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# 2-[(Diphenylphosphino)methyl]-6-methylpyridine (PN) coordination chemistry at triosmium clusters: Regiospecific ligand activation and DFT evaluation of the isomeric $Os_3(CO)_{10}(PN)$ clusters



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This paper is dedicated to our colleague Professor W.A. Herrmann on the occasion of his 65th birthday. Herzlichen Glückwunsch zum Geburtstag!

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## ABSTRACT

The reaction of 2-[(diphenylphosphino)methyl]-6-methylpyridine (PN) with Os<sub>3</sub>(CO)<sub>12-n</sub>(MeCN)<sub>n</sub> [where n = 0 (1), 1 (2), 2 (3)] has been investigated. Os<sub>3</sub>(CO)<sub>12</sub> reacts with PN in the presence of Me<sub>3</sub>NO to afford the clusters  $Os_3(CO)_{11}(\kappa^1-PN)$  (4) and  $1,2-Os_3(CO)_{10}(\kappa^1-PN)_2$  (5). X-ray diffraction analyses confirm the equatorial coordination of the phosphine(s) in 4 and 5, with the two phosphines in the latter cluster exhibiting a 1,2-trans orientation about the Os-Os vector that contains the two ligands. Treatment of the MeCN-substituted cluster Os<sub>3</sub>(CO)<sub>11</sub>(MeCN) and PN (1:1 ratio) in CH<sub>2</sub>Cl<sub>2</sub> gives clusters 4 and 5, in addition to HOs<sub>3</sub>( $\eta^1$ -Cl)(CO)<sub>10</sub>( $\kappa^1$ -PN) (**6**) as a result of competitive activation of the reaction solvent. Cluster 6 contains 48e and the diffraction structure reveals the presence of axial chloride and equatorial phosphine ligands which are located on adjacent osmium atoms. The bridging hydride ligand in 6 spans the Cl,P-substituted Os-Os vector. The reaction of Os<sub>3</sub>(CO)<sub>10</sub>(MeCN)<sub>2</sub> with PN furnishes 5, 6, and 1,1- $Os_3(CO)_{10}(\kappa^2-PN)$  (7) in yields that are dependent on the reagent stoichiometry and reaction solvent. The solid-state structure of 7 confirms the chelation of the PN ligand to a single osmium atom via the pyridine and phosphine moieties at axial and equatorial sites, respectively. The bonding in 7 relative to other possible stereoisomers has been explored by DFT calculations, and the diffraction structure is computed as the thermodynamically most stable form of this cluster. Cluster 4 is photosensitive and CO loss gives 7, in addition to the formation of the dihydride H<sub>2</sub>Os<sub>3</sub>(CO)<sub>8</sub>[µ-CH(NC<sub>5</sub>H<sub>3</sub>)CH<sub>2</sub>PPh<sub>2</sub>] (8), whose origin derives from the double metalation of the C-6 methyl group of the PN ligand in 7. Photolysis of 7 yields 8 without detectable observation of the expected intermediate hydride  $HOs_3(CO)_9[\mu-CH_2(NC_5H_3)]$ CH<sub>2</sub>PPh<sub>2</sub>]. The PN ligand in 7 undergoes P–C bond activation in toluene at 110 °C to afford the 50e cluster  $Os_3(CO)_9(\mu-C_6H_4)(\mu-PPh)$  (9), which contains face-capping benzyne and phosphinidene moieties. The bonding between the benzyne moiety and the opened Os<sub>3</sub> frame in 9 has been examined computationally, and these data are discussed relative to  $\sigma$  and  $\pi$  bonding contributions from the metalated aryl ring to the cluster polyhedron.

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## 1. Introduction

Bidentate compounds that contain both phosphorus and nitrogen donors have been extensively investigated as ligand auxiliaries in a variety of important catalytic transformations [1]. Additional interest in such hard-soft ligand combinations stems from their potential hemilabile behavior and the inherent regio- and stereochemical asymmetry that the two different pnictogen donors impart to a transition metal(s) upon coordination. Of the many different phosphorus—nitrogen-based ligand systems known, 2-(diphenylphosphino)pyridine (dpppy) represents one of the forerunners in this genre of bidentate ligands, and the ability of dpppy to bind a single metal (chelate) and tether adjacent metals (bridge) in polynuclear compounds is well documented. The plethora of reactivity and structural reports underscores the early popularity and importance of this particular compound as a ligand [2]. The high rigidity and short bite angle in dpppy severely limit its coordinative flexibility in reactions with metal clusters. And chelation of a single metal center in a polynuclear cluster by dpppy is rare compared to the bridging of adjacent metal centers observed in the majority of structurally characterized clusters containing this ligand [3].

Increasing the flexibility of the backbone in dpppy through the inclusion of one extra carbon spacer has been examined. Here



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researchers have investigated 2-(diphenylphosphinomethyl)pyridine (dppmp) in order to study the effect that a saturated methylene moiety imparts on the coordinative flexibility and chemical reactivity vis-à-vis dpppy. Dppmp is easily synthesized from 2picoline and Ph<sub>2</sub>PCl (Eq. (1)), and numerous derivatives have been prepared through modification of this protocol [4]. As a ligand dppmp can function as both a chelating and bridging ligand with mononuclear and simple dinuclear metal compounds. However, to our knowledge no structurally characterized examples containing dppmp-substituted polynuclear metals exist, and questions concerning bonding preference and chemical stability of this ligand at polynuclear metal clusters remain unanswered.



Given our interest in the fluxionality and reactivity of diphosphine and diimine ligands at Os<sub>3</sub> clusters [5], we wished to examine the reactivity of a suitable bidentate phosphorus-nitrogen donor with  $Os_3(CO)_{12-n}(MeCN)_2$  [n = 0 (**1**), n = 1 (**2**), 2 (**3**)]. A mixed phosphorus-nitrogen donor would allow us to study the synergistic and regiochemical aspects related to the mode of ligand coordination in the Os<sub>3</sub> product(s) and bond activation of the mixed ligand upon thermolysis and photolysis. While many potential phosphorus-nitrogen donor candidates for study exist, recent reports on 2-[(diphenylphosphino)methyl]-6-methylpyridine (PN) as a ligand with mononuclear ruthenium and rhodium compounds stand out [6]. The resulting PN-substituted products were shown to exhibit extremely high turnover numbers in the transfer hydrogenation of acetophenone by 2-propanol and the ROMP of norbornene. Herein we report our results on the reaction of the mixed pnictogen 2-[(diphenylphosphino)methyl]-6-methylpyridine (PN) with a series of triomsium clusters. This particular PN compound was chosen as a ligand for study because its coordination at an intact metal cluster, which has not previously explored, would allow us to probe for possible cluster-promoted regioselective bond activation of the methyl and phenyl substituents in PN.

