

α -Diimine Ligand Coordination and C–H Bond Activation in the Reaction of $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ with 6-R-2,2'-Bipyridine (where R = Et, Ph): X-ray Diffraction Structures of the Ortho-Metalated Hydride Clusters $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{10}\text{H}_6\text{-6-R})$

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Abstract The reactivity of the labile cluster $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ (**1**) with the monofunctionalized heterocyclic ligands 6-R-2,2'-bipyridine (where R = Et, Ph) has been investigated. The alkyl-substituted heterocycle 6-Et-2,2'-bipyridine reacts with **1** in refluxing CH_2Cl_2 to give an isomeric mixture of $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{12}\text{H}_{11})$ due to cyclometalation of the side-chain ethyl group (**2**) and ortho metalation of the unsubstituted bipyridine ring (**3**). The solid-state structure of the latter cluster, $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{10}\text{H}_6\text{-6-Et})$ (**3**), has unequivocally established the site of the C–H bond activation in the product. Treatment of **1** with the aryl-substituted ligand 6-Ph-2,2'-bipyridine proceeds similarly with ortho metalation at the ancillary phenyl group and the C-6' ortho site of the unsubstituted bipyridine ring, as verified by ^1H NMR spectroscopy. The X-ray diffraction structure of the thermodynamically more stable bipyridine-metalated cluster $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{10}\text{H}_6\text{-6-Ph})$ (**5**) has been determined. The course of these reactions

is discussed with respect to our recent study involving the reaction of cluster **1** with the ligand 6-Me-2,2'-bipyridine.

Keywords α -Diimine ligand · Triosmium clusters · Cyclometalation · Ortho metalation · Ligand substitution

Introduction

Within the pharmaceutical industry the selective functionalization of alkaloid C–H bonds remains under active investigation [1, 2]. The principal interest in such chemical transformations derives from a combination of environmental, safety, and financial considerations. While many traditional organic reagents are known for their stoichiometric ability to convert a C–H bond within a heterocyclic molecule into a more versatile functional group, all too many times such reactions are accompanied by low yields and harsh reaction conditions; this latter complication negates the presence of many ancillary functional groups that could be used in subsequent modifications of the heterocyclic platform. In today's extraordinarily competitive and atom-driven economy, transition-metal catalysis offers promising solutions for the directed elaboration of C–H bonds in nitrogenous heterocycles [3]. Numerous approaches involving the catalytic construction of important heterocyclic platforms exist, with the formation of highly fused indole motifs via tandem C–H activations, regiospecific arylation of azoles, and alkyne coupling with arylamines to give bicyclic pyrroles representing some of the more elegant synthetic paradigms in the literature [4–7].

Our interest in the activation of nitrogen-containing heterocycles stems from our recent report involving the reaction of the labile cluster $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ with the alkyl-substituted ligand 6-Me-2,2'-bipyridine [8]. Here

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C–H bond activation was observed at the side-chain methyl group (cyclometalation) and at the ortho site of the unsubstituted bipyridine ring (ortho metalation) to furnish the isomeric hydride-bridged clusters $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{11}\text{H}_9)$, as illustrated in Scheme 1. Independent control experiments subsequently established the cyclometalated hydride as the kinetic product of C–H bond activation and the ortho-metalation product as the thermodynamically more stable isomer. The conversion of the kinetically formed hydride to the thermodynamic hydride was also probed by us through a combination of kinetic measurements and isotope studies, and evidence for a rate-limiting step involving the reductive coupling of the bridging hydride and the cyclometalated alkyl group to give a transient Os_3 cluster possessing a sigma-bound methyl group was presented.

In order to test the generality and regioselectivity of the above C–H bond activations with different monosubstituted 2,2'-bipyridines, we have explored the reaction of cluster 1 with the heterocyclic ligands 6-R-2,2'-bipyridine (where R = Et, Ph). Herein, we present our results showing that the coordination of 6-Et-2,2'-bipyridine ligand proceeds in a fashion similar to that found by us for the 6-Me-2,2'-bipyridine ligand. In the case of the phenyl-substituted derivative 6-Ph-2,2'-bipyridine, two different ortho metalation products are observed, with the thermodynamically more stable

