arif, A. M.; Gladysz, J. A. Chem. Eur. J. 1998, 4, 1033. (e) Deeming, A. J.; Stchedroff, M. J.; Whittaker, C.; Arce, A. J.; Sanctis, Y. D.; Steed, J. W. J. Chem. Soc., Dalton Trans. 1999, 3289. (f) Édwards, A. J.; Gallop, B. F. G.; Köhler, J. U.; Lewis, J.; Raithby, P. R. Angew. Chem., Int. Ed. Engl. **1994**, *33*, 1093. (g) Li, Y.; Wong, W. T. Dalton Trans. 2003, 398. (h) Bruce, M. L.; Humphrey, P. A.; Schmutzler, R.; Skelton, B. W.; White, A. H. J. Organomet. Chem. 2004, 689, 2415. (i) Su, M. D.; Liao, H. Y.; Chu, S. Y.; Chi, Y.; Liu, C. S.; Lee, F. J.; Peng, S. M.; Lee, G. H. Organometallics 2000, 19, 5400. (j) Morrison, E. D.; Geoffroy, G. L. J. Am. Chem. Soc. 1985, 107, 254. (k) Lavigne, G.; Kaesz, H. D. J. Am. Chem. Soc. 1984, 106, 4647. (1) Cherkas, A. A.; Taylor, N. J.; Carty, A. J. J. Chem. Soc., Chem. Commun. 1990, 385. (m) Johnson, B. F. G.; Lewis, J.; Pippard, D. A. J. Chem. Soc., Dalton Trans. 1981, 407. (n) Lu, K. L.; Chen, H. J.; Lu, P. Y.; Li, S. Y.; Hong, F. E.; Peng, S. M.; Lee, G. H. Organometallics 1994, 13, 585.

10.1021/ic0504310 CCC: \$30.25 © 2005 American Chemical Society Published on Web 08/04/2005

chemistry.² *N*-Isocyanoiminetriphenylphosphorane (CNNP-Ph₃) 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 CNNPPh₃ 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 CNNPPh₃ 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

- (3) (a) Weinberger, B.; Fehlhammer, W. P. Chem. Ber. 1985, 118, 42.
 (b) Weinberger, B.; Degel, F.; Fehlhammer, W. P. Chem. Ber. 1985, 118, 51.
- (4) Weinberger, B.; Fehlhammer, W. P. Angew. Chem., Int. Ed. Engl. 1980, 19, 480.
- (5) Fan, J. S.; Lee, F. Y.; Chiang, C. C.; Chen, H. C.; Liu, S. H.; Wen, Y. S.; Chang, C. C.; Li, S. Y.; Chi, K. M.; Lu, K. L. J. Organomet. Chem. 1999, 580, 82.
- (6) (a) Hahn, F. E.; Langenhahn, V.; Meier, N.; Lugger, T.; Fehlhammer, W. P. Chem. Eur. J. 2003, 9, 704. (b) Takahashi, T.; Tsai, F. Y.; Li, Y.; Nakajima, K. Organometallics 2001, 20, 4122. (c) Santos, A. M.; Romao, C. C.; Kuhn, F. E. J. Am. Chem. Soc. 2003, 125, 2414. (d) Aggarwal, V. K.; Fulton, J. R.; Sheldon, C. G.; de Vicente, J. J. Am. Chem. Soc. 2003, 125, 6034. (e) Santos, A. M.; Pedro, F. M.; Yogalekar, A. A.; Lucas, I. S.; Romao, C. C.; Kuhn, F. E. Chem. Eur. J. 2004, 10, 6313.
- (7) (a) Motoyama, Y.; Kawakami, H.; Shimozono, K.; Aoki, K.; Nishiyama, H. Organometallics 2002, 21, 3408. (b) Nair, V.; Rajesh, C.; Vinod, A. U.; Bindu, S.; Sreekanth, A. R.; Mathen, J. S.; Balagopal, L. Acc. Chem. Res. 2003, 36, 899.

