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# Synthesis of $[{Os_3(CO)_{10}(\mu_2-H)}_2{\{\mu_2,\mu_2-NC_6H_4C_6H_4N\}}]$ and $[{Os_3(CO)_9(\mu_2-H)PPh_3}_2{\{\mu_2,\mu_2-NC_6H_4C_6H_4N\}}]$ : Carbon–carbon bond formation promoted by organorhodium species

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Dedicated to D.M.P. Mingos.

#### Abstract

Synthesis and characterization of linked cluster  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (1) from the reaction of  $[Os_3Rh(\mu-H)_3(CO)_{12}]$  with aniline in the presence of an excess amount of 4-vinyl phenol in refluxing heptane is reported. A similar reaction with  $[Os_3(CO)_{10}(NCMe)_2]$  as starting material gave a known compound,  $[Os_3(CO)_{10}(\mu_2-H)(\mu_2-HNC_6H_5)]$  (2). The treatment of complexes 1 and 2 with Wilkinson's catalyst in refluxing heptane respectively, yielded  $[{Os_3(CO)_9(\mu_2-H)PPh_3}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (3). An interesting and unexpected C–C coupling of phenyl-amido ligands was observed in complexes 1 and 3, which is believed to be catalysed by the organometallic rhodium species. The newly synthesized compounds 1 and 3 were fully characterized by IR, <sup>1</sup>H NMR spectroscopy, mass spectroscopy, elemental analysis, and X-ray crystallography. Both structures 1 and 3 comprise two triangles of osmium atoms. The two triangular osmium metal cores are linked by a bi-amido ligand via the two nitrogen atoms N(1) and N(1)\* and N(1) and N(2), at their equatorial sites. The electronic absorption spectra of complexes 1, 2, and 3 display both low energy absorption,  $d\pi$  (Os)  $\rightarrow \pi^*$  (amido) metal-to-ligand charge-transfer (MLCT) transition, and  $\pi \to \pi^*$  intra-ligand electronic transitions of the amido and bi-amido ligands. © 2005 Elsevier B.V. All rights reserved.

Keywords: Carbon-carbon bond formation; Rhodium compound; Osmium cluster; X-ray crystal structures

#### 1. Introduction

The chemistry of the transition-metal-catalysed coupling of various reagents to generate new carbon-carbon bonds is currently a field of great interest [1–3]. Organometallic compounds may be regarded as model compounds for intermediates in the catalytic processes. Over the years, new C-C bond formations that are derived from different organic ligands catalysed by a wide range of transition metal complexes have been reported. Organoruthenium, iron, and platinum are good candidates for the promotion of the carbon-carbon bond formation. Girolami and co-

\* Corresponding author. Fax: +852 25472933/28571586. E-mail address: wtwong@hkucc.hku.hk (W.-T. Wong). workers reported the carbon-centered coupling of two propadiene molecules with a ruthenium complex resulted into  $[Cp_2^*Ru_2(\eta^3:\eta^3-C_6H_8)Cl_4]$  [4]. Other studies have revealed that the C–C coupling of arenes by cationic Pt(II) complexes into biaryls is also possible. The Pt–biaryl complexes can then be oxidatively cleaved to generate free biaryls, which offers a new perspective for the synthesis of organic compounds [1]. In addition to these organometallic complexes, a great deal of work has also been devoted to the use of the rhodium complexes [5–7]. The C–C coupling reaction of olefins and diphenyldiazomethane catalysed by cationic rhodium(I) complexes has been previously reported by Werner and co-workers [8].

In the context of our studies on the reaction of  $[Os_3Rh(\mu-H)_3(CO)_{12}]$  with aniline, we have been able to isolate a linked bis-triosmium metal clusters in which the

metal triangles are bridged by a biphenyl-amido ligand  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (1). To our knowledge, biphenyl-amido containing cluster complex is very rare. Gunnoe reported an aryl-coupled binuclear compound by the oxidation of the Ru(II) amido complexes TpRuL<sub>2</sub>(NHPh), (Tp = Hydridotris(pyrazolylborate); L = CO, PMe\_3, or P(OMe)\_3) [9]. Herein, we report the synthesis of  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (1) and  $[Os_3(CO)_{10}(\mu_2-H)(\mu_2-HNC_6H_5)]$  (2) from the reaction of  $[Os_3Rh(\mu-H)_3(CO)_{12}]$  and  $[Os_3(CO)_{10}(NCMe)_2]$  with aniline respectively, and the reactivity of both complexes 1 and 2 with Wilkinson's catalyst. Studies on the cleavage of the Os-bi-phenyl amido complexes to generate free biphenyl diamine are underway.