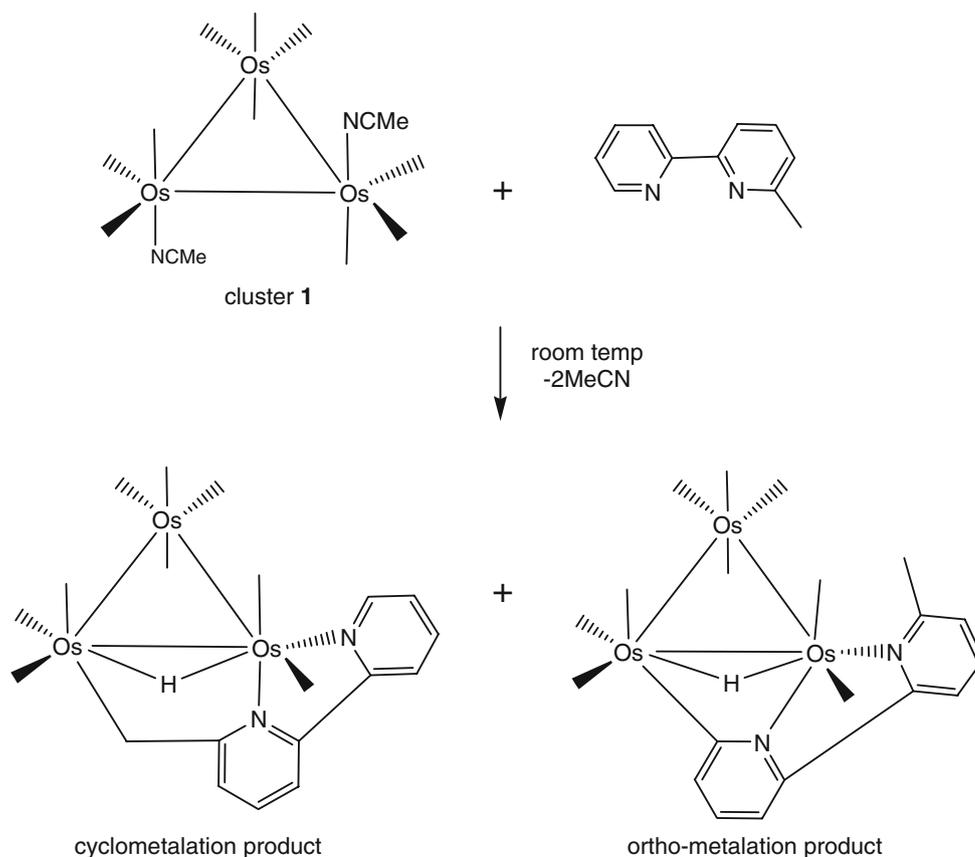
hydride originating from C–H bond activation at C(6)' of the bipyridine ring. The X-ray structure associated with the thermodynamically more stable hydride-bridged cluster from each bipyridine ligand is presented and discussed.

Experimental Section

Materials and Equipment

The $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ used in the current study was prepared from $\text{Os}_3(\text{CO})_{12}$ and Me_3NO (anhydrous) in the presence of MeCN according to the published procedure, [9] with the parent cluster $\text{Os}_3(\text{CO})_{12}$ synthesized from OsO_4 (Engelhard) and CO in a 450-mL Parr Series 4560 benchtop-mini reactor [10]. The heterocyclic ligand 6-Et-2,2'-bipyridine was synthesized from 2,2'-bipyridine following the procedure of Rillema et al. with replacement of MeLi by EtLi, [11] while 6-Ph-2,2'-bipyridine was prepared via the Kröhnke synthesis starting with 2-acetylpyridine [12, 13]. The following chemicals $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$, 2-acetylpyridine, 3-(dimethylamino)propiofenone hydrochloride, EtLi [0.5 M in benzene/cyclohexane (90/10)], and 2,2'-bipyridine were purchased from Aldrich Chemical Co. and used as received, except for $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ whose waters of hydration were removed by

Scheme 1 Hydride clusters isolated from the reaction of $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ with 6-Me-2,2'-bipyridine



azeotropic distillation using benzene. All reaction solvents were either distilled from an appropriate drying agent under argon or obtained from an Innovative Technology solvent purification system. All distilled solvents were handled via inert-atmosphere techniques, and when not in use these solvents were stored in Schlenk vessels equipped with Teflon stopcocks [14].