Inorganic Chemistry, Vol. 44, No. 18, 2005 6425

^{*} To whom correspondence should be addressed. E-mail: lu@ chem.sinica.edu.tw.

[†] Academia Sinica.

[‡] National Chung Cheng University.

studies on the chemistry of metal isocyanide complexes,^{4,8,9} we have been interested in the reactivity of CNNPPh₃containing 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 CNNPPh₃ with the hydridotriosmium complex H₂Os₃(CO)₁₀. Their coordination modes are reported here for the first time.

Results and Discussion

Reaction of H₂Os₃(CO)₁₀ with CNNPPh₃. The purple hydridotriosmium cluster H₂Os₃(CO)₁₀ was prepared by bubbling hydrogen into a solution of Os₃(CO)₁₂ in refluxing *n*-octane over a 2 h period.¹¹ The H₂Os₃(CO)₁₀ produced was then dissolved in CH₂Cl₂ and treated with CNNPPh₃ at room temperature to afford a yellow complex, (μ -H)Os₃(CO)₁₀-(μ_2 - η^2 -C(H)NNPPh₃) (**1**), and a small amount of an orange complex, (μ -H)Os₃(CO)₁₀(μ_2 - η^1 -CHPPh₃) (**2**, eq 1).



The FAB mass spectrum of **1** showed a molecular ion peak at m/z 1161, which corresponds to an adduct of H₂Os(CO)₁₀ and CNNPPh₃. The ¹H NMR spectrum of **1** showed a bridging hydride peak at δ -15.49 ppm, phenyl proton signals in the δ 7.47–7.58 ppm region, and another proton signal at δ 8.82 ppm. In the ³¹P{¹H} NMR spectrum, the triphenyl phosphine group gave rise to a singlet at δ 8.09 ppm, demonstrating that the CNNPPh₃ is not coordinated to the osmium cluster in the terminal mode. [cf. the terminal CNNPPh₃ ligands in complexes ReBr(CO)₃(CNPh)(CNNPPh₃) and ReBr(CO)₃(CNPr)(CNNPPh₃) resonate at δ 32.36 and 32.14, respectively].⁵ The heteronuclear ¹H–¹³C (HMQC) spectrum showed that the proton at δ 8.82 was bound to the carbon atom (*C*NNPPh₃) at δ 155.5 ppm. These findings



Figure 1. ORTEP diagram of $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2$ - η^2 -C(H)NNPPh₃) (1).

indicate the reaction involves the insertion of an isocyanide into the metal-hydride bond.¹²

An X-ray structure analysis of 1 was undertaken to investigate the exact coordination characteristics of the CNNPPh3 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)NNPPh₃ moiety coordinate at two axial sites of the Os(2)–Os(3) vector forming a μ_2 - η^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 $(\mu$ -H)₂Os₃(CO)₁₀ with CNNPPh₃ 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 hydridotrios-mium cluster with an isocyanide ligand (CNR) forms adducts of the type H₂Os₃(CO)₁₀(CNR) (R = C₆H₅, Me, Bu^t).^{12a,b} Although we were unable to detect any reaction intermediates, we propose that the hydridotriosmium cluster reacts with CNNPPh₃ initially forming H₂Os₃(CO)₁₀(CNNPPh₃), and this reaction is followed by the insertion of isocyanide into the metal hydride to afford complex **1**. Other related triosmium

^{(8) (}a) Lu, K. L.; Chen, C. C.; Lin, Y. W.; Gau, H. M.; Hong, F. E.; Wen, Y. S. Organometallics **1993**, *12*, 2188. (b) Lu, K. L.; Chung, M. L.; Lu, P. Y.; Gau, H. M.; Hong, F. E.; Wen, Y. S. Organometallics **1994**, *13*, 3177. (c) Huang, J. Y.; Lin, K. J.; Chi, K. M.; Lu, K. L. J. Chem. Soc., Dalton Trans. **1997**, 15.