#### 2. Experimental

#### 2.1. General procedures

All of the reactions and manipulations were carried out under nitrogen using Schlenk techniques unless otherwise stated. The glassware was pre-dried in an oven (~120 °C) before use. The reactions were monitored by both IR spectroscopy and analytical thin-layer chromatography (Merck Kieselgel 60  $F_{254}$ ), and the products were separated by thin-layer chromatography on plates that are coated with silica (Merck Kieselgel 60  $F_{254}$ ). Dichloromethane (Ajax, AR) was distilled over calcium hydride. *n*-Hexane (Ajax, AR) was purified by distillation in the presence of sodium-benzophenone. All of the other solvents were of analytical grade and were freed from oxygen by degassing and saturating with nitrogen atmosphere before use.

The starting materials  $[Os_3Rh(\mu-H)_3(CO)_{12}][10]$ ,  $[Os_3(\mu-H)_3(CO)_{12}][10]$ ,  $[Os_3(\mu-H$  $H_{2}(CO)_{10}$ [11],  $[Os_3(CO)_{10}(NCMe)_2]$  [12], and [{Rh(CO)<sub>2</sub>Cl}<sub>2</sub>] [13] were prepared according to literature procedures. All of the chemicals, unless otherwise stated, were purchased commercially and used as received. Infrared spectra were recorded on a Bio-Rad FTS-165 IR spectrometer, using 0.5 mm CaF<sub>2</sub> solution cells. <sup>1</sup>H NMR was obtained on a Bruker DPX400 spectrometer using CD<sub>2</sub>Cl<sub>2</sub> and referenced to SiMe<sub>4</sub> ( $\delta = 0$ ). Positive ionization fast atom bombardment (FAB) mass spectra were recorded on a Finnigan MAT 95 mass spectrometer, using 3-nitrobenzyl alcohol as the matrix solvent. GC-MS spectra were obtained on a GCD series II gas chromatograph electron ionization detector. UV-Vis electronic absorption spectra were obtained from a microprocessor-controlled HP 8450P array spectrophotometer using a quartz cell with a path length of 1 cm. Elemental analyses were performed by the Department of Chemistry, City University of Hong Kong.

# 2.1.1. Synthesis of $[ \{ Os_3(CO)_{10}(\mu_2 - H) \}_2 \{ \mu_2, \mu_2 - NC_6H_4C_6H_4N \} ]$ (1)

 $[Os_3Rh(\mu-H)_3(CO)_{12}]$  (100 mg, 0.10 mmol) and aniline (9.2 mg, 0.10 mmol) with an excess amount of 4-vinylphenol were stirred in refluxing heptane (50 cm<sup>3</sup>) under a nitrogen atmosphere for 2 h. The solution gradually turned from yellow to yellow brown with some brown oily product. The solution was then filtered and the volume was reduced to 5 cm<sup>3</sup> in vacuo. Purification was accomplished by TLC using hexane– $CH_2Cl_2$  (3:1 v/v) as an eluent to yield complex 1 as a major purple red compound in a 43% yield (75.35 mg, 0.04 mmol). Two other uncharacterized yellow bands in very low yields were observed. Elemental Anal. Calc. for C<sub>32</sub>H<sub>10</sub>N<sub>2</sub>O<sub>20</sub>Os<sub>6</sub>: C, 20.40; H, 0.54; N, 1.49. Found: C, 20.55; H, 0.60, N, 1.50%. The IR spectrum was  $[v(CO), cm^{-1}, CH_2Cl_2]$ : 2110vs, 2077vs, 2054s, 2033w, 2014 br. MS (FAB +ve) m/z: 1883 [M]<sup>+</sup>, observed 914 [M/2-CO]<sup>+</sup>. The <sup>1</sup>H NMR study at 298 K comprised two sets of signals 1a and 1b at a ratio of approximately 2:1 and showed the presence of two isomers, **1a**:  $\delta$  7.92 (m, 4H, aryl H),  $\delta$  7.54 (m, 4H, aryl H),  $\delta$  -19.65 (s, 2H, Os-H) 1b:  $\delta$  7.44 (m, 4H, aryl H),  $\delta$  6.71 (m, 4H, aryl H),  $\delta$  -10.41 (s, 2H, Os-H). Single crystals of 1 that were suitable for X-ray studies were obtained by the gasphase diffusion of hexane into CH<sub>2</sub>Cl<sub>2</sub> solution.