The reported IR data were recorded on a Nicolet 6700 FT-IR spectrometer in 0.1 mm NaCl cells, while the ^1H NMR data were recorded either at 200 MHz on a Varian Gemini-200 spectrometer or at 500 MHz on a Varian VXR-500 spectrometer. The ESI-APCI mass spectrum for **5** was recorded at the UC San Diego mass spectrometry facility in the positive ionization mode.¹

Reaction of $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ with 6-Et-2,2'-bipyridine

To a small Schlenk tube under argon was placed 0.18 g (0.19 mmol) of **1** and 40 mg (0.22 mmol) of 6-Et-2,2'-bipyridine, followed by ca. 50 mL of CH_2Cl_2 . The solution was then stirred for 45 min at room temperature, at which point the vessel was placed in an oil bath and heated at 40 °C for 7 h, slowly turning red-orange in color. Upon cooling, TLC analysis using CH_2Cl_2 /hexane (2:3) revealed the presence of three spots corresponding to a trace amount of the known chloride-bridged cluster $\text{HOs}_3(\text{CO})_{10}(\mu\text{-Cl})$, and clusters **2** and **3**, along with a considerable amount of material that remained at the origin. **2** and **3** were subsequently isolated by preparative chromatography over silica gel using the aforementioned eluent mixture. Yield of red-orange **2**: 21 mg (11%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2082 (s), 2041 (s), 2006 (vs), 1988 (s), 1956 (sh), 1933 (m) cm^{-1} . The ^1H NMR (CDCl_3): δ -19.85 (hydride), 2.06 (d, 3H, Me, $J = 7$ Hz), 3.30 (q, 1H, methine, $J = 7$ Hz), 7.41 (m, 1H), 7.48 (d, 1H, $J = 8$ Hz), 7.67 (t, 1H, $J = 8$ Hz), 7.78 (d, 1H, $J = 8$ Hz), 7.90 (t, 1H, $J = 8$ Hz), 8.20 (d, 1H, $J = 8$ Hz), 9.28 (d, 1H, $J = 7$ Hz). Yield of red-orange **3**: 39 mg (20%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2074 (s), 2055 (m), 2028 (s), 2005 (vs), 1980 (sh, s), 1945 (m) cm^{-1} . ^1H NMR (CDCl_3): δ -15.45 (hydride), 1.40 (t, 3H, Me, $J = 7$ Hz), 2.90 (bq, 2H, methylene, $J = 7$ Hz), 6.97 (d, 1H, $J = 6$ Hz), 7.15 (m, 1H), 7.76 (bt, 1H, 6 Hz), 8.13 (d, 1H, $J = 8$ Hz), 8.54 (d, 1H, $J = 8$ Hz), 8.58 (d, 1H, $J = 6$ Hz).

¹ While the four bipyridine-substituted clusters **2–5** were subjected to mass spectrometric investigation, **2–4** were unstable and decomposed during sample preparation or in the mass spectrometer. Only **5** afforded meaningful mass spectral data.

Reaction of $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ with 6-Ph-2,2'-bipyridine

About 75 mg (0.080 mmol) of **1** and 19 mg (0.082 mmol) of 6-Ph-2,2'-bipyridine were treated with ca. 25 mL of CH_2Cl_2 and then stirred at room temperature for 1 hr, after which time the dark red-colored solution was heated at 40 °C for 6 h. The solution was allowed to cool and the solution examined by TLC, which revealed the presence of unreacted **1**, trace amounts of clusters $\text{HOs}_3(\text{CO})_{10}(\mu\text{-Cl})$, **4**, and **5**, the latter which was formed the major product. A considerable amount of decomposed material was observed at the origin of the plate that did not exhibit any significant mobility by TLC using a variety of common solvents. Column chromatography over silica gel using CH_2Cl_2 /hexane (15:85) afforded **4**, with **5** eluted after the mobile phase was changed to CH_2Cl_2 /hexane (1:4). Yield of red-orange **4**: 2 mg (2%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2080 (s), 2041 (s), 2010 (vs), 1981 (s), 1953 (m), 1937 (m) cm^{-1} . ^1H NMR (CDCl_3): δ -21.83 (hydride), 7.36–7.57 (m, 9H), 7.91 (t, 1H, $J = 8$ Hz), 8.07 (d, 1H, $J = 8$ Hz). Yield of yellow-orange **5**: 21 mg (25%). IR (CH_2Cl_2): $\nu(\text{CO})$ 2066 (s), 2052 (s), 2038 (vs), 2024 (sh), 1997 (s), 1985 (s), 1927 (m) cm^{-1} . ^1H NMR (CDCl_3): δ -15.80 (hydride), 7.20 (t, 1H, $J = 5$ Hz), 7.38 (t, 1H, *p*-Ph, $J = 8$ Hz), 7.56 (t, 2H, *m*-Ph, $J = 8$ Hz), 7.84 (bt, 1H, $J = 8$ Hz), 8.11 (bd, 2H, $J = 7$ Hz), 8.32 (d, 2H, *o*-Ph, $J = 8$ Hz), 8.63 (d, 1H, $J = 6$ Hz), 8.72 (d, 1H, $J = 8$ Hz). ESI-MS (m/z): 1054.78 [**5**]⁺ and ions for the loss of CO (1–5).