^{(9) (}a) Lu, K. L.; Lee, H. H.; Wang, C. M.; Wen, Y. S. Organometallics 1994, 13, 593. (b) Fan, J. S.; Lin, J. T.; Chang, C. C.; Chou, S. J.; Lu, K. L. Organometallics 1995, 14, 925. (c) Lee, F. Y.; Huang, J. J.; Chen, Y. J.; Lin, K. J.; Lee, G. H.; Peng, S. M.; Hwu, J. R.; Lu, K. L. J. Organomet. Chem. 2005, 690, 441.

^{(10) (}a) Takeda, N.; Kajiwara, T.; Suzuki, H.; Okazaki, R.; Tokitoh, N. *Chem. Eur. J.* **2003**, *9*, 3530. (b) Hahn, F. E.; Plumed, C. G.; Munder, M.; Lugger, T. *Chem. Eur. J.* **2004**, *10*, 6285.

^{(12) (}a) Adams, R. D.; Golembeski, N. M. J. Am. Chem. Soc. 1979, 101, 2579. (b) Adams, R. D.; Golembeski, N. M. Inorg. Chem. 1979, 18, 1909. (c) Tanase, T.; Ohizumi, T.; Kobayashi, K.; Yamamoto, Y. Organometallics 1996, 15, 3404. (d) Antinolo, A.; Carrillo-Hermosilla, F.; Fajardo, M.; Garcia-Yuste, S.; Otero, A.; Camanyes, S.; Maseras, F.; Moreno, M.; Lledos, A.; Lluch, J. M. J. Am. Chem. Soc. 1997, 119, 6107. (e) Visser, C.; van den Hende, J. R.; Meetsma, A.; Hessen, B.; Teuben, J. H. Organometallics 2001, 20, 1620. (f) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. Organometallics 2003, 22, 4084.

⁽¹³⁾ Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. Chem. Soc., Perkin Trans. 2 1987, S1.



Figure 2. ORTEP diagram of $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2$ - η^1 -CHPPh₃) (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.

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 N₂ molecule. The ¹H NMR spectrum of complex 2 showed a bridging hydride as a double-doublet centered at δ -16.67 ppm, another double-doublet resonance at δ 4.70 ppm integrating as one proton, and phenyl protons at δ 7.44– 7.64. The triphenylphosphine group gives rise to a resonance at 47.77 ppm in the ³¹P 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 ¹³C NMR spectrum of 2 is consistent with this unidentified bridging atom being a

(14) Yin, C. C.; Deeming, A. J. J. Organomet. Chem. 1977, 133, 123.

(15) Adams, R. D.; Katahira, D. A.; Yang, L. W. J. Organomet. Chem. 1981, 219, 85.

(16) (a) Day, M.; Espitia, D.; Hardcastle, K. I.; Kabir, S. E.; Rosenberg, E.; Gobetto, R.; Milone, L.; Osella, D. Organometallics **1991**, *10*, 3550.
(b) Kabir, S. E.; Rosenberg, E.; Day, M.; Hardcastle, K. I.; Irving, M. J. Cluster Sci. **1994**, *5*, 481. (c) Kabir, S. E.; Rosenberg, E.; Stetson, J.; Yin, M.; Ciurash, J.; Mnatsakanova, K.; Hardcastle, K. I.; Noorani, H.; Movsesian, N. Organometallics **1996**, *15*, 4473.

Table 1. Crystal Data and Refinement of	
$(\mu$ -H)Os ₃ (CO) ₁₀ $(\mu_2$ - η^2 -C(H)NNPPh ₃) (1),	
$(\mu-H)Os_3(CO)_{10}(\mu_2-\eta^1-CHPPh_3)$ (2), and $(\mu-H)$)
$_{3Os_{3}(CO)_{9}(\mu_{3}-\eta^{1}-CCO_{2}CH_{2}Ph)}$ (3)	