## 2. Experimental section

#### 2.1. Materials and equipment

 $Os_3(CO)_{12}$  (1) was synthesized from  $OsO_4$  and CO in a Parr Series 4560 autoclave (450 mL capacity) [7], and the parent cluster was used as the starting material for the preparation of  $Os_3(CO)_{11}(MeCN)$  (2), and  $Os_3(CO)_{10}(MeCN)_2$  (3) [8]. The 2-[(diphenylphosphino)methyl]-6-methylpyridine (PN) employed in our studies was prepared from 2,6-lutidine and Ph<sub>2</sub>PCl according to the procedure of Lugan and Lavigne [6c].  $OsO_4$  was purchased from Electron Microscopy Sciences, and the organic chemicals  $Me_3NO \cdot xH_2O$ , Ph<sub>2</sub>PCl, 2,6-lutidine, and BuLi (2.5 M in hexanes) were obtained from Aldrich Chemical Co. With the exception of the Me<sub>3</sub>NO  $\cdot xH_2O$  that was azeotropically dried using benzene solvent, all other starting reagents were used as received. The reaction solvents were obtained from an Innovative Technology (IT) solvent purification system or were distilled under argon from a suitable drying agent prior to use [9]. All NMR solvents were purchased from Cambridge Isotope Laboratories; the aromatic solvent  $C_6D_6$  was purified by bulb-to-bulb distillation from sodium/benzophenone ketyl while the CDCl<sub>3</sub> was distilled in a similar fashion from  $P_2O_5$ . The photolysis experiments were performed at 366 nm ( $\pm 20$  nm) using GE blacklight bulbs or at 254 nm using a high-pressure mercury lamp (200 W) that was configured to an Oriel 68805 universal power supply; the latter photolyses were conducted in quartz NMR tubes that were equipped with a J-Young valve. The combustion analyses were performed by Atlantic Microlabs, Norcross, GA.

## 2.2. Instrumentation

The IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer, and the <sup>1</sup>H NMR spectra were recorded at 400 or 500 MHz on Varian VNMRS-400 and VNMRS-500 spectrometers, respectively. The reported <sup>1</sup>H assignments were corroborated through the use of COSY, HMQC, HMBC, and NOESY pulse sequences. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on the latter spectrometer at 202 MHz and are referenced to external H<sub>3</sub>PO<sub>4</sub> (85%), whose chemical shift was set at  $\delta = 0$ . The ESI-APCI mass spectrum was recorded at the UC San Diego mass spectrometry facility in the positive ionization mode.

## 2.3. Synthesis of 4 and 5 from 1 and PN

To 0.10 g (0.11 mmol) of **1** in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> under argon was added 32 mg (0.11 mmol) of PN, followed by 17 mg (0.22 mmol) of Me<sub>3</sub>NO. The reaction solution was stirred overnight at room temperature and then examined by TLC analysis (1:1 Et<sub>2</sub>O/hexane), which revealed the presence of clusters **4** ( $R_f = 0.48$ ) and **5** ( $R_f = 0.30$ ), in addition to unreacted **1**. The two products were subsequently isolated by column chromatography over silica gel using the aforementioned solvent system, after which both products were recrystallized from benzene/CH<sub>2</sub>Cl<sub>2</sub> (**4**) and hexane/CH<sub>2</sub>Cl<sub>2</sub> (**5**). The spectroscopic data for all new products are summarized in Table 1. Yield **4**: 40% (52 mg). Anal. Calcd (found) for C<sub>30</sub>H<sub>18</sub>NO<sub>11</sub>Os<sub>3</sub>P·3/4benzene: C, 33.70 (33.45); H, 1.83 (2.14). Yield **5**: 30% (47 mg). Anal. Calcd (found) for C<sub>48</sub>H<sub>36</sub>N<sub>2</sub>O<sub>10</sub>Os<sub>3</sub>P<sub>2</sub>: C, 40.22 (40.14); H, 2.53 (2.57).

#### 2.4. Synthesis of 4, 5, and 6 from 2 and PN

To a medium Schlenk tube under argon flush was added 0.15 g (0.16 mmol) of **2** and 50 mL of CH<sub>2</sub>Cl<sub>2</sub>, followed by the addition of 48 mg (0.16 mmol) of PN. The solution was stirred for 1.5 h at room temperature and then examined by TLC analysis using 1:1 Et<sub>2</sub>O/ hexane as the eluent. The presence of **4** (major) and **5** (minor) was noted, along with a third slower moving spot at  $R_f = 0.21$  corresponding to cluster **6**. The three products were isolated by column chromatography and recrystallized from hexane/CH<sub>2</sub>Cl<sub>2</sub>. The yield for clusters **4** and **5** was 50% (95 mg) and 20% (47 mg), respectively. Yield of **6**: 15 mg (8%). Anal. Calcd (found) for C<sub>29</sub>H<sub>19</sub>ClNO<sub>10</sub>Os<sub>3</sub>P·1/2hexane: C, 31.43 (31.98); H, 2.13 (2.28). Repeating this reaction using toluene as the solvent furnished only **4** (50%) and **5** (25%).

#### 2.5. Reaction of 3 with PN

#### 2.5.1. Reaction of 3 and PN in toluene

To 0.10 g (0.11 mmol) of **3** in 25 mL of toluene was added dropwise, through the use of a syringe pump, 31 mg (0.11 mmol) of PN dissolved in 5 mL of toluene. The reaction mixture was stirred at room temperature for 2 h, after which time TLC examination (7:3 Et<sub>2</sub>O/hexane) revealed the presence of starting cluster, **5**, and **7** (major product) as the only mobile materials. Attempts to purify **7** 