X-ray Diffraction Data for Clusters **3** and **4**

Tables 1 and 2 contain the X-ray data and processing parameters and selected bond distances and angles, respectively, for the triosmium clusters **3** and **5**. Single crystals of **3** and **5** suitable for X-ray diffraction analysis were grown at 5 °C from CH_2Cl_2 solutions containing each cluster that had been layered with hexane. The X-ray data for **3** (UNT) were collected on an APEX II CCD-based diffractometer at 100(2) K. The frames were integrated with the available APEX2 [15] software package using a narrow-frame algorithm, and the structure was solved and refined using the SHELXTL program package [16]. The diffraction data on **5** (SDSU) were collected at 200(2) K on a Bruker X8 APEX CCD diffractometer, and the frames were integrated with the available SAINT software package using a narrow-frame algorithm, [17] and the structure solved and refined using the available SHELXTL program package [17]. Both molecular structures were checked by using PLATON, [18] and all non-hydrogen atoms were refined with anisotropically, with the carbon-bound hydrogens assigned to calculated positions and allowed to ride on the attached carbon atom. The bridging hydride in **5** was not located during refinement. The refinement for **3**

Table 1 X-ray crystallographic data and processing parameters for clusters **3** and **5**

CCDC entry no.	710508	710509
Cryst system	Monoclinic	Triclinic
Space group	P2(1)/n	P – 1
<i>a</i> (Å)	10.8330(3)	11.2631(7)
<i>b</i> (Å)	15.3680(4)	11.2073(7)
<i>c</i> (Å)	14.0384(4)	11.8638(6)
α (°)		70.594(3)
β (°)	102.159(1)	74.975(3)
γ (°)		67.710(3)
<i>V</i> (Å ³)	2284.7(1)	1291.6(1)
Mol formula	C ₂₁ H ₁₂ N ₂ O ₉ Os ₃	C ₂₅ H ₁₁ N ₂ O ₉ Os ₃
fw	1006.93	1053.96
Formula units per cell (<i>Z</i>)	4	2
<i>D</i> _{calcd} (Mg/m ³)	2.927	2.710
λ (Mo K α) (Å)	0.71073	0.71073
μ (mm ⁻¹)	16.699	4.041
Absorption correction	Semi-empirical from equivalents	SADABS
Abs corr factor	0.4390/0.2292	0.1561/0.09554
Total reflections	25949	34890
Independent reflections	4513	8860
Data/res/parameters	4513/4/348	8860/0/352
R1 [<i>I</i> ≥ 2 σ (<i>I</i>)] ^a	0.0187	0.0478
<i>w</i> R2 ^b	0.0403	0.1171
GOF on <i>F</i> ²	1.013	1.046
$\Delta\rho$ (max), $\Delta\rho$ (min) (e/Å ³)	1.058, -0.914	3.161, -2.322

$$^a R1 = \frac{\sum \|F_o\| - |F_c|}{\sum |F_o|}$$

$$^b R2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

converged at *RI* = 0.0187 and *wR2* = 0.0403 for 4513 independent reflections with *I* > 2 σ (*I*), while **5** gave convergence values of *RI* = 0.0478 and *wR2* = 0.1202 for 8860 independent reflections with *I* > 2 σ (*I*).