	C ₂₉ H ₁₇ N ₂ O ₁₀ Os ₃ P	C ₂₉ H ₁₇ O ₁₀ Os ₃ P	C ₃₆ H ₂₀ O ₂₂ Os ₆
fw	1155.00	1127.00	1945.67
Т, К	293(2)	293(2)	293(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	triclinic
space group	C2/c	P1	P1
<i>a</i> , Å	32.61(2)	9.174(2)	8.287(2)
b, Å	13.157(2)	11.905(2)	14.998(3)
<i>c</i> , 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
$D_{\rm calcd}$, g cm ⁻³	2.372	2.408	2.825
μ (Mo K α), 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

```
<sup>a</sup> R1 = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. wR2 = {\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum |F_{o}| [w(F_{o}^{2})^{2}]}<sup>1/2</sup>.
```

Table 2.	Selected	Bond	Distances	(Å)	and	Angles	(deg)	for
u-H)Os ₃ ($CO)_{10}(\mu_2 -$	η^2 -C(I	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)		
$\Omega s^2 - \Omega s^3 - N1$	(7, 2(2))				

carbon, the chemical shift of which is $\delta -1.20$ ppm, with a coupling constant of $J_{\rm CP} = 25.2$ Hz, indicating that carbon was bound to a PPh₃ group. The ¹H-¹³C (HMQC) spectrum also indicated that this carbon was also bound to a proton, which resonated at δ 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 PPh₃ group ($J_{\rm HP} = 6.9$ Hz) and the bridging hydride ($J_{\rm HH} = 4.2$ Hz). This conclusion was confirmed by the heteronuclear ¹H-¹⁵N (HMQC) spectrum, which shows no cross signals. These results indicate that complex **2** contains a unique phosphine-stabilized μ_{2} -alkylidyne C(H)(PPh₃) moiety, which is zwitterionic in

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(\mu$ -H)Os₃(CO)₁₀(μ ₂- η ¹-CHPPh₃) (**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–CH₃ single bond (1.83(3) and 1.84(2) Å) in two ylide complexes.^{13,17,18} There are many phosphinestabilized zwitterionic hydrocarbyl ligands in the literature.^{19,20} The structure of **2** resembles that of the methylene cluster (μ -H)(μ -CH₂)Os₃(CO)₁₀.²¹

The conversion of **1** to **2** occurred when a CDCl₃ 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 CDCl₃ 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 CDCl₃ at 40, 50, and 55 °C are 3.95×10^{-5} , 1.74×10^{-4} , and 3.09×10^{-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 δ

- (17) Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernandez-Baeza, J.; Jones, P. G.; Sheldrick, G. M.; Espinet, P. J. Chem, Soc., Dalton Trans. 1985, 1163.
- (18) (a) Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. Organometallics 1983, 2, 1336. (b) Fuchs, A.; Gudat, D.; Nieger, M.; Schmidt, O.; Sebastian, M.; Nyulaszi, L.; Niecke, E. Chem. Eur. J. 2002, 8, 2188. (c) Falvello, L. R.; Llusar, R.; Margalejo, M. E.; Navarro, R.; Urriolabeitia, E. P. Organometallics 2003, 22, 1132.
- (19) (a) Cherkas, A. A.; Doherty, S.; Cleroux, M.; Hogarth, G.; Randall, L. H.; Breckenridge, S. M.; Taylor, N. J.; Carty, A. J. *Organometallics* **1992**, *11*, 1701. (b) Mott, G. N.; Carty, A. J. *Inorg. Chem.* **1983**, *22*, 2726.
- (20) (a) Sanctis, Y. D.; Arce, A. J.; Ganavera, F.; Machado, R.; Deeming, A. J.; Gonzalez, T.; Galarza, E. J. Organomet. Chem. 2004, 689, 2025.
 (b) Arce, A. J.; Machado, R.; Sanctis, Y. D.; Capparelli, M. V.; Atencio, R.; Manzur, J.; Deeming, A. J. Organometallics 1997, 16, 1735.
- (21) Schultz, A. J.; Williams, J. M.; Calvert, R. B.; Shapley, J. R.; Stucky, G. D. Inorg. Chem. 1979, 18, 319.
- (22) Uedelhoven, W.; Neugebauer, D.; Kreissl, F. R. J. Organomet. Chem. 1981, 217, 183.



