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Platinum-Osmium Heterometallic Clusters Containing N-Heterocyclic Carbene Ligands and an Electron Deficient Tetraosmium Byproduct

Yu Liu,^[a] Rakesh Ganguly,^[a] Han Vinh Huynh,^[b] and Weng Kee Leong^{*[a]}

Abstract: The room temperature reaction of $[\text{Os}_3(\text{CO})_{12}]$ (**1**) with three molar equivalents of $[\text{PtCl}(\text{allyl})(\text{NHC})]$ (**2**) in the presence of KO^tBu afforded the heterometallic clusters $[\text{PtOs}_3(\text{CO})_{12}(\text{NHC})]$ (**3**), $[\text{Pt}_2\text{Os}_3(\text{CO})_{12}(\text{NHC})_2]$ (**4**) and $[\text{Pt}_3\text{Os}_3(\text{CO})_{12}(\text{NHC})_3]$ (**5**), together with a trace amount of the tetraosmium cluster $[\text{Os}_4(\text{CO})_{10}(\mu\text{-H})_2(\text{NHC})]$ (**6**). The reaction pathway is thus similar to that for Pd analogues, with the exception of cluster **6**. Unlike their Pd analogues, however, these clusters do not appear to readily interconvert. With a valence electron count of 58, the clusters **6** are deficient by four electrons.

Introduction

N-heterocyclic carbenes are now ubiquitously used as ligands in organometallic chemistry.^[1] In most cases, they are used to stabilize discrete metal centers, while cluster-NHC chemistry has been less explored. Transition metal clusters have found interesting applications and, in particular, heteronuclear organometallic clusters have been utilised as core-source precursors for bimetallic nanoparticles; this allowed for control over the composition, particle size and homogeneity.^[2] For example, we have shown that cluster-derived ruthenium-platinum nanoparticles are very active heterogeneous catalysts for the steam reforming of ethanol.^[3] Similarly derived ruthenium-osmium nanoparticles also show activity for CO oxidation,^[4] and osmium-platinum bimetallic systems have been shown to be active as fuel cell catalysts.^[5] In our previous work, we have demonstrated that the $[\text{Pd}(\text{NHC})]$ fragments, generated from the Pd^{II} complexes of the type $[\text{PdCl}(\text{allyl})(\text{NHC})]$, can readily add across the Os-Os bonds in osmium carbonyl clusters to afford a series of clusters with a raft-like Os_3Pd_n core.^[6] In this paper, we wish to report our extension of that synthetic methodology to obtain bimetallic OsPt clusters.

Results and Discussion

The room temperature reaction of $[\text{Os}_3(\text{CO})_{12}]$ (**1**) with three molar equivalents of $[\text{PtCl}(\text{allyl})(\text{NHC})]$ (**2**), via the reaction of $[\text{Os}_3(\text{CO})_{12}]$ with $[\text{PtCl}(\text{allyl})(\text{NHC})]$, where NHC = SIPr [N, N'-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene] (**a**), IPr [N, N'-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene] (**b**) or IMes [N, N'-dimesitylimidazolin-2-ylidene] (**c**), in the presence of a base (KO^tBu) afforded the new clusters $[\text{PtOs}_3(\text{CO})_{12}(\text{NHC})]$ (**3**), $[\text{Pt}_2\text{Os}_3(\text{CO})_{12}(\text{NHC})_2]$ (**4**) and $[\text{Pt}_3\text{Os}_3(\text{CO})_{12}(\text{NHC})_3]$ (**5**), together with a trace amount of the tetraosmium cluster $[\text{Os}_4(\text{CO})_{10}(\mu\text{-H})_2(\text{NHC})]$ (**6**) (Scheme 1). With increasing reaction time or amount of **2** relative to **1**, the formation of **5** was favoured over **3** and **4**. The reaction thus follows the same general course as for the Pd analogues, with the exception of cluster **6**, which was not observed in the reactions involving the Pd analogues. All the clusters have been characterized spectroscopically and analytically; for clusters **3a**, **3c**, **4a**, **4c**, **5b**, **6a** and **6b**, they have also been characterized by single-crystal X-ray crystallographic studies.

Scheme 1. Reaction of $[\text{Os}_3(\text{CO})_{12}]$ (**1**) and $[\text{PtCl}(\text{allyl})(\text{NHC})]$ (**2**).

ORTEP plots showing the molecular structures of **3a**, **4a** and **5b** are given in Figure 1. They may be compared with their Pd analogues,^[6] as well as their phosphine analogues, viz., $[\text{Os}_3(\text{CO})_{12}\{\text{Pt}(\text{P}^i\text{Bu}_3)_n\}]$ ($n = 1\text{-}3$, **3'**-**5'**, respectively).^[7] They have similar overall structural features; all the metal cores comprise a triangular arrangement of three Os atoms, with a Pt atom bridging one to three of the Os-Os edges, respectively. It is also noteworthy that the structures of both **4a** and **4c** resemble that of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{IPr})_2]$ rather than the "spike" structure of $[\text{Pd}_2\text{Os}_3(\text{CO})_{12}(\text{SIPr})_2]$.^[6] Compared to the phosphine derivatives, a notable difference is the presence of more bridging CO ligands in the NHC derivatives. This probably reflects the greater electron donor ability of the NHCs;^[8] an increase in electron density on the metal core is known to favor carbonyl ligands adopting a bridging mode.^[9]