2.1.2. Synthesis of  $[Os_3(CO)_{10}(\mu_2-H)(\mu_2-HNC_6H_5)]$  (2)

To a solution of  $[Os_3(CO)_{10}(NCMe)_2]$  (100 mg, 0.11 mmol) in heptane (50 ml), one equivalent of aniline (10.2 mg, 0.11 mmol) was added. The yellow solution was allowed to heat under reflux for 2 h until the reaction mixture changed gradually to brown. The solvent was then removed in vacuo and redissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>). Purification by TLC using *n*-hexane– $CH_2Cl_2$  (3:1 v/v) as an eluent gave a lilac compound 2 in a 40% yield (41.45 mg, 0.04 mmol) together with two uncharacterized light purple bands. Elemental Anal. Calc. for C<sub>16</sub>H<sub>6</sub>NO<sub>10</sub>Os<sub>3</sub>: C, 20.38; H, 0.64; N, 1.49. Found: C, 20.45; H, 0.66; N, 1.50%. The IR spectrum was  $[v(CO), cm^{-1}, CH_2Cl_2]$ : 2113vs, 2074vs, 2062vs, 2026vs, 2012vs, 1981m. MS (FAB +ve) m/z: 943  $[M]^+$ ; observed: 915  $[M-CO]^+$ . The <sup>1</sup>H NMR study at 298 K,  $\delta$  7.46 (t, 2H, aryl H),  $\delta$  6.97 (s, 1H, aryl H),  $\delta$ 6.71 (d, 2H, aryl H), 3.43 (s, 1H, NH),  $\delta$  -10.47 (s, 1H, Os-H). No single crystals of 2 that were suitable for Xray studies were obtained.

# 2.1.3. Synthesis of $[ \{Os_3(CO)_9(\mu_2-H)PPh_3\}_2 \{\mu_2,\mu_2-NC_6H_4C_6H_4N\} ]$ (3)

Both compounds 1 (100 mg, 0.05 mmol) and 2 (100 mg, 0.11 mmol) with an excess amount of Wilkinson's catalyst respectively, were stirred overnight in refluxing heptane (50 cm<sup>3</sup>) for 24 h. Both the solutions turned from orange red to light brown. The solvent was then removed in vacuo to give a brown solid material, which was redissolved in 2–3 cm<sup>3</sup> of dichloromethane. The residue was chromatographed on TLC using *n*-hexane–CH<sub>2</sub>Cl<sub>2</sub> (3:1 v/v) as an eluent to give a blue complex **3** as the major product. The reaction of both compounds **1** and **2** yielded 40% of complex **3**, that is (48.2 mg, 0.02 mmol) and (96.4 mg, 0.04 mmol), respectively. Elemental *Anal.* Calc. for C<sub>68</sub>H<sub>40</sub>N<sub>2</sub>Os<sub>6</sub>O<sub>18</sub>P<sub>2</sub>: C, 34.37; H, 1.70; N, 1.18. Found: C, 34.50, H, 1.65; N, 1.20%. The IR spectrum was [v(CO),

cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>]: 2083s, 2048s, 2006vs. MS (FAB +ve) m/z: 2409 [M]<sup>+</sup>; observed: 2353 [M–2CO]<sup>+</sup>. The <sup>1</sup>H NMR study at 298 K comprised two sets of signals **3a** and **3b** at a ratio of approximately 1:1, and showed the presence of two isomers in the range of  $\delta$  6.45–7.60 (m, 16H, aryl H),  $\delta$  7.20–7.45 (m, 60H, PPh<sub>3</sub>), and  $\delta$  –14.05 to –14.15 (m, 4H, Os–H). Single crystals of **3** that were suitable for Xray studies were obtained by the vapour diffusion of octane into CH<sub>2</sub>Cl<sub>2</sub> solution.