Figure 3. ORTEP diagram of $(\mu$ -H)₃Os₃(CO)₉ $(\mu_3$ - η^1 -CCO₂CH₂Ph) (3).

Table 4. Selected Bond Distances (Å) and Angles (deg) of $(\mu$ -H)₃Os₃(CO)₁₀(μ -CCO₂CH₂Ph) (**3**)

	Bond D	istances	
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)
	D 1		
	Bond A	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)

-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 (μ-H)₃Os₃(CO)₉(μ₃-η¹-CCO₂CH₂Ph) (**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.



Although the ³¹P NMR spectrum of **3** showed no resonance signals, surprisingly, its ¹H NMR spectrum showed aromatic protons at δ 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 μ_3 -alkylidyne ligand where the symmetrically triply bridged CCO₂CH₂Ph fragment is lying perpendicular to and above the triosmium triangle. The Os–C distances are as follows:

Novel Osmium Azine and Ylide Complexes

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, ¹H 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 PhCH₂O 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 $Os_3(CO)_{10}(\mu$ -CO)(μ -CH₂) occurs, resulting in the formation of $(\mu-H)_2Os_3(CO)_9(\mu_3-1,2-\eta^2-\eta_3)$ 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 $(\mu$ -H)₂Os₃(CO)₁₀ with CNNPPh₃ were obtained. The products include the first example of a coordinated phosphinazine ligand (in 1), a phosphine-stabilized μ_2 -alkylidyne (2), and a μ_3 -alkylidyne (3) formed via CO insertion, C–C coupling, and hydrogen migration.

Experimental Section

General Data. The ligand CNNPPh₃ 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 CaH₂ (hexane, CH₂Cl₂, CHCl₃) 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 H₂**Os**₃**(CO)**₁₀ with CNNPPh₃. Bubbling hydrogen through a refluxing solution of Os₃(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 CH₂Cl₂ (80 mL) and treated with a solution of CNNPPh₃ (36.3 mg 0.120 mmol) in CH₂Cl₂ (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 CH₂Cl₂/hexane (50:50) afforded a yellow compound $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2-\eta^2$ -C(H)NNPPh₃) (1) in 59% yield (75.4 mg, 0.065 mmol) and a small amount of an orange complex (µ-H)Os₃(CO)₁₀(µ-CHPPh₃) (2) in 6% yield (7.2 mg, 6.4 µmol). Anal. Calcd for C₂₇H₁₇N₂O₁₀POs₃ (1): C, 30.16; H, 1.48; N, 2.43. Found: C, 29.95; H, 1.82; N, 2.31. IR (CH₂Cl₂): v_(CO) 2101 (w), 2059 (s), 2048 (m), 2013 (vs), 1986 (m) cm⁻¹. ¹H NMR (CDCl₃): δ 8.82 (s, 1 H, CH), 7.50 (m, 15 H, Ph), -15.49 (s, 1 H, Os-H-Os) ppm. ¹³C NMR (CDCl₃): δ 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. ³¹P NMR (CDCl₃): δ 8.09 ppm. Mass (FAB, Os¹⁹²): 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 $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2 - \eta^1$ -CHPPh₃) (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 CHCl3 (80 mL), treated with CNNPPh₃ (50.4 mg 0.167 mmol) in CHCl₃ (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 CH2-Cl₂/hexane (50:50) afforded an orange complex $(\mu$ -H)Os₃(CO)₁₀- $(\mu_2 - \eta^1$ -CHPPh₃) (2) in 55% yield (102.9 mg, 0.091 mmol). For 2: Calcd for C₂₉H₁₇O₁₀Os₃P: C, 30.91; H, 1.52. Found: C, 30.88; H, 1.61. IR (CH₂Cl₂): v_(CO) 2089 (m), 2042 (vs), 2031 (m), 2003 (s), 1993 (s), 1956 (s) cm^{-1.1}H NMR (CDCl₃): δ 7.44–7.64 (m, 15 H, Ph), 4.70 (dd, 1 H, CH, $J_{\text{HP}} = 6.9$ Hz, $J_{\text{HH}} = 4.2$ Hz), -16.67 (dd, 1 H, Os-H-Os, $J_{\rm HH}$ = 4.2 Hz, $J_{\rm HP}$ = 1.0 Hz) ppm. ¹³C NMR (CDCl₃): δ 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. ³¹P NMR (CDCl₃): δ 47.77 ppm. Mass (FAB, Os¹⁹²): *m*/*z* 1133 (M⁺), 1105 (M⁺ - CO), 1077 $(M^+ - 2CO)$, 1049 $(M^+ - 3CO)$, 1021 $(M^+ - 4CO)$.