Results and Discussion

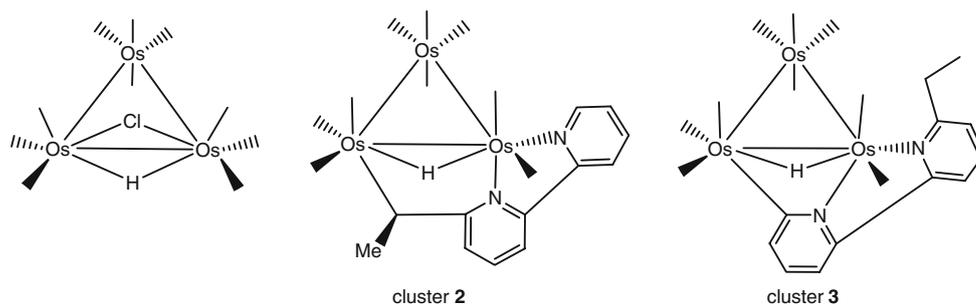
Synthesis, Spectroscopic Properties, and X-Ray Diffraction Structure of **3**

Treatment of cluster **1** with a slight excess of 6-Et-2,2'-bipyridine in refluxing CH₂Cl₂ led to the rapid consumption of **1** and the formation of three new spots as assessed by TLC analysis. The putative cluster Os₃(CO)₁₀(6-Et-2,2'-bipyridine) containing a chelating diimine ligand was not observed under the given reaction conditions. Control experiments from our earlier study employing the 6-Me-2,2'-bipyridine ligand have demonstrated that the formation of Os₃(CO)₁₀(6-Me-2,2'-bipyridine) is accompanied by rapid cyclometalation and ortho metalation sequences.

Table 2 Selected bond distances (Å) and angles (°) in the clusters **3** and **5**

3			
<i>Bond distances</i>			
Os(1)–Os(2)	2.8852(3)	Os(1)–Os(3)	2.9136(2)
Os(2)–Os(3)	2.8941(3)	Os(3)–N(1)	2.044(4)
Os(3)–N(2)	2.166(4)	Os(1)–C(14)	2.122(4)
Os(1)–H(1)	1.80(6)	Os(3)–H(1)	1.71(6)
<i>Bond angles</i>			
N(1)–Os(3)–N(2)	75.6(1)	N(1)–Os(3)–Os(2)	85.4(1)
N(1)–Os(3)–Os(1)	67.7(1)	N(2)–Os(3)–Os(2)	98.15(9)
N(2)–Os(3)–Os(1)	137.65(9)	C(9)–Os(3)–Os(1)	110.4(1)
C(1)–Os(1)–Os(3)	115.9(1)	C(3)–Os(1)–Os(3)	105.4(1)
C(8)–Os(3)–Os(1)	109.7(1)	C(2)–Os(1)–Os(2)	86.2(1)
C(4)–Os(2)–Os(1)	99.3(1)		
5			
<i>Bond distances</i>			
Os(1)–Os(3)	2.8806(4)	Os(1)–Os(2)	2.9307(3)
Os(2)–Os(3)	2.9082(3)	Os(2)–N(1)	2.058(4)
Os(2)–N(2)	2.163(5)	Os(1)–C(10)	2.116(5)
<i>Bond angles</i>			
N(1)–Os(2)–N(2)	75.4(2)	N(1)–Os(2)–Os(3)	87.1(1)
N(1)–Os(2)–Os(1)	67.5(1)	N(2)–Os(2)–Os(3)	106.2(1)
N(2)–Os(2)–Os(1)	140.2(1)	C(4)–Os(2)–Os(1)	109.4(2)
C(3)–Os(1)–Os(2)	109.0(1)	C(2)–Os(1)–Os(2)	110.1(2)
C(5)–Os(2)–Os(1)	109.5(2)	C(1)–Os(1)–Os(3)	92.6(2)
C(8)–Os(3)–Os(1)	93.2(2)		

Apparently, the same scenario is followed in the case of the 6-Et-2,2'-bipyridine ligand. The reaction products were subsequently isolated by column chromatography and characterized in solution by IR and ¹H NMR spectroscopies. The structures of the three products are depicted on the next page. The trace amount of the known cluster HOs₃(CO)₁₀(μ -Cl) isolated (<1%) was easily identified by its characteristic IR and NMR data and by comparison to an independently prepared sample [19, 20]. The hydride-bridged isomers HOs₃(CO)₉(N₂C₁₂H₁₁) are derived from the cyclometalation of the side-chain ethyl group and ortho metalation of the unsubstituted bipyridine ring affording **2** and **3**, respectively. These two clusters were obtained in 11 and 20% yields, respectively. The ¹H NMR spectra for clusters **2** and **3** were instrumental in helping assign the identity of the isomeric hydrides. Here seven distinct aryl resonances were found in the aromatic region of **2** from δ 7.41 to 9.28 consistent with an intact bipyridine platform. Moreover, the down-field doublet centered at δ 9.28 serves as a diagnostic marker for the *ortho* or 6' hydrogen on the unsubstituted bipyridine ring [21, 22]. Activation of one of the methylene C–H bonds on the ethyl substituent is supported by the presence of quartet and doublet resonances at δ 3.30 and δ 2.06 in an integral ratio of 1:3, respectively. The C–H bond activation that