#### 2.1.4. Crystallography

All pertinent crystallographic data and other experimental details are summarized in Table 5. Crystals suitable for X-ray analyses were glued on glass fibres with epoxy resin or sealed in a 0.3 mm glass capillary. Intensity data were collected at an ambient temperature on a Bruker AXS SMART CCD diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda =$ 0.71073 Å). All structures were solved by direct methods (SHELX97) [14] and expanded by Fourier-difference technique (DIRDIF99) [15]. All metal atoms were anisotropically refined in 1, and the rest were refined isotropically. All metal, nitrogen and phosphorous atoms with some carbon atoms were refined anisotropically in 3, except C(8) and the carbon atoms of the bi-amido phenyl ligands were refined isotropically. The hydrogen atoms were generated in their ideal position and were included in the structure factor calculations using the riding mode, but were not refined for all of the structures. The metal-hydrido atoms were placed in their ideal position, but were not refined. Due to the highly disordered nature of the solvent molecule in compound 3, the carbon and hydrogen atoms of the octane molecule were only refined with their xyz position, and a long C-C bond distance and a bad angle were observed. Some residue peaks in the final differences Fourier map were also observed in 3, which may be due to the presence of another highly disorder solvent moiety, several attempts were made to model the solvent molecule, but an unreasonable chemical structure was found. Therefore, no modeling was made for the residue electron density observed. The calculations were performed on a Silicon Graphics computer using teXsan [16] crystallographic software package.

## 3. Results and discussion

Treatment of  $[Os_3Rh(\mu-H)_3(CO)_{12}]$  with 1 equivalent of aniline in the presence of an excess amount of 4-vinylphenol in heptane  $(50 \text{ cm}^3)$  under reflux for 2 h yielded a purple red product  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6H_4C_6-}$  $H_4N$ ] (1) in a 43% yield and two other uncharacterized yellow bands in very low yields upon TLC separation on silica, see Scheme 1. The IR spectra of cluster 1 gave peaks in the range of  $2014-2110 \text{ cm}^{-1}$ , which indicates the presence of terminal bonded carbonyl ligands only. The <sup>1</sup>H NMR spectrum of compound 1 in CD<sub>2</sub>Cl<sub>2</sub> at room temperature comprises two sets of signals at a relative ratio of 2:1 in the aromatic and hydride regions where the two sets of signals have a similar coupling pattern, which indicates that two isomers are present in solution. The presence of the isomers may be due to the hindered rotation about the C-C bond that links the two tri-osmium cluster units, see Scheme 2. The <sup>1</sup>H NMR spectra at 298 K of both of the isomers consists of two aromatic signals, 1a:  $\delta$  7.92,  $\delta$ 7.54; **1b**:  $\delta$  7.44,  $\delta$  6.71, and one hydride signal, **1a**:  $\delta$ -19.65 and **1b**:  $\delta$  -10.41, which confirms the presence of the biphenyl-amido ligand and the metal hydride. The positive FAB mass spectrum of 1 exhibits an envelope that is centered at m/z = 914, which suggests the cleavage of the bi-amido ligand at the C–C bond, leading to the formation of 2 { $Os_3(CO)_{10}(\mu_2-H)(\mu_2-NC_6H_4)$ } units with a stepwise loss of carbonyl ligands (see Table 1). To establish the molecular structure of 1, an X-ray analysis was carried out on a purple red crystal that was obtained by the slow evaporation of n-hexane into CH<sub>2</sub>Cl<sub>2</sub> solution below -5 °C over a period of a few days. The structure is shown in Fig. 1, together with the atomic labeling scheme, selected



Scheme 1. Reagent and conditions: (i) aniline, 4-vinylphenol, heptane, reflux; (ii) aniline, heptane, reflux; (iii) Wilkinson's catalyst, heptane, reflux.