In-Situ ¹H NMR Study on the Transformation of 1 to 2. A solution of $(\mu$ -H)₂Os₃(CO)₁₀ (25 mg, 0.029 mmol) in CDCl₃ (0.4 mL) in an NMR tube was treated with CNNPPh₃ (8.8 mg, 0.029 mmol) in CDCl₃ (0.2 mL). The reaction was monitored by ¹H NMR spectroscopy at 313, 323, and 328 K. The spectral data showed that the complex $(\mu$ -H)Os₃(CO)₁₀(μ ₂- η ²-C(H)NNPPh₃) (1) was produced as the initial product, and then was slowly converted to $(\mu$ -H)Os₃(CO)₁₀(μ ₂- η ²-CHPPh₃) (2) in quantitative yield.

Thermolysis of $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2 - \eta^2$ -CHPPh₃) (2). A solution of $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2$ - η^2 -CHPPh₃) (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 ¹H NMR spectrum of the crude products indicated the presence of a number of species with hydride peaks at δ -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 CH₂Cl₂/hexane (50:50) afforded colorless compound $(\mu$ -H)₃Os₃(CO)₉ $(\mu_3$ - η^1 -CCO₂CH₂Ph) (3) in 9.3% yield (8 mg, 8.21 μ mol). 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

^{(23) (}a) Sievert, A. C.; Srickland, D. S.; Shapley, J. R.; Steinmentz, G. R.; Geoffroy, G. L. Organometallics **1982**, *1*, 214. (b) Shapley, J. R.; Srickland, D. S.; St. George, G. N.; Churchill, M. R.; Bueno, C. Organometallics **1983**, *2*, 185.

serious overlapping and the complexity of the spectrum. IR (CH₂-Cl₂): $\nu_{(CO)}$ 2087 (s), 2026 (vs), 1668 (s, ester) cm⁻¹. ¹H NMR (CDCl₃): δ 7.43–7.24 (m, 5H, Ph), 5.27 (s, 2H, OCH₂Ph), -19.42 (s, 3H, Os–H–Os) ppm. Mass (FAB, Os¹⁹²): *m/z* 978 (M⁺), 871 (M⁺ – OCH₂Ph), 843 (M⁺ – OCH₂Ph – CO), 815 (M⁺ – OCH₂-Ph – 2CO), 787 (M⁺ – OCH₂Ph – 3CO).

Crystallographic Analysis. Crystals of $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2-\eta^2$ -CHNNPPh₃) (1) and $(\mu$ -H)Os₃(CO)₁₀ $(\mu_2-\eta^1$ -CHPPh₃) (2) were grown from a mixture of CH₂Cl₂ 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 K α 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 WINGX²⁴ and SHELX²⁵ software packages.

Acknowledgment. We thank Academia Sinica and the National Science Council of Taiwan for financial support.

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.

IC050431O

⁽²⁴⁾ Farrugia, L. J. J. Appl. Crystallogr. 1999, 32, 837.

⁽²⁵⁾ Sheldrick, G. M. SHELX-97 (including SHELXS and SHELXL); University of Gottingen: Gottingen, Germany, 1997.