Table 1

S	nectrosco	nic	data	for	the	clusters	4-	_g a
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Cluster	IR, $cm^{-1}$	<sup>1</sup> H NMR, δ	$^{31}$ P NMR, $\delta$
4	2106 (m), 2053 (s), 2034 (m),	2.35 (3H, s, Me), 4.13 (2H, d, CH <sub>2</sub> , <sup>2</sup> J <sub>P-H</sub> = 11 Hz),	-4.93
	2017 (vs), 1996 (m), 1986 (m),	6.04 (1H, d, py H <sub>3</sub> , ${}^{3}J_{H-H} = 7.5$ Hz),	
	1777 (sh, m)	6.88 (1H, d, py $H_{5}$ , ${}^{3}J_{H-H} = 7.5 Hz$ ),	
		7.15 (1H, t, py H <sub>4</sub> , ${}^{3}J_{H-H} = 7.5$ Hz),	
		7.35–7.48 (10 H, m, aryl)	
5 <sup>b</sup>	2084 (m), 2027 (s), 2011 (sh, m),	2.31 (6H, s, Me), 4.08 (4H, broad, CH <sub>2</sub> ),	-10.13, -6.59,
	1997 (vs), 1964 (b, m)	6.05 (2H, broad singlet, py, $H_3$ ),	-5.24
		6.83 (2H, d, py $H_5$ , ${}^3J_{H-H} = 7.5 Hz$ ),	
		7.09 (2H, t, py H <sub>4</sub> , ${}^{3}\!J_{\rm H-H} =$ 7.5 Hz),	
		7.35 (6 H, broad, aryl), 7.45 (4 H, broad, aryl)	
6	2114 (m), 2078 (s), 2063 (s),	$-16.11$ (1H, d, hydride, ${}^{2}J_{P-H} = 11$ Hz),	-6.36
	2030 (vs), 2020 (sh, s), 1976 (b, m)	2.38 (3H, s, Me), 4.39 (2H, m, CH <sub>2</sub> ),	
		6.22 (1H, d, py H <sub>3</sub> , ${}^{3}J_{H-H} = 8$ Hz),	
		7.95 (1H, d, py H <sub>5</sub> , ${}^{3}J_{H-H} = 8$ Hz),	
		7.25 (1H, t, py H <sub>4</sub> , ${}^{3}J_{H-H} = 8$ Hz),	
		7.45—7.62 (10 H, m, aryl)	
7	2087 (m), 2044 (sh, m), 2037 (s),	3.11 (3H, s, Me),	22.57
	2000 (b, vs), 1987 (sh, s), 1970 (sh),	4.47 (1H, dd, CH <sub>2</sub> , ${}^{2}J_{P-H} = 16$ Hz, ${}^{2}J_{H-H} = 8$ Hz),	
	1950 (b, m), 1928 (sh, w), 1906 (sh)	5.21 (1H, t, CH <sub>2</sub> , ${}^{2}J_{P-H} = 8$ Hz, ${}^{2}J_{H-H} = 8$ Hz),	
		6.98 (4H, m, aryl), 7.33 (1H, d, py, ${}^{3}\!J_{\rm H-H} = 8$ Hz),	
		7.52 (2H, m, aryl), 7.55 (1H, d, py, ${}^{3}J_{H-H} = 8$ Hz),	
		7.60 (1H, t, py H <sub>4</sub> , ${}^{3}J_{H-H} = 8$ Hz),	
		7.78 (4H, m, aryl)	
8 <sup>c</sup>	2087 (s), 2044 (s), 2005 (vs),	-14.21 (1H, s, hydride),	20.62
	1987 (m), 1953 (m)	$-13.14$ (1H, d, hydride, ${}^{2}J_{P-H} = 9$ Hz),	
		2.70 (1H, dd, CH <sub>2</sub> , ${}^{2}J_{H-H} = 16$ Hz, ${}^{2}J_{P-H} = 5.2$ Hz),	
		3.50 (1H, dd, CH <sub>2</sub> , ${}^{2}J_{H-H} = 16$ Hz, ${}^{2}J_{P-H} = 12.8$ Hz),	
		5.49 (1H, s, benzylidene CH),	
		5.94 (1H, d, py H <sub>3</sub> , ${}^{3}J_{H-H} = 7.6$ Hz),	
		6.24 (1H, d, py H <sub>5</sub> , ${}^{3}J_{H-H} = 7.6$ Hz),	
		6.61 (1H, t, py H <sub>4</sub> , ${}^{3}J_{H-H} = 7.6$ Hz),	
		6.83–7.05 (8H, m, aryl), 7.47–7.53 (2H, m, aryl)	
9	2065 (vs), 2042 (s), 2007 (s),	7.09 (2H, m, benzyne),	221.45
	1990 (m), 1968 (sh, w), 1942 (sh, w)	7.41 (3H, m, PPh aryl),	
		7.60 (4H, m, PPh aryl and benzyne)	

<sup>a</sup> All IR spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub> and the NMR spectra recorded in CDCl<sub>3</sub> at room temperature, unless otherwise noted.

<sup>b 31</sup>P NMR spectrum recorded at 333 K in CDCl<sub>3</sub>.

<sup>c</sup> NMR spectra recorded in C<sub>6</sub>D<sub>6</sub>.

by column chromatography were accompanied by excessive decomposition with isolated yields <5%. Cluster **5** was the major species isolated by chromatography, and the yield of **5** after recrystallization was 46 mg (30% yield). Repeating the reaction with a twofold excess of PN relative to **3** did not significantly increase the yield of the chelate cluster **7**. Here **5** (61 mg; 40%) was again isolated as the major after chromatography, followed by recrystallization.

## 2.5.2. Reaction of **3** and PN in $CH_2Cl_2$

This experiment was carried out exactly as described above (1:1 stoichiometry) except for the use of  $CH_2Cl_2$  as the reaction solvent. The reaction solution was examined after 1 h by TLC, to reveal the presence of the PN-substituted clusters **5** (25%), **6** (40%), and **7** (5%), and the known cluster HOs<sub>3</sub>( $\mu$ -Cl)(CO)<sub>10</sub> (10%) [10]; the identity of the latter cluster was confirmed by TLC and <sup>1</sup>H NMR comparisons against an independently prepared sample of this cluster. Increasing the PN amount twofold relative to **3** afforded the disubstituted cluster **5** (40%), **6** (5%), and a trace amount of **7**.

#### 2.6. Preparation of 7 from 4 and Me<sub>3</sub>NO

To 0.15 g (0.13 mmol) of **4** in a medium Schlenk tube was added 50 mL of toluene via cannula, followed by the addition of 12 mg (0.16 mmol) of  $Me_3NO$ . The vessel was sealed and the solution was stirred overnight at room temperature. TLC examination of the reaction solution the following day confirmed the presence of **7** as the principal product, in addition to a small amount of material that remained at the origin of the TLC plate. The IR spectrum of the solution before purification was in concert with the desired

product, which was subsequently purified by recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> to give **7** as a yellow solid in 45% yield (66 mg). ESI-MS: m/z 1165.53 [M + Na]<sup>+</sup>, and ions for the loss of 1–3 CO molecules.

## 2.7. Synthesis of 8 from the photochemical activation of 7

To a 5 mm NMR tube equipped with a J-Young valve was added 50 mg (0.044 mmol) of **7** and 0.7 mL of  $C_6D_6$ . The tube was sealed and the contents were evacuated by three freeze–pump–thaw degas cycles, after which the NMR tube was irradiated at 366 nm. The progress of the reaction was monitored by NMR spectroscopy, with complete consumption of the starting cluster and formation of **8** achieved after several days. The solvent was removed and the crude product taken up in hexane and placed in the freezer at 5 °C in order to induce crystallization. **8** was isolated as a yellow solid in 90% yield (48 mg). Anal. Calcd (found) for  $C_{27}H_{18}NO_8Os_3P$  hexane: C, 33.79 (34.00); H, 2.73 (2.91).

#### 2.8. Synthesis of **9** from the thermolysis of **7**

The thermolysis reaction was carried out in a heavy-walled Carius tube that was charged with 0.10 g (0.088 mmol) of **7** and 25 mL of toluene. After the reaction solution was deoxygenated by three freeze–pump–thaw degas cycles, the Carius tube was sealed and heated at 110 °C for 48 h. TLC analysis (1:1 Et<sub>2</sub>O/hexane) of the cooled reaction solution confirmed the loss of **7** and the presence of fast moving yellow spot at  $R_f = 0.71$ , which was subsequently identified as **9**. Some decomposition was observed in this reaction,

on the basis of a small amount of material that remained the origin of the TLC plate. The desired product was purified by column chromatography over silica gel, followed by recrystallization from heptane/benzene, to give 9 in 70% yield (62 mg). Anal. Calcd (found) for C<sub>21</sub>H<sub>9</sub>O<sub>9</sub>Os<sub>3</sub>P·heptane: C, 30.52 (30.94); H, 2.09 (2.26).