 $\frac{O_{S}}{H} \xrightarrow{N} O_{S}$ 

Scheme 2. A possible isomerisation process of  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\{\mu_2,\mu_2-NC_6H_4C_6H_4N\}}]$  (1).

bond distances and angles of cluster 1 are presented in Table 2 and the relevant structural parameters are listed in Table 5. The structure of 1 comprises two triangles of osmium atoms with 10 terminal carbonyl groups each. The two triangular osmium metal core are linked by a biamido ligand which is formed via the coupling of the  $C(14)-C(14^*)$  bond, 1.37 Å, which is short enough to have multiple bond character. Complex 1 sits on a crystallographic center of symmetry at the mid point of the  $C(14)-C(14^*)$  bond. The bi-amido ligand symmetrically bridges Os(1)-Os(3) and  $Os(1)^*-Os(3)^*$  of the triosmium metal clusters via the two nitrogen atoms N(1) and  $N(1)^*$ , respectively. The bi-amido moiety in this complex contains a C=N double bond (1.26(5) Å), which is not commonly observed. Similar geometric bridging arrangements have been found in  $[Os_3(CO)_{10} \{\mu - N(H)(C_5H_3NBr)\}$ - $\{\mu - N(C_{10}H_{13}NO)\}$  [17],  $[Os_3(\mu - H)(CO)_{10}(\mu - N = C(H)CF_3)]$ [18], and  $[Os_3(\mu-H)(CO)_{10}(\mu-N=C(H)Et)]$  [19], in which the

Table 2

Selected bond distances (A) and angles (°) for cluster 1			
Os(1)–Os(2)	2.846(3)	Os(1)–Os(3)	2.810(2)
Os(1)–N(1)	2.07(3)	Os(2)-Os(3)	2.846(3)
Os(3)-N(1)	2.06(4)	N(1)-C(11)	1.26(5)
C(11)-C(12)	1.45(6)	C(11)-C(16)	1.45(6)
C(12)-C(13)	1.36(6)	C(13)-C(14)	1.45(6)
C(14)-C(15)	1.47(5)	C(14)-C(15)	1.37(1)
C(15)-C(16)	1.36(6)		
Os(2)-Os(1)-Os(3)	60.41(6)	Os(3)-Os(2)-Os(1)	59.16(6)
Os(2)–Os(3)–Os(1)	60.43(6)	Os(3)-N(1)-Os(1)	85(1)

N-C bond lies between 1.29(3) and 1.38(5) Å. Within the molecule, N(1), C(11), C(12), C(13), C(14), C(15), and C(16) form a plane that is almost perpendicular to the osmium triangle of Os(1), Os(2), and Os(3) with a dihedral angle of 68.13°. The hydride ligand was not located directly in the analysis, but the bending of the equatorial carbonyl groups C(3) O(3) and C(8) O(8) away from the Os(1)-Os(3)edge suggests that it lies in the plane of the imido ligand that bridges across the Os(1)-Os(3) edge. To gain insight into the mechanism by which the bi-amido ligand is formed, we treated  $[Os_3(CO)_{10}(NCMe)_2]$  with aniline in refluxing heptane for 2 h to compare with the former reaction product. The analysis shows that no coupling of the amido ligands has occurred, and the known cluster,  $[Os_3(CO)_{10}(\mu_2-H)(\mu_2-HNC_6H_5)]$  (2), is obtained instead [20]. This suggests that the rhodium metal in the cluster  $[Os_3Rh(\mu-H)_3(CO)_{12}]$  plays an important role in the formation of the C–C bond in  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6-}$  $H_4C_6H_4N$ ] (1). There are some examples of rhodiumcatalysed coupling reactions [2,6,7]. In addition to rhodium metal, organoruthenium and platinum have been shown to be able to promote C-H bond activations and C-C bond formation between other unsaturated hydrocarbons [1,4]. Treatment of the two products  $[{Os_3(CO)_{10}(\mu_2-H)}]_2$ - $\{\mu_{2},\mu_{2}-NC_{6}H_{4}C_{6}H_{4}N\}\]$  (1) and  $[Os_{3}(CO)_{10}(\mu_{2}-H)(\mu_{2}-HN C_6H_5$ ] (2) with an excess amount of Wilkinson's catalyst in refluxing heptane respectively, gave the same blue complex  $[{Os_3(CO)_9(\mu_2-H)PPh_3}_2{\mu_2,\mu_2-NC_6H_4C_6-H_4N}]$  (3) in roughly 40% yield upon TLC separation on silica, see Scheme 1. The compound 3 was characterized by spectroscopic and crystallographic techniques. The IR, <sup>1</sup>H NMR, and mass spectroscopy data for the new complex is fully consistent with those of solid-state structures (see