accompanies **2** gives rise to a single diastereomer where the methyl group is assumed to adopt an exo or anti orientation relative to the Os₃ core. **2** exhibits a high-field hydride resonance at $\delta -19.85$ that is in concert with the chemical shift reported by us for the related cyclometalated cluster $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{11}\text{H}_9)$ formed from **1** and 6-Me-2,2'-bipyridine. While not examined in detail, a preliminary NMR study conducted in C_6D_6 at elevated temperature confirmed the conversion of **2**→**3**, supporting **2** as the kinetically controlled cluster in this isomeric mixture. Unfortunately, X-ray quality crystals of **2** proved elusive, despite repeated attempts to grow such crystals.

The ^1H NMR spectrum of **3** revealed the presence of a high-field bridging hydride at $\delta -15.45$, along with an intact ethyl group based on the recorded triplet and quartet resonances at $\delta 1.40$ (3H) and $\delta 2.90$ (2H), respectively. That the hydride ligand in **3** originates from an ortho metalation of the bipyridine ring is underscored by the observation of six distinct aromatic hydrogens from $\delta 6.97$ to 8.58. The unequivocal identity of **3** was established by

X-ray diffraction analysis, with the thermal ellipsoid plot of **3** depicted in the left-hand side of Fig. 1. The chelation of both nitrogen atoms to the Os(3) center and the ortho metalation of the original C(14)–H bond of the ancillary bipyridine ligand to the Os(1) atom are immediately confirmed in Fig. 1. **5** contains $48e^-$ and is electron precise according to conventional electron counting rules [23]. The Os–Os bond lengths range from 2.8852(3) Å [Os(1)–Os(2)] to 2.9136(2) Å [Os(1)–Os(3)], and the mean distance of 2.8976 Å is fully consistent with a polyhedral core predicated on three Os–Os single bonds. The Os(3)–N(1) [2.044(4) Å] and Os(3)–N(2) [2.166(4) Å] bond distances and bond angle of 75.6(1)° for the N(1)–Os(3)–N(2) linkage agree closely with those values reported for other diimine-chelated Os₃ clusters [8, 24, 25]. The Os(1)–C(14) bond length of 2.122(4) Å is congruent with those bond distances reported in related osmium clusters possessing an ortho-metalated ligand [26, 27]. The bridging hydride that was located during refinement spans the Os(1)–Os(3) vector, the longest of the three Os–Os vectors, and is in