## 2.9. X-ray crystallographic data

Single crystals of **4**–**7** and **9** were grown by slowly evaporating the CH<sub>2</sub>Cl<sub>2</sub> solvent from hexane/CH<sub>2</sub>Cl<sub>2</sub> solutions containing each cluster at 5 °C. All X-ray diffraction examinations were carried out using a Bruker SMART APEX2 CCD-based X-ray diffractometer equipped with a low-temperature cryostat (Oxford Instruments) and a Mo-target X-ray tube ( $\lambda = 0.71073$  Å). With the exception of **6**. whose X-ray data were collected at room temperature, the X-ray data for the other clusters were collected at 100(2) K. Data collection. indexing, and initial cell refinements were carried out using APEX2 [11], with the frame integrations and final cell refinements carried out using SAINT [12]. An absorption correction was applied to each system using the program SADABS [13], and all non-hydrogen atoms were refined anisotropically. The bridging hydride in 6 was located during refinement and refined isotropically, while all remaining hydrogen atoms in all of the other structures were placed in idealized positions and were refined using a riding model. The highly disordered molecule of CH<sub>2</sub>Cl<sub>2</sub> extant in 7 was treated using the PLATON/SQUEEZE program [14]; this treatment gave an electron count in the unit cell of 32 electrons/cell that is close to the required value for one CH<sub>2</sub>Cl<sub>2</sub> molecule (42 electrons/cell). The reported structures were solved and refined using the SHELXTL program package software [15]. Refinement details and structural parameters for these structures are summarized in Table 2.

#### 2.10. Computational methodology and modeling details

The reported calculations were performed with the hybrid DFT functional B3LYP, as implemented by the Gaussian 09 program package [16]. This functional utilizes the Becke three-parameter

#### Table 2

X-ray crystallographic data and processing parameters for the clusters 4-7, and 9.



Fig. 1. Thermal ellipsoid plot of the molecular structure of 4 at the 50% probability level. Selected bond distances (Å) and angles (deg) for the diffraction structure: Os(1)-Os(2) = 2.8801(2), Os(1) - Os(3) = 2.8907(2), Os(2) - Os(3) = 2.9150(2), Os(2) - Os(3) = 0.9150(2), Os(3) = 0.9150(2), Os(2) - Os(3) = 0.9150(2), Os(2) = 0.9150(2),P(1) = 2.345(1), P(1)-Os(2)-Os(1) = 165.87(3), P(1)-Os(2)-Os(3) = 106.84(2), C(5)-Os(3) = 106.84(2),Os(2)-P(1) = 89.2(1), C(6)-Os(2)-P(1) = 89.8(1), C(7)-Os(2)-P(1) = 99.0(1).

exchange functional (B3) [17], combined with the correlation functional of Lee, Yang and Parr (LYP) [18]. The Os atoms were described by Stuttgart–Dresden effective core potentials (ecp) and an SDD basis set, while a 6-31G(d') basis set was employed for the remaining atoms.

All reported geometries correspond to fully optimized groundstate structures based on positive eigenvalues obtained from the analytical Hessian. The computed frequencies were used to make zero-point and thermal corrections to the electronic energies; the reported enthalpies are quoted in kcal/mol relative to the

Compound	4	5	6	7	9
CCDC entry no.	889198	889199	889197	889196	889200
Cryst system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P -1	P -1	P -1	P -1	P21/c
a, Å	11.3969(5)	12.191(2)	11.344(1)	10.1087(7)	14.625(1)
b, Å	11.5122(5)	13.746(2)	16.286(2)	10.3833(7)	15.557(1)
<i>c</i> , Å	14.1471(6)	16.615(3)	19.029(2)	16.678(1)	20.488(2)
α, deg	72.425(1)	66.871(2)	111.754(1)	73.747(1)	
$\beta$ , deg	73.549(1)	88.256(2)	98.109(1)	73.368(1)	95.111(1)
$\gamma$ , deg	67.277(1)	63.791(2)	90.048(1)	80.865(1)	
V, Å <sup>3</sup>	1602.6(1)	2262.5(7)	3227.0(6)	1604.4(2)	4642.7(6)
Mol formula	C <sub>30</sub> H <sub>18</sub> NO <sub>11</sub> Os <sub>3</sub> P	C48H36N2O10Os3P2	C <sub>29</sub> H <sub>19</sub> ClNO <sub>10</sub> Os <sub>3</sub> P	$C_{29}H_{18}NO_{10}Os_3P \cdot 1/2CH_2Cl_2$	$C_{21}H_9O_9Os_3P$
Fw	1170.02	1433.33	1178.47	1184.48	1006.85
Formula units per cell (Z)	2	2	4	2	8
D <sub>calcd</sub> (Mg/m <sup>3</sup> )	2.425	2.104	2.426	2.452	2.881
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu$ (mm <sup>-1</sup> )	11.973	8.536	11.971	12.040	16.499
Absorption correction	Semiempirical from	Semiempirical from	Semiempirical from	Semiempirical from	Semiempirical from
	equivalents	equivalents	equivalents	equivalents	equivalents
Abs corr factor	0.4055/0.1857	0.7374/0.2553	0.4671/0.3073	0.4241/0.1969	0.4585/0.1983
Total reflections	14616	27622	39299	18912	46956
Independent reflections	6971	9958	14177	6993	9890
Data/res/parameters	6971/0/410	9958/0/588	14177/0/821	6993/0/398	9890/0/613
$R1^{a} [I \geq 2\sigma(I)]$	0.0223	0.0159	0.0345	0.0238	0.0231
wR2 <sup>b</sup> (all data)	0.0556	0.0376	0.0863	0.0730	0.0495
GOF on F <sup>2</sup>	1.037	1.001	1.022	1.009	1.015
$\Delta \rho(\max), \Delta \rho(\min) (e/Å^3)$	1.228, -1.288	1.241/-0.842	2.823/-0.775	1.351/-1.507	2.813/-2.195

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|0;$ <sup>b</sup>  $R1 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ 



**Fig. 2.** Thermal ellipsoid plot of the molecular structure of **5** at the 50% probability level. Selected bond distances (Å) and angles (deg) for the diffraction structure: Os(1) - Os(3) = 2.9230(4), Os(1) - Os(2) = 2.9266(4), Os(2) - Os(3) = 2.8914(5), Os(2) - P(2) = 2.3454(7), Os(3) - P(1) = 2.3473(7), P(2) - Os(2) - Os(3) = 161.02(2), P(2) - Os(2) - Os(1) = 103.57(2), P(1) - Os(3) - Os(2) = 164.24(2), P(1) - Os(3) - Os(1) = 105.42(2).

specified standard. The natural charges and Wiberg indices were computed using Weinhold's natural bond orbital (NBO) program [19,20]. The geometry-optimized structures presented here have been drawn with the *JIMP*2 molecular visualization and manipulation program [21].