Table I		
Spectroscopic dat	a for compo	unds 1-3

1	1 1		
Cluster	IR spectra <sup>a</sup> v(CO)/cm <sup>-1</sup>	Mass spectra <sup>b</sup> $m/z$	1H NMR spectra <sup>c</sup> $\delta$ , J/Hz
1	2110vs, 2077vs, 2054s, 2033w, 2014br	914 [M/2-CO] <sup>+</sup>	At 298 K for <b>1a</b> : $\delta$ 7.92 (m, 4H, aryl H), $\delta$ 7.54 (m, 4H, aryl H), $\delta$ –19.65 (s, 2H, Os–H) <b>1b</b> : $\delta$ 7.44 (m, 4H, aryl H), $\delta$ 6.71 (m, 4H, aryl H), $\delta$ –10.41 (s, 2H, Os–H)
2	2113vs, 2074vs, 2062vs, 2026vs, 2012vs, 1981m	915 [M-CO] <sup>+</sup>	At 298 K, $\delta$ 7.46 (t, 2H, aryl H), $\delta$ 6.97 (s, 1H, aryl H), $\delta$ 6.71 (d, 2H, aryl H), $\delta$ 3.43 (s, 1H, NH), $\delta$ –10.47 (s, 1H, Os–H)
3	2083s, 2048s, 2006vs	2353 [M-2CO] <sup>+</sup>	At 298 K for <b>3a</b> and <b>3b</b> : $\delta$ 6.45–7.60 (m, 16H, aryl H), $\delta$ 7.20–7.45 (m, 60H, PPh <sub>3</sub> ), and $\delta$ –14.05 to –14.15 (m, 4H, Os–H)

<sup>a</sup> Recorded in CH<sub>2</sub>Cl<sub>2</sub> unless otherwise stated.

<sup>b</sup> Positive FAB MS; the calculated values are in parentheses.

<sup>c</sup> Recorded in  $CDCl_2$  for 1–3.



Fig. 1. The molecular structure of  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (1) with the atom numbering scheme.

Table 1). Only terminal carbonyls were observed in the IR region ( $v_{CO}$  2200–1600) for the complex in solution. The FAB mass spectra of cluster 3 showed the corresponding parent molecular ion peak at m/z 2353 (calc. 2409), which reveals the loss of two CO units. The <sup>1</sup>H NMR spectrum of compound 3 in CD<sub>2</sub>Cl<sub>2</sub> at room temperature comprises two sets of signals at a relative ratio of 1:1 in the aromatic and hydride regions, and shows the presence of two isomers in the range of  $\delta$  6.45–7.60 (m, 16H, aryl H),  $\delta$ 7.20–7.45 (m, 60H, PPh<sub>3</sub>), and  $\delta$  –14.05 to –14.15 (m, 4H, Os-H). It is suggested that the presence of the two isomers in solution is due to a similar C-C bond rotation process proposed for 1. To elucidate the structure of cluster 3, an X-ray analysis was carried out on a blue crystal that was grown by the slow evaporation of an octane/CH<sub>2</sub>Cl<sub>2</sub> solution at -5 °C over a period of a few days. The molecular structure of  $[{Os_3(CO)_9(\mu_2-H)PPh_3}_2{\mu_2,\mu_2-NC_6H_4C_6-$ 