Another difference is the fairly flat Os_3Pt_n metal cores in clusters **3-5** (maximum deviation of 0.077 Å from the Os_3Pt_n plane), in contrast to the rather puckered cores of the phosphine

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analogues, which have the Pt atoms lying significantly out of the Os₃ planes (maximum deviation of 0.441 Å from the Os₃Pt_n plane).^[10] This may be due to the bulky aromatic substituents on the NHC ligands, which tend to occupy the space above and below the plane of the metal core to reduce steric interactions; in the phosphine analogues there is less of such a constraint. The Pt-bridged Os–Os bonds are significantly elongated compared to the unbridged Os–Os bonds; the former ranges from 2.9437(4) Å in **4a** to 2.9007(5) Å in **3a**, while the latter ranges from 2.8707(5) Å in **3a** to 2.8260(5) Å in **4a**. The Os–Pt bonds are also shorter (range: 2.6629(7) to 2.7452(4) Å) than those of the phosphine analogues **3'–5'** (range: 2.7880(5) to 2.8602(9) Å).

Figure 1. ORTEP plots for **3a** (top), **4a** (middle) and **5b** (bottom). Thermal ellipsoids are drawn at 50% probability level. All hydrogen atoms have been omitted for clarity.

Unlike their Pd analogues, the clusters **3–5** are relatively stable in solution and do not appear to interconvert readily. For instance, the ¹⁹⁵Pt{¹H} NMR spectra of **4a** and **4b** showed only one signal each, which remained the same even at low temperature (–80 °C for **4a** and –60 °C for **4b**); this is consistent with retention of their solid-state structures, i.e., there is no detachment and reattachment of the [Pt(NHC)] unit. A variable temperature ¹³C{¹H} NMR experiment on a ¹³C-enriched sample of **4a** over the temperature range –80 °C to –20 °C showed that the CO ligands were undergoing fast exchange, with complete collapse of the signals at room temperature. The most likely CO exchange mechanism is that of a “merry-go-round” which also involves the bridging ligands (Figure S4).^[11]

The VT ¹H NMR spectra of both **4a** and **4b** showed two sets of CH signals for the ⁱPr group at 193 K, which broadened on warming, finally collapsing into a sharp set of signals above –20 °C; that for **4a** is shown in Figure 2. Likewise, that for **4c** showed two sets of signals for the ortho-CH₃ groups at –80 °C, which collapsed into one set on warming. Since the two ⁱPr groups on the same phenyl ring in **4a** are diastereotopic, as are the two ortho-CH₃ groups on the same phenyl ring in **4c**, the changes in these VT NMR spectra may be accounted for by restricted rotation of the phenyl rings about the N–C_{ipso} bond (Figure S5).

Figure 2. Variable temperature ¹H NMR spectra (d₈-toluene) of **4a**.

In contrast, the ¹H NMR spectrum of **5b** showed only one set of NHC signals at both ambient temperature and –80 °C. The room temperature ¹³C{¹H} NMR spectrum showed two resonances of equal intensities at δ 195.8 and 189.2 ppm for the carbonyl ligands, and a carbene signal at 212.9 ppm; no satellites due to ¹⁹⁵Pt–¹³C coupling were observed, although this is not uncommon.^[12] The carbonyl resonances cannot be assigned definitively as bridging carbonyls can be shifted upfield to δ 175.2 ppm, and terminal carbonyls can be shifted downfield to δ 201.1 ppm (e.g. in the iridium cluster TMBA₂[Ir₆(CO)₁₅]).^[13] The room temperature ¹⁹⁵Pt{¹H} NMR spectrum also showed only one resonance at δ –3286 ppm. All these suggest that **5b** is not fluxional.

The isolation of the platinum-free by-products **6** is notable as it suggests a rare NHC transfer from Pt to Os. The molecular structure of **6** is interesting; an ORTEP plot showing the molecular structure of **6a** is given in Figure 3. Two bridging hydrido ligands were located through potential energy calculations with the XHYDEX program.^[14] The general structural features are similar

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to those for the known cluster $[\text{Os}_4(\mu\text{-H})_4\text{CO}]_{11}(\text{IMes})$, which has one carbonyl and additional two hydrido ligands (Figure S6). With a valence electron count of 58, the clusters **6** are therefore deficient by four electrons in accordance with the EAN rule. This suggests that clusters **6** may be capable of ligand addition reactions and indeed, in the presence of CO gas, a solution of **6b** changed from dark green to yellow, and this is reversed under vacuum (Figure S7).

Figure 3. ORTEP plot for $[\text{Os}_4(\text{CO})_{10}(\mu\text{-H})_2(\text{SIPr})]$ (**6a**). Thermal ellipsoids are drawn at 50% probability level. Organic hydrogen atoms have been omitted for clarity.