#### 3. Results and discussion

## 3.1. Reaction of $Os_3(CO)_{12}$ (1) with PN

Treatment of a CH<sub>2</sub>Cl<sub>2</sub> solution containing equimolar amounts of **1** and PN with a measured excess of the oxidative-decarbonylation reagent Me<sub>3</sub>NO [22] furnishes the PN-substituted clusters **4** and **5**. Both **4** and **5** were obtained as reaction products independent of the stoichiometry of **1**:Me<sub>3</sub>NO employed, and we had to settle on the separation of the binary mixture in order to isolate pure samples of each cluster. Repeating this reaction with an increased PN:**1** ratio led to the predictable gain in **5** at the expense of **4**. Both PN-substituted clusters were isolated by column chromatography over silica gel and characterized in solution by IR and NMR spectroscopies. Eq. (2) summarizes this reaction that yields **4** and **5**.



**Fig. 3.** Thermal ellipsoid plot of the molecular structure of **6** at the 50% probability level. Selected bond distances (Å) and angles (deg) for the diffraction structure: Os(1) - Os(2) = 2.8989(4), Os(1) - Os(3) = 3.0274(5), Os(2) - Os(3) = 2.8758(4), Os(1) - H(1) = 1.79(9), Os(3) - H(1) = 1.89(9), Os(1) - P(1) = 2.363(2), Os(3) - Cl(1) = 2.472(2), P(1) - Os(1) - Os(2) = 167.44(4), P(1) - Os(1) - Os(3) = 109.60(4), C(8) - Os(3) - Cl(1) = 174.7(2), C(9) - Os(3) - Cl(1) = 83.9(2), C(9) - Os(3) - Os(1) = 115.5(2).

spectral data reported for a diverse group of phosphine-substituted Os<sub>3</sub> clusters [23]. The <sup>31</sup>P NMR spectrum recorded for **5** at room temperature revealed the presence of three broad singlets, whose integration confirmed the existence of a 1:1 mixture of stereoisomers based on **5**. This ratio remained unchanged when the <sup>31</sup>P NMR spectrum was recorded at 333 K. While specific <sup>31</sup>P assignments cannot be made based on these data, the two stereoisomers are attributed to the 1,2-Os<sub>3</sub>(CO)<sub>10</sub>(PN)<sub>2</sub> clusters, where the ancillary PN ligands are attached to adjacent osmium centers at equatorial sites that differ only by the P–Os–Os–P dihedral angle [24]. Leong and Liu have observed this exact phenomenon in the case of 1,2-Os<sub>3</sub>(CO)<sub>10</sub>(PPh<sub>3</sub>)<sub>2</sub> [25].

The crystal structures of **4** and **5** were established by X-ray crystallography, and the solid-state structures for **4** and **5** are shown in Figs. 1 and 2, respectively. Here the coordination of the phosphorus group to the cluster, as opposed to the pyridyl moiety,



The pertinent spectral data for **4** and **5**, as well as the other new products, are reported in Table 1; the v(CO) frequencies for the terminal carbonyl groups and the NMR data are consistent with the

is confirmed in each case. The mean Os–Os bond distance in **4** (2.8953 Å) and **5** (2.914 Å) fall within acceptable ranges found for the Os–Os distances in the other  $Os_3(CO)_{12-n}P_n$  clusters (where

n = 1, 2) [23,25,26]. To our knowledge **4** and **5** represent the first structurally characterized metal clusters containing a coordinated PN ligand(s) [27]. The remaining bond distances and angles in **4** and **5** are unremarkable and require no comment.

## 3.2. Reaction of $Os_3(CO)_{11}(MeCN)$ (2) with PN

The reaction of the labile cluster **2** with PN was next examined. Cluster 2 reacts rapidly with one equivalent of PN in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, to afford cluster 4 as the major product (50%); accompanying the reaction are clusters 5 and 6 in 20 and 8% yields, respectively. The <sup>1</sup>H NMR spectrum of **6** shows the expected number of resonances for the coordinated PN ligand, in addition to a high-field doublet (1H) at  $\delta$  –16.11, which supports the presence of a bridging hydride ligand. The structure of 6, which exists in the unit cell as two independent molecules, was subsequently determined by X-ray diffraction analysis. No significant differences exist between the two structures, and the ORTEP plot of the molecular structure of one of the two molecules of 6 is shown in Fig. 3, where the coordination of the PN ligand, one terminal chloride, and a bridging hydride are confirmed. The bridging hydride in each molecule of **6** was located during data reduction and refined isotropically in the analysis. Assuming that the chloride and hydride ligands both function as one-electron donors, cluster 6 is best viewed as electron precise with an electron count of 48e. The PN and chloride ligands are situated at equatorial and axial positions at the Os(1) and Os(3) atoms, respectively, while the hydride ligand H(1) is of the edge-bridging variety, spanning the Os(1)–Os(3) vector. The Os–Os bond distances range from 2.8758(4) Å [Os(2)– Os(3) to 3.0274(5) Å Os(1)-Os(3), with the longest of the three Os-Os bond distances associated with the hydride-bridged metal-metal bond [28].

In comparison to the numerous Os<sub>3</sub> clusters that possess an edgebridging chloride ligand, the presence of a terminal chloride ligand remains a rarity. Apart from 6, other structurally characterized triosmium clusters having a terminal chloride ligand include H<sub>2</sub>Os<sub>3</sub>( $\eta^{1}$ -Cl)(CO)<sub>8</sub>[ $\mu_3$ -C(4-methylquinol-8-yl)], HOs<sub>3</sub>( $\eta^1$ -Cl)(CO)<sub>10</sub>(CNPr), and  $H_2Os_3(\eta^1-Cl)(CO)_9(\mu-NH_2)$  [29]. The presence of the terminal chloride ligand in 6 must derive from the CH<sub>2</sub>Cl<sub>2</sub> solvent, and this was easily verified by repeating the reaction with toluene as the solvent; use of toluene gave only 4 and 5. The point at which  $CH_2Cl_2$  undergoes activation remains unclear, but pure samples of 4 and 5 kept under an argon atmosphere show no evidence for reaction with CH<sub>2</sub>Cl<sub>2</sub>. Finally, the introduction of a chloride ligand(s) into the coordination sphere of different clusters is known to occur in thermolysis and photolysis reactions that have been conducted in the presence of a chlorinated solvent [29c,30]. In some of these paradigms, a free-radical chain process is unquestionably operative but it is unlikely the only route by which the halide is incorporated into the final product.