 $H_4N$ ] (3) is shown in Fig. 2, and the associated bond lengths and interbond angles are presented in Table 3. The analysis reveals that the structure of cluster **3** is very similar to that of complex 1, which contains two triangular osmium metal cores, [Os(1)-Os(2), 2.825(1); Os(2)-Os(3),2.859(1); Os(1)–Os(3), 2.850(1); Os(4)–Os(5), 2.822(1);  $O_{s}(5)-O_{s}(6)$ , 2.847(1) and  $O_{s}(4)-O_{s}(6)$ , 2.849(1)], that are linked by a C-C (C(60)-C(61), 1.41(2)) coupled bi-amido ligand that bridges the Os(1)-DOs(2) and Os(4)-Os(5)edges through N(1) and N(2) at the equatorial sites. It only differs in the terminal ligands, in which one of the terminal carbonyl groups is replaced by a PPh<sub>3</sub> ligand. Both of the C-N bond in the bi-amido moiety are double bond (1.35(2) Å), which compares well with similar systems [17–19]. The two phenyl ring in 3 are found to be co-planar to each other with a small dihedral angle of 3.465°. Hence, the atoms N(1), C(55), C(56), C(57), C(58), C(59), C(60)



Fig. 2. The molecular structure of  $[{Os_3(CO)_9(\mu_2-H)PPh_3}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (3) with the atom numbering scheme.

Table 3 Selected bond distances (Å) and angles (°) for cluster **3** 

Selected bolid distances (A) and angles ( ) for cluster 5			
Os(1)–Os(2)	2.825(9)	Os(1)–Os(3)	2.850(1)
Os(1) - N(1)	2.08(2)	Os(2) - Os(3)	2.859(1)
Os(2)–N(1)	2.04(1)	Os(4) - Os(5)	2.822(1)
Os(4) - Os(6)	2.849(1)	Os(4)–N(2)	2.04(1)
Os(5) - Os(6)	2.847(1)	Os(5)–N(2)	2.04(2)
N(1)-C(55)	1.35(2)	N(2)-C(64)	1.35(2)
C(55)-C(56)	1.42(3)	C(55)-C(58)	1.45(2)
C(56)-C(57)	1.38(2)	C(57)-C(60)	1.39(2)
C(58)-C(59)	1.34(3)	C(59)–C(60)	1.48(3)
C(60)-C(61)	1.41(2)	C(61)-C(62)	1.46(3)
C(61)-C(66)	1.42(2)	C(64)-C(65)	1.42(3)
C(65)-C(66)	1.37(3)		
Os(2)-Os(1)-Os(3)	60.49(3)	Os(3)-Os(1)-Os(1)	60.19(3)
Os(2) - Os(3) - Os(1)	59.31(3)	Os(5)-Os(4)-Os(6)	60.27(3)
Os(6)-Os(5)-Os(4)	60.32(3)	Os(5)-Os(6)-Os(4)	59.40(3)
Os(2)-N(1)-Os(1)	86.7(5)	Os(5)-N(2)-Os(4)	87.6(5)

C(61), C(62), C(63), C(64), C(65), C(66), and N(2) can be regarded as a plane and makes an angle of 69.00(1)° and  $67.65(3)^{\circ}$  with the osmium triangles, Os(1), Os(2) and Os(3) and Os(4), Os(5) and Os(6), respectively. The plane is nearly co-planar with one of the phenyl rings of each of the PPh<sub>3</sub> units, i.e., C(25) to C(30) and C(49) to C(54), respectively, with dihedral angles of only  $9.55(2)^{\circ}$  and 9.82(2)°. The hydride ligand was not located directly in the analysis, but both the bridged and unbridged Os-Os bonds in cluster 3 show only a little variation in bond distance, and therefore the two hydrido ligands are located according to the bending of the equatorial carbonyl groups C(2) O(2) and C(4) O(4) away from the Os(1)-Os(2) edge, and C(11) O(11) and C(14) O(14) bending away from the Os(4)-Os(5) edge. The coupling of the two coordinated amido ligands {NC<sub>6</sub>H<sub>5</sub>} in **2** that leads to [{Os<sub>3</sub>(CO)<sub>9</sub>( $\mu_2$ -H)PPh<sub>3</sub> $_{2\mu_2,\mu_2}$ -NC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>N] (**3**) is observed, which further suggests the function of organorhodium species in promoting C-H bond activation and C-C bond formation between the amido ligands.