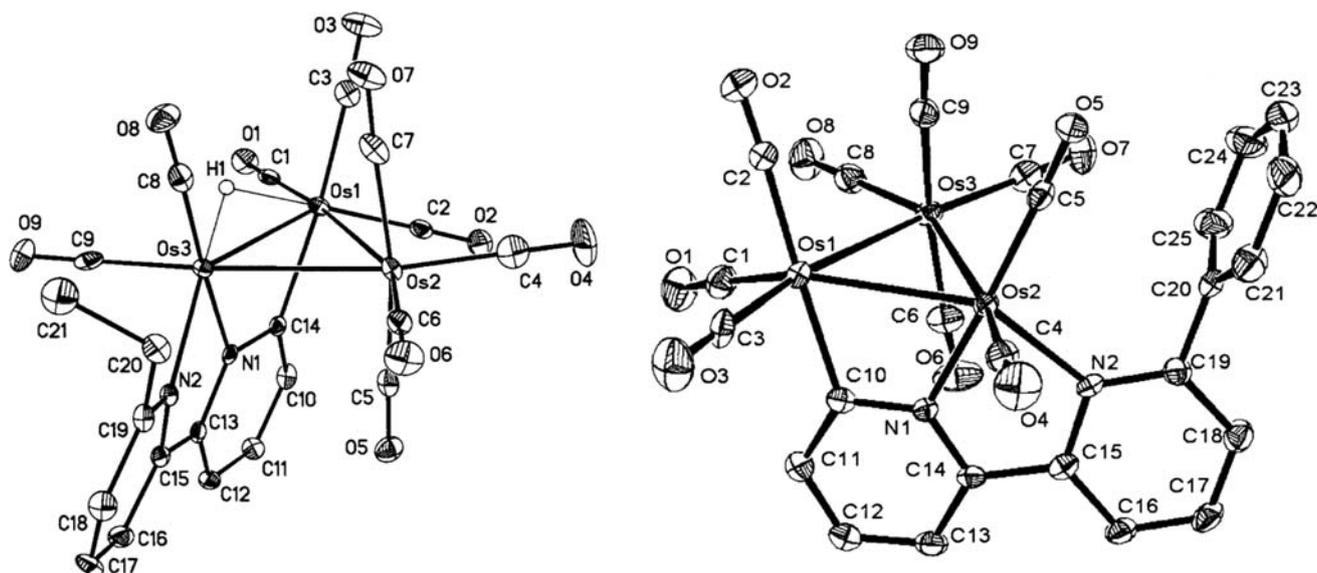
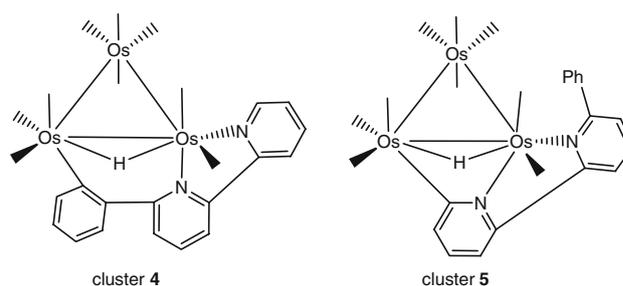


Fig. 1 Thermal ellipsoid plot of the ortho-metalated clusters **3** (left) and **5** (right) showing the thermal ellipsoids at the 50% probability level. Hydrogen atoms except H(1) in **3** are omitted for clarity

keeping with established bond-length trends in polynuclear clusters [28]. The bridging H(1) atom lies below the trimetallic plane that is capped by the axially disposed bipyridine ligand and bisects the C(1)–Os(1)–C(3) and C(8)–Os(3)–C(9) angles. The opening of the cis-equatorial C(1)–Os(1)–Os(3) and C(9)–Os(3)–Os(1) angles and the cis-axial C(3)–Os(1)–Os(3) and C(9)–Os(3)–Os(1) to well over 105° further strengthens the refined locus for the H(1) atom about the Os(1)–Os(3) bond. Similar hydride-induced structural effects in other polynuclear systems, have been documented [29, 30]. The remaining bond distances and angles are unremarkable and require no comment.

Synthesis, Spectroscopic Properties, and X-ray Diffraction Structure of **5**

The reaction between **1** and 6-Ph-2,2'-bipyridine was next pursued due to our interest in C–H bond selectivity as a function of the different ortho-metalation pathways available to substituted heterocyclic ligands. The initial product of ligand coordination, namely Os₃(CO)₁₀(6-Ph-2,2'-bipyridine), will lose CO and generate the unsaturated cluster Os₃(CO)₉(6-Ph-2,2'-bipyridine), which in turn will serve as the platform for the ensuing ortho metalation at either the phenyl group or the unsubstituted bipyridine ring. While the cyclometalation of the C(6)' alkyl group in Os₃(CO)₁₀(6-R-2,2'-bipyridine) has already been demonstrated as a kinetically controlled manifold, [8] no data exist for C–H bond selectivity between different aryl sites in this genre of cluster. Refluxing **1** and 6-Ph-2,2'-bipyridine in CH₂Cl₂ at 40 °C furnished three new spots, as assessed by TLC monitoring of the reaction solution. As with our earlier reaction, TLC analysis revealed a trace amount of HO₃(CO)₁₀(μ-Cl), in addition to two new spots attributed to the cluster compounds **4** (minor) and **5** (major), whose structures are shown to the right. The isomeric HO₃(CO)₉(N₂C₁₆H₁₁) clusters were isolated by chromatographic separation and characterized by spectroscopic methods, along with mass spectrometry and X-ray diffraction analysis in the case of **5**. The ¹H NMR spectrum of **4** exhibited a singlet resonance at δ –21.83, whose high-field location is consistent with the presence of bridging hydride, while the aromatic hydrogens appeared as an overlapping multiplet of 9H from δ 7.37 to 7.57, along with a single hydrogen triplet and doublet at δ 7.91 and δ 8.07. The 9:1:1 integral ratio displayed by these aryl hydrogens indicates that the bridging hydride originates from the ancillary heterocyclic ligand. Repeated attempts to grow single crystals of **4** were met with failure. The structure of **4** may, however, be reasonably assigned based on the ¹H NMR spectral data and the results obtained from an NMR thermolysis experiment conducted at 70–75 °C, where the isomerization of **4**→**5** was observed in C₆D₆. Accordingly,