# 3.3. Synthesis of **7** and DFT evaluation of the bridged and chelated stereoisomers

The reaction between **3** and PN is rapid, and the product distribution is dependent on the reaction solvent and reagent stoichiometry. Treatment of an equimolar mixture of reagents in CH<sub>2</sub>Cl<sub>2</sub> furnishes the PN-containing products **5** (25%), **6** (40%), and **7** (5%), in addition to the known cluster HOs<sub>3</sub>( $\mu$ -Cl)(CO)<sub>10</sub> (10%), whose identity was established through TLC and spectroscopic comparisons against an independently prepared sample of this cluster [10a]. The yields of these products are estimates based on TLC analysis of the crude mixture. Cluster **7** is unstable on common chromatographic supports and attempts to isolate **7** by column chromatography were met with extensive and unacceptable material loss. Performing the chromatographic separation under an inert atmosphere and at low temperature did not improve the

#### Table 3

Selected X-ray diffraction and DFT bond distances (Å) and angles (deg) in 7 (A1) and 9 (C1).

	X-ray	DFT
7 (A1)		
Bond distances		
Os(1)-Os(2)	2.8853(3)	2.9877
Os(1) - Os(3)	2.8959(3)	2.9920
Os(2) - Os(3)	2.9131(3)	3.0243
Os(3)-N(1)	2.291(4)	2.422
Os(3)–P(1)	2.298(1)	2.371
Bond angles		
C(9)-Os(3)-C(10)	85.9(2)	87.5
C(9) - Os(3) - N(1)	170.9(2)	170.3
C(10) - Os(3) - N(1)	87.3(2)	87.5
C(9) - Os(3) - P(1)	96.8(2)	96.3
C(10) - Os(3) - P(1)	100.7(2)	102.0
N(1) - Os(3) - P(1)	78.4(1)	76.5
C(10) - Os(3) - Os(1)	107.3(2)	103.7
N(1) - Os(3) - Os(1)	102.8(1)	102.5
P(1) - Os(3) - Os(1)	152.00(3)	154.28
N(1) - Os(3) - Os(2)	93.9(1)	95.8
P(1) - Os(3) - Os(2)	92.45(3)	94.80
9 (C1)		
Bond distances		
$Os(1) \cdots Os(2)$	3.9899(4)	4.0683
Os(1) - Os(3)	2.7880(3)	2.8698
Os(2)-Os(3)	2.9292(3)	3.0283
Os(1)-P(1)	2.339(1)	2.379
Os(2)–P(1)	2.306(1)	2.359
Os(3)–P(1)	2.420(1)	2.477
Os(1) - C(10)	2.308(5)	2.371
$Os(1)\cdots C(11)$	2.922(5)	3.056
Os(2) - C(15)	2.120(5)	2.150
Os(3) - C(10)	2.182(5)	2.240
C(10)-C(15)	1.424(8)	1.440
C(10)-C(11)	1.427(7)	1.431
C(11)-C(12)	1.366(8)	1.391
C(12)-C(13)	1.385(8)	1.402
C(13)-C(14)	1.393(8)	1.399
C(14) - C(15)	1.389(8)	1.405
Bond angles		
Os(1)-Os(3)-Os(2)	88.478(9)	87.180
Os(1) - P(1) - Os(2)	118.42(6)	118.33
P(1)-Os(2)-C(15)	80.7(1)	81.9
P(1)-Os(3)-C(10)	77.5(1)	77.5
P(1)-Os(1)-C(10)	76.8(1)	77.0
Os(1)-C(10)-Os(3)	76.7(2)	76.9
C(10)-C(15)-Os(2)	111.7(4)	113.6

situation; cluster **7** could be isolated free of accompanying byproducts using **4** as the starting reagent (*vide infra*). Finally, the effect of doubling the concentration of PN to **3** was examined in CH<sub>2</sub>Cl<sub>2</sub>, and here the amount of **5** increased but not that of **7**. Of further interest in this last reaction is the significant diminution in the yields of **6** and HOs<sub>3</sub>( $\mu$ -Cl)(CO)<sub>10</sub>, which was observed in trace amounts by TLC analysis. Clearly a complex relationship exists between the initial concentrations of **3** and PN and the two cluster products derived from the activation of the halogenated solvent.

The reaction between **3** and PN in toluene yields **5** and **7** as the principal substitution products. Using a 1:1 reagent stoichiometry gives **5** and **7** in 30 and 40% yields (TLC). The crude yield of **7** was maximized at 60% when a 1:2 ratio of **3**:PN was employed, and multiple recrystallizations eventually furnished **7** in yields <20%. We were able to synthesize **7** in higher yield from **4** and Me<sub>3</sub>NO, as outlined in Eq. (3). This particular protocol furnished **7** with minimal side-products and in yields >80% when **4** was treated with a slight excess of Me<sub>3</sub>NO in toluene. Pure **7** could be obtained by simply washing the crude product with multiple portions of hexane or recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub>.



7 was characterized in solution by IR and NMR spectroscopies. Of note in the <sup>1</sup>H NMR spectrum is the diastereotopic nature of the methylene hydrogens associated with the 2-(diphenylphosphino) methyl moiety. These hydrogens appear as separate resonances at  $\delta$  4.47 and  $\delta$  5.21 and display doublet of doublets and triplet splitting patterns, respectively. The coordination mode adopted by the PN ligand in 7 was unequivocally established by X-ray diffraction analvsis. Selected bond distances and angles are reported in Table 3, and Fig. 4 (left-hand side) shows the thermal ellipsoid plot of the molecular structure of 7, where chelation of the PN ligand at axial (N) and equatorial (P) sites at the Os(3) center is confirmed. As mentioned earlier, 7 is the first structurally characterized metal cluster that contains the compound PN as a bidentate ligand. The axial versus equatorial coordination of the pyridyl moiety in 7 is in keeping with the stereochemical preference of such ligands in trimetallic clusters [31]. The metallic core consists of a triangular array of osmium atoms where the Os-Os bond distances range from 2.8853(3) Å [Os(1)-Os(2)] to 2.9131(3) Å [Os(2)-Os(3)]. The Os(3)-N(1) [2.291(4) Å] and Os(3)–P(1) [2.298(1) Å] bond distances are consistent with those Os-N(pyridyl) and Os-P distances found in the dpppy-substituted osmium clusters  $Os_3(CO)_{10}(\mu$ -dpppy) [32],  $H_4Os_4(CO)_{10}(\mu$ -dpppy) [33], and  $HOs_3(CO)_9(\mu$ -PhPpy) [34]. The ten carbonyl groups are all linear in nature and do not exhibit any unusual distances and angles. The bonding in 7 was also explored by DFT, and the geometry-optimized structure of A1 is displayed alongside the X-ray diffraction structure of 7 in Fig. 4. The optimized structure of A1 shows a good correspondence with the solid-state

structure, as verified by a comparison of the selected bond distances and angles (experiment versus theory) in Table 3.

The stability of the chelated PN ligand in **7** relative to other possible PN coordination modes was investigated computationally by DFT [35]. Fig. 5 shows the energy ordering of several different isomeric chelated and bridged clusters based on **7**. The dissimilar pnictogen atoms in PN lead to a greater number of possible coordination modes for the PN ligand when regio- and stereochemical aspects are considered relative to symmetrical bidentate PP and NN ligands. Species **A1** is the thermodynamically most stable form of this cluster, a feature that reconciles theory with the experimentally determined solid-state structure. The equatorially bridged species **A2** lies 6.6 kcal/mol higher in enthalpy than **A1**, while the equatorially chelated species **A3**, which represents a commonly observed coordination motif for rigid diphosphines having a two-carbon backbone [5a,d], is computed to be higher in enthalpy than **A1** by 8.0 kcal/mol.