#### 3.1. Electronic absorption spectra

The UV–Vis spectral data for complexes 1–3 in CH<sub>2</sub>Cl<sub>2</sub> are summarized in Table 4. The absorptions in the lower energy region (ca. 402–547 nm) are attributed to electronic transitions that arise from the  $d\pi$  (Os)  $\rightarrow \pi^*$  (amido) MLCT transition, and are similar to those observed in a triosmium metal cluster that contains an azo ligand at ca. 516 nm with an extinction coefficient of 7217 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> [21]. In addition to the low energy absorption, the absorptions in the higher energy region (ca. 264–334 nm) are assigned to the  $\pi \rightarrow \pi^*$  intra-ligand electronic transitions of the amido

Table 4

Cluster	Electronic absorption $\lambda_{max}/nm (\epsilon/dm^3 mol^{-1} cm^{-1})^a$
1	318 (3103), 547 (1028)
2 3	334 (1606), 546 (324) 264 (15822), 402 (833)

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 298 K.

	Compound	
	1	3
Empirical formula	Os <sub>6</sub> C <sub>32</sub> H <sub>10</sub> N <sub>2</sub> O <sub>20</sub>	Os <sub>6</sub> C <sub>68</sub> H <sub>40</sub> N <sub>2</sub> O <sub>18</sub> P <sub>2</sub>
Formula weight	1883.63	2409.31
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (#14)	P1 (#2)
a (Å)	7.361(2)	11.007(3)
b (Å)	30.711(7)	18.114(6)
<i>c</i> (Å)	9.356(2)	20.762(7)
α (°)	90	75.00(1)
β (°)	100.28(1)	75.22(1)
γ (°)	90	87.13(1)
$V(Å^3)$	2081.1(9)	3865.6(21)
Z value	2	2
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	3.006	2.070
<i>F</i> (000)	1664	2226
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	183.12	99.21
Temperature (K)	298	298
Reflection collected	13 223	24 443
Unique reflection	4820	16843
Observed reflection $[I > 2.00\sigma(I)]$	2185	12076
Final $R, R_{\rm w}$	0.055, 0.086	0.055, 0.066

and bi-amido ligands that are attached to the tri-osmium metal clusters. Similar absorption bands were found for the corresponding untreated aniline and free biphenyl-4,4'-diamine ( $H_2NC_6H_4C_6H_4NH_2$ ) ligand.

### 4. Conclusions

In this work, we demonstrate the coupling of two phenyl amido units  $\{NC_6H_5\}$  into a biphenyl amido ligand via the formation of a C-C bond in the two newly formed complexes  $[{Os_3(CO)_{10}(\mu_2-H)}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (1) and  $[{Os_3(CO)_9(\mu_2-H)PPh_3}_2{\mu_2,\mu_2-NC_6H_4C_6H_4N}]$  (3) (see Table 5). We could not establish the mechanistic details for the coupling reactions, but we have found the key element in the reaction that is responsible for the promotion of the C-C bond formation. The rhodium metal in either the starting material which is  $[Os_3Rh(\mu-H)_3(CO)_{12}]$  for compound 1 or the Wilkinson's catalyst in catalyzing cluster 2 is believed to play a very important role in the catalytic reaction. No formation of bi-phenyl amido ligands was observed without the present of the Rh metal. These complexes display intense purple and blue colours, and show both low and high energy absorption peaks in the electronic absorption spectra, which are assigned as the  $d\pi$  (Os)  $\rightarrow \pi^*$ (amido) MLCT transition and the  $\pi \rightarrow \pi^*$  intra-ligand electronic transitions of the amido and bi-amido ligands.

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#### Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC287374– CCDC287375. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.12.046.

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