the ortho metalation of the ancillary phenyl moiety in **4** represents the kinetic path for C–H activation.

The ¹H NMR spectrum of the thermodynamically more stable cluster **5** exhibits a high-field hydride at δ –15.80, in addition to seven distinct sets of aromatic resonances from δ 7.20 to 8.72 whose total integral value of 11 hydrogens reinforces a C–H activation originating from the heterocyclic ligand. The assignments for the ortho, meta, and the para hydrogens of the phenyl ring that are quoted in the experimental section were established via a two-dimensional ¹H COSY experiment. The ESI mass spectrum of **5** displayed a strong molecular ion at m/z 1054.78 and peaks corresponding to the sequential loss of up to five CO groups. The X-ray structure of **5** is shown in Fig. 1. **5** contains an ortho-metalated bipyridine ring that is bound to the Os(1)–Os(2) vector via the C(10) and N(1) atoms, respectively. The Os–Os bond distances in **5** follow closely those distances found in **3**, with the hydride assumed to bridge the longer Os(1)–Os(2) vector of 2.9307(3) Å based on the bond-length alterations in the Os₃ core and the opening of the angle in the C(4)–Os(2)–Os(1) [$109.4(2)^\circ$], C(3)–Os(1)–Os(2) [$109.0(1)^\circ$], C(2)–Os(1)–Os(2) [$110.1(2)^\circ$], and C(5)–Os(2)–Os(1) [$109.5(2)^\circ$] linkages. The Os(2)–N(2) [2.163(5) Å] and Os(2)–N(1) [2.058(4) Å] bond distances and the N(1)–Os(2)–N(2) bond angle of $75.4(2)^\circ$ are in excellent agreement with those values reported found by us for cluster **3** and HO₃(CO)₉(N₂C₁₀H₆-6-Me), [8] and the corresponding ortho-metalated cluster HO₃(CO)₉(N₂C₁₀H₇) that was isolated from the high-temperature thermolysis of Os₃(CO)₁₂ with 2,2'-bipyridine by Deeming and co-workers [24]. The phenyl group that is defined by the atoms C(20)–C(25) is nearly orthogonal to the bipyridine platform in order to minimize unfavorable van der Waals between the phenyl group and the axial C(5)O(5). The nine terminal CO groups exhibit bond distances and angles consistent within acceptable limits.

Conclusions

Ligand chelation and C–H bond activation of the mono-substituted 6-R-2,2'-pyridines (where R = Et, Ph) with

$\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ occur rapidly to afford a pair of isomeric hydride-bridged clusters $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{21}\text{H}_{11})$ (**2** and **3** for $\text{R} = \text{Et}$) and $\text{HOs}_3(\text{CO})_9(\text{N}_2\text{C}_{16}\text{H}_{11})$ (**4** and **5** for $\text{R} = \text{Ph}$). The triosmium clusters **2** (cyclometalation) and **4** (ortho metalation) that originate from the unsaturated intermediate $\text{Os}_3(\text{CO})_9(6\text{-R-}2,2'\text{-pyridine})$ represent kinetically controlled products from the activation of the 6-substituent. Transformation of the kinetic hydrides into the thermodynamically more stable hydride-bridged clusters **3** and **5** is accompanied by the ortho metalation of the unsubstituted pyridine ring, as verified by X-ray structural analyses. Future studies will investigate the selectivity in the C–H bond activation in other heterocyclic substrates as a function of the ring size and heteroatom using **1** and related mixed-metal clusters.

Supplementary Material

Crystallographic data for **3** (710508) and **5** (710509), in CIF format, have been deposited with the Cambridge Crystallographic Data Centre (CCDC). Copies of these latter data may be obtained free of charge via www.ccdc.cam.ac.uk/data_request/Cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

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