The effect of the PN coordination mode on the charge distribution and bond indices in A1-A7 was explored by NBO analysis. Table 4 shows the natural charges and Wiberg indices for selected atoms in the isomeric clusters. All of the osmium atoms exhibit a negative charge and the pyridyl-substituted osmiums are the least electron rich of the metal centers. The nitrogen atoms all carry a negative charge and the charge density is relatively unaffected by the site of coordination in the cluster. The phosphorus atoms all display a positive charge, with the computed charges ranging from 1.37 to 1.24. The clusters having an axial phosphine are expected to experience less efficient overlap between the Os and P centers, which in turn manifests itself in a lower positive charge on the pnictogen center as opposed to their equatorial counterparts. The Wiberg bond indices, which serve as a measure of bond strength, are more or less uniform within the different bond groups. The computed indices for the Os-Os, Os–P, and Os–N vectors are consistent with the accepted singlebond designation for these groups.

## 3.4. Photochemical activation of 4 and 7 to give 8

Optical excitation of 4 or 7, using either near-UV of UV light, leads to loss of CO and formation of the dihydride cluster 8 (Eq.



Fig. 4. Thermal ellipsoid plot of the molecular structure of 7 at the 50% probability level (left) and the optimized B3LYP structure of A1 (right).



Fig. 5. Ground-state enthalpy ordering of the isomeric clusters Os<sub>3</sub>(CO)<sub>10</sub>(PN). All enthalpy values are in kcal/mol relative to species A1.

(4)), whose origin derives from the double metalation of the 6-Me group associated with the PN ligand. Photochemically promoted C–H bond activation of chelated bidentate ligands in Os<sub>3</sub> clusters is common [36], and the mechanism responsible for C–H bond activation of the methyl group in related nitrogen-based ligands coordinated to Os<sub>3</sub> clusters has been investigated [5,37]. That **4** undergoes an initial loss of CO, followed by chelation of the pendant  $\kappa^1$ -PN ligand to give **7**, was confirmed in those reactions that were monitored by NMR spectroscopy. Loss of two additional molecules of CO in **7** ultimately furnishes **8**. Prolonged irradiation is required to drive these reactions to completion, behavior that

we attribute to the low quantum efficiency for CO loss as opposed to dynamics stemming from the activation of the C–H bonds. For those reactions that were monitored by NMR spectroscopy, no evidence was seen for the expected intermediate hydride  $HOs_3(CO)_9[\mu-CH_2(NC_5H_3)CH_2PPh_2]$ , which once formed must undergo rapid conversion to the dihydride. **8** was isolated by column chromatography, and the <sup>1</sup>H NMR spectrum revealed the presence of a pair of high-field hydrides at  $\delta$  –14.31 and –13.14 and a benzylidene (CH) singlet at  $\delta$  5.49, all of which derive from the original 6-Me group in **7**. As found in **7**, the methylene hydrogens belonging to the 2-(diphenylphosphino)methyl moiety in **8** are

#### Table 4

Selected natural charges and Wiberg bond indices for the isomeric clusters  $Os_3(CO)_{10}(PN)$  (A1-A7).<sup>a</sup>

$Os_2$ $Os_1$ $Os_3$ $Os_3$ $Os_3$		$OS_1 OS_2 OS_3 OS_3 OS_3 OS_1 OS_3 OS_3 OS_1 OS_3 OS_3 OS_3 OS_3 OS_3 OS_3 OS_3 OS_3$	$Os_2 \xrightarrow{P} Os_3$ $Os_1 \xrightarrow{Os_2} Os_3$	$N = \begin{bmatrix} 0 & S_2 \\ 0 & S_2 \\ 0 & S_1 \\ 0 & S_1 \\ 0 & S_3 \end{bmatrix}$		
1,1-N <sub>ax</sub> ,P <sub>eq</sub>	$1,2-N_{eq},P_{eq}$	$1,1-N_{eq},P_{eq}$	$1,1-N_{eq},P_{ax}$	1,2-N <sub>ax</sub> ,P <sub>ax</sub>	1,2-N <sub>ax</sub> ,P <sub>eq</sub>	$1,2-N_{eq},P_{ax}$

	A1	A2	A3	A4	A5	A6	A7
Atomic charge							
Os <sub>1</sub>	-1.39	-0.99	-1.37	-1.40	-0.72	-0.86	-0.97
Os <sub>2</sub>	-1.41	-1.31	-1.35	-1.34	-1.43	-1.38	-1.34
Os <sub>3</sub>	-0.94	-1.44	-1.04	-0.89	-1.43	-1.46	-1.35
Р	1.33	1.37	1.37	1.24	1.31	1.37	1.29
Ν	-0.42	-0.39	-0.38	-0.40	-0.45	-0.43	-0.39
Wiberg index							
$Os_1 - Os_2$	0.43	0.53	0.42	0.41	0.49	0.44	0.55
$Os_1 - Os_3$	0.48	0.44	0.41	0.42	0.37	0.50	0.44
$Os_2 - Os_3$	0.46	0.45	0.51	0.53	0.41	0.45	0.40
Os-P	0.76	0.80	0.81	0.68	0.74	0.80	0.74
Os-N	0.40	0.43	0.45	0.42	0.23	0.32	0.43

<sup>a</sup> Atom orientation and numbering scheme for the Os<sub>3</sub> clusters depicted above. Only the Os, P, and N atoms and selected CO ligands are shown.

diastereotopic, and they appear as two separate doublet of doublets at  $\delta$  2.70 and 3.50.



We were able to obtain two preliminary X-ray diffraction structures of **8** that confirmed the activation of the 6-Me group, but the crystals were of poor quality and twinned. Attempts to grow high quality crystals of 8 that were not twinned failed, and the convergence values for those crystals that did furnish a diffraction structure were unacceptably high (>13%) and accompanied by disordered solvent and phenyl groups. Accordingly, we resorted to DFT calculations to establish the bonding of the PN residue to the Os<sub>3</sub> frame and the locus of the hydrides ligands in 8. The geometry-optimized structure of the dihydride cluster **B1** is shown below. The hydrides bridge adjacent Os-Os edges, with one located in the plane of the metals and the other situated below the metallic frame opposite the face-capping PN ligand. The computed charges and Wiberg indices for **B1** are summarized in Table 5. These data are consistent with the computational results reported by us for related phosphine-substituted Os<sub>3</sub> clusters [38]. The double metalation found in the conversion of  $A1 \rightarrow B1 + CO$ (2 equivs) is endergonic by 2.3 kcal/mol, and the principal driving force is the entropic release of the CO molecules. The computed  $\Delta S$ value is 68.8 eu, which translates to 34.4 eu per CO, and is in excellent agreement with the ortho-metalation thermodynamics computed for the conversion of  $HOs_3(CO)_8(\kappa^2-bcpd)(\mu-SC_6H_4Me-$ 4) to  $H_2Os_3(CO)_7(\kappa^2-bcpd)(\mu-SC_6H_3Me-4)$  [38a].