The ^1H NMR spectra of **6a-c** show four hydrido resonances in the -6 to -10 ppm range, which is unusually downfield, and is probably related to the electron-deficiency. For example, the ^1H NMR spectrum of **6b** shows one set of resonances for the IPr ligand but four hydrido resonances at -7.57, -7.67, -8.42 and -9.17 ppm, of differing intensities; the second and last are broad and of much lower intensities compared to the other two. The ^1H EXSY spectrum taken at room temperature indicated exchange between resonance C and the two A resonances, as well as with resonance B, but there was no exchange between the A and B resonances (Figure 4). These suggest that three mutually exchanging isomers are present in solution, and that there is an exchange pathway that connects isomer A to isomer B, via isomer C. A consistent set of assignments and exchange pathway is also given in Figure 4. The resonances A1 and A2 have been assigned to isomer A, which corresponds to that observed in the solid-state, while isomers B and C have two equivalent bridging hydrido ligands each. The presence of three isomers and the exchange pattern is reminiscent of that in the heterotetranuclear cluster $[\text{RuOs}_3(\mu\text{-H})_2(\text{CO})_{12}]$; the Os atom carrying the NHC ligand in **6** is equivalent to the Ru atom in the latter.^[15]

Conclusions

In conclusion, we have found that the reaction of $[\text{PtCl}(\text{allyl})(\text{NHC})]$ with $[\text{Os}_3(\text{CO})_{12}]$ afforded NHC-containing,

stable, heterometallic OsPt clusters with 3:1, 3:2, and 3:3 metal ratios, in much the same way as their Pd analogues. Understanding such reactivity is important and paves the way towards mixed-metal materials with well-defined metal compositions. Interestingly, the cluster $[\text{Os}_4(\text{CO})_{10}(\mu\text{-H})_2(\text{NHC})]$, which appears to be highly electron deficient (by four electrons according to the EAN rule) and capable of absorbing CO, was also isolated from these reactions. Its isolation provides a hint that NHC transfer from Pt to Os is possible. Unfortunately, it was only obtained in very low yields; alternative high yield routes to **6** will be desirable.

Figure 4. Room temperature ^1H EXSY spectrum (d_8 -toluene) for **6b**, and the proposed isomers and exchange pathway.

Experimental Section

General procedures. All manipulations involving organometallic compounds were carried out under argon using standard Schlenk techniques. Solvents used in reactions were of AR grade, and were dried under the appropriate drying agent and distilled under argon; and they were stored in flasks fitted with Teflon valves prior to use. TLC separations were carried out on Merck silica gel 60 Å F₂₅₄ 20×20 cm² plates. NMR spectra were collected using a JEOL ECA 400, ECA 400-SL, BBFO1, or AV 300 NMR spectrometer, while variable temperature and 2D NMR spectra were obtained on a Bruker BBFO2 NMR spectrometer, with chemical shifts referenced to residual solvent peaks. Mass spectrometry was carried out in the ESI mode with a waters Q-ToF Premier Micromass instrument. Elemental analyses were performed in-house. $[\text{Os}_3(\text{CO})_{12}]$ was purchased from Oxkem. $[\text{Os}_3(\text{CO})_{12}]$ was

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isotopically enriched to approximately 30% with ^{13}C -labelled carbon monoxide from Cambridge Isotopes, following the reported method.^[16] The platinum complexes **2b** and **2c** were prepared according to the literature method,^[17] while **2a** was prepared via Ag transmetallation.^[18] Other reagents were used as obtained from commercial sources. Elemental analyses were performed by the microanalytical laboratory at NUS.

Reaction of 1 and 2. In a typical experiment, KO^tBu, **1** and **2** were dissolved in IPA (10 ml). After stirring at room temperature for several hours, the solvent was removed under vacuum, the residue redissolved in the minimum volume of DCM and subjected to TLC separation to afford the cluster products. The quantities of reactants used and product yields are summarized in Table S1, and the characterization data given in Tables S2-5.

X-ray crystallographic studies. The crystals were mounted on quartz fibers. X-ray diffraction data were collected on a Bruker X8 APEX Single-Crystal X-ray Diffractometer at 103(2) K, using Mo K α radiation, with the SMART programs.^[19] Reflections data was processed and corrected for Lorentz and polarization effects with SAINT,^[20] and for absorption effects with SADABS.^[21] Heavy atoms were located by direct methods, and subsequent difference maps were used for locating the light, non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined with a riding model. In the final model all non-hydrogen atoms were given anisotropic displacement parameters. Structural solution and refinement were carried out using the SHELXTL suite of programs.^[22] Solvates were found in the crystals of **3a**, **3c**, **4a** and **4c**, and were refined with appropriate restraints. The crystal and refinement data are given in Tables S6 and S7.

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Keywords: transition metal carbonyl compounds · heterometallic · platinum · osmium · NHC · electron deficient

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Entry for the Table of Contents

Reaction of the [Pt(NHC)] fragment with [Os₃(CO)₁₂] gives planar Os₃Pt_n (n = 1-3) heterometallic clusters, and a highly electron-deficient NHC-derivatized tetrahedral Os₄ cluster.

Heterometallic clusters

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