3.5. Thermal decomposition of the PN ligand in 7 to give 9

Thermolysis of cluster **7** in toluene at 110 °C furnishes **9** (Eq. (5)), whose formation is accompanied by loss of the pyridyl moiety and activation of the  $Ph_2P$  group. Of all of the clusters reported here, **9** is by far the most stable, and it was isolated by chromatography in 70% yield. Thermolysis of **4** in toluene affords **9**, albeit in slightly

#### Table 5

Selected natural charges and Wiberg bond indices for the clusters  $H_2Os_3(CO)_8[\mu-CH(NC_5H_3)CH_2PPh_2]$  (**B1**) and  $Os_3(CO)_9(\mu-C_6H_4)(\mu-PPh)$  (**C1**).<sup>a</sup>



	B1	C1
Atomic charge		
Os <sub>1</sub>	-1.21	-1.15
Os <sub>2</sub>	-1.08	-1.30
Os <sub>3</sub>	-1.19	-1.30
P	1.33	0.95
Ν	-0.41	
C <sub>1</sub>	-0.42	-0.21
C <sub>6</sub>		-0.01
H <sub>1</sub>	0.14	
H <sub>2</sub>	0.09	
Wiberg index		
$Os_1 - Os_2$	0.24	0.04
$Os_1 - Os_3$	0.29	0.40
$Os_2 - Os_3$	0.49	0.34
Os <sub>1</sub> -P		0.85
Os <sub>2</sub> –P	0.75	0.88
Os <sub>3</sub> –P		0.63
Os-N	0.50	
Os <sub>1</sub> -C <sub>1</sub>	0.69	0.43
Os <sub>3</sub> –C <sub>1</sub>	0.69	0.61
$Os_2 - C_6$		0.75
$C_1 - C_6$		1.25
$C_1 - C_2$		1.26
C <sub>2</sub> -C <sub>3</sub>		1.47
$C_3 - C_4$		1.39
C <sub>4</sub> -C <sub>5</sub>		1.43
$C_5 - C_6$		1.41
Os <sub>1</sub> -H <sub>1</sub>	0.40	
Os <sub>3</sub> -H <sub>1</sub>	0.37	
Os <sub>1</sub> -H <sub>2</sub>	0.41	
Os <sub>2</sub> -H <sub>2</sub>	0.38	

<sup>a</sup> Atom orientation and numbering scheme for the Os<sub>3</sub> clusters depicted above.

lower yields. The IR and NMR properties of **9** closely match those spectroscopic data reported for  $Os_3(CO)_9(\mu-C_6H_4)(\mu-PR)$  (where R = Me, Et) [39,40]. Particularly diagnostic is the low-field <sup>31</sup>P resonance at  $\delta$  221.45, which signals the transformation of the original phosphine moiety to a phosphinidene ligand.



**9** was structurally characterized by X-ray crystallography, and Fig. 6 shows one of the two independent molecules of **9** found in



Fig. 6. Thermal ellipsoid plot of the molecular structure of 9 at the 50% probability level (left) and the optimized B3LYP structure of C1 (right).

the unit cell: the thermal ellipsoid plot of the molecular structure confirms the activation of the PN ligand and the capping of the two Os<sub>3</sub> faces by benzvne and phenylphosphinidene moieties. 9 contains 50e, assuming that the face-capping ligands each function as 4e donors, and is structurally similar to  $Os_3(CO)_9(\mu-C_6H_4)(\mu-PR)$ [39]. The dihedral angle formed by the planes defined by the benzyne carbons and osmium metals is ca. 73°, and the organic fragment is tipped toward the metallic plane in order to facilitate the transfer of  $\pi$  electron density to Os(1) center. The Os(2)–C(15) and Os(3) - C(10) vectors exhibit distances of 2.120(5) and 2.182(5) Å, bond lengths that are best reconciled as Os–C  $\sigma$  bonds. The longer Os(1)–C(10) bond distance [2.308(5) Å] compares well to that distance reported in the EtP- and MeP-capped clusters  $Os_3(CO)_9(\mu-C_6H_4)(\mu-PR)$  [39]. The internuclear distance between the Os(1) and Os(2) atoms is 3.9899(4) Å and this exceeds the van der Waals radii for the two osmium atoms, preventing any significant orbital overlap between these two metals [41]. The observed bond distances and angles associated phosphinidene moiety and the nine terminal carbonyl ligands are unremarkable and require no comment.

The asymmetric coordination of the benzyne moiety to the osmium atoms in  $Os_3(CO)_9(\mu-C_6H_4)(\mu-PR)$  has been the subject of discussion with respect to the  $\sigma$  and  $\pi$  contributions from the organic fragment to the Os3 core [39,40]. On the basis of crystallographic and VT NMR data, Deeming and coworkers have presented compelling evidence for a benzyne bonding model that involves one  $\pi$  and two  $\sigma$  components [39b]. The former interaction is best viewed as originating from a benzyne molecular orbital of suitable  $\pi$  symmetry with the wingtip osmium that is not  $\sigma$ -bound to the C<sub>6</sub>H<sub>4</sub> ring. In order to better address this bonding conundrum in 9, we have performed DFT calculations on 9 and have computed the atomic charges and Wiberg indices. The B3LYP-optimized structure of C1 is shown alongside the structure of 9 in Fig. 6. Good visual agreement exists between the pair of structures in the Figure, and the bond distances and angles in Table 3 track reasonably well. The Wiberg indices computed for C1 reinforce the bonding model advocated by Deeming. The stronger Os–C  $\sigma$  bonds are assigned to the Os(3)-C(1) and Os(2)-C(6) vectors, which display a bond index of 0.61 and 0.75, respectively. The weaker  $\pi$  component that arises from the overlap of the Os(1) and C(1) atoms reveals a Wiberg index of 0.43. The overlap between the C(6) atom and the Os(1) and Os(3) centers is negligible based on bond indices of 0.06.

## 4. Conclusions

The ability of 2-[(diphenylphosphino)methyl]-6-methylpyridine (PN) to serve as a ligand in the osmium clusters based on  $Os_3(CO)_{12-n}(MeCN)_n$  has been investigated. Bidentate coordination of PN is demonstrated in the case of **7**, whose X-ray structure reveals a chelated PN ligand having axial pyridyl and equatorial phosphine moieties. The energies of alternative stereoisomers based on **7** have been computed by electronic structure calculations, and the solid-state structure has been confirmed as the ground-state minimum. **7** is thermally and photochemically sensitive, and the decomposition products **8** and **9** have been isolated and shown to derive from a combination of C–H and P–C bond cleavages. The reaction of PN with other metal clusters is under investigation, and our results will be published in due course.

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#### Appendix A. Supplementary material

CCDC 889198, 889199, 889197, 889196, and 889200 contain the supplementary crystallographic data for this paper. These data may be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif. Atomic co-ordinates of the DFT data reported here are available from MGR upon request.

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