PAPER www.rsc.org/dalton | Dalton Transactions

Activation of two C–H bonds of NHC N-methyl groups on triosmium and triruthenium carbonyl clusters†

Javier A. Cabeza,*[a] Ignacio del Río,[a] Daniel Miguel,[b] Enrique Pérez-Carreño[c] and M. Gabriela Sánchez-Vega[a]

Received 6th December 2007, Accepted 7th February 2008
First published as an Advance Article on the web 28th February 2008
DOI: 10.1039/b718770j

The thermolysis of the NHC triosmium cluster $[Os_3(Me_2Im)(CO)_{11}]$ (**1a**; $Me_2Im =$ 1,3-dimethylimidazol-2-ylidene) in toluene at reflux temperature sequentially affords the edge-bridged cluster $[Os_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}MeImCH_2)(CO)_{10}]$ (**2a**) and the face-capped derivative $[Os_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}MeImCH)(CO)_9]$ (**3a**). These products result from the sequential oxidative addition of one (**2a**) and two (**3a**) N–methyl C–H bonds of the original NHC ligand. The related face-capped triruthenium cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}MeImCH)(CO)_9]$ (**3b**) has been prepared by heating the NHC triruthenium cluster $[Ru_3(Me_2Im)(CO)_{11}]$ (**1b**) in THF at reflux temperature. In this case, the pentanuclear derivatives $[Ru_5(Me_2Im)(\mu_4\text{-}\kappa^2\text{-}CO)(CO)_{14}]$ (**4b**) and $[Ru_5(Me_2Im)_2(\mu_4\text{-}\kappa^2\text{-}CO)(CO)_{13}]$ (**5b**) are minor reaction products, but a ruthenium cluster analogous to **2a** has not been obtained. The face-capped oxazole-derived NHC triruthenium cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}OxCH)(CO)_9]$ (**3c**; $MeOx =$ *N*-methyloxazol-2-ylidene) is the only isolated product of the thermolysis of $[Ru_3(MeOx)(CO)_{11}]$ (**1c**) in THF at reflux temperature.

Introduction

We have recently reported the reactivity of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ with a variety of N-heterocyclic carbenes (NHCs) at room temperature,[1] showing that $[Ru_3(CO)_{12}]$ reacts easily with 1,3-dimethylimidazol-2-ylidene (Me_2Im), more slowly with N-methyloxazol-2-ylidene (MeOx), and very slowly with 1,3-dimesitylimidazol-2-ylidene (Mes_2Im) to give the corresponding CO substitution products $[Ru_3(NHC)(CO)_{11}]$, but it does not react with the very bulky 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene ($Dipph_2Im$). DFT calculations revealed that $[Ru_3(Dipph_2Im)(CO)_{11}]$ is a minimum in the corresponding potential energy surface; therefore, the absence of reaction between $[Ru_3(CO)_{12}]$ and $Dipph_2Im$ has a kinetic origin associated with the large volume of this NHC. $[Os_3(CO)_{12}]$ reacts with Me_2Im to give $[Os_3(Me_2Im)(CO)_{11}]$. However, MeOx is not basic enough and Mes_2Im and $Dipph_2Im$ are too bulky to react with $[Os_3(CO)_{12}]$, which is less reactive than $[Ru_3(CO)_{12}]$. Therefore, the reactions of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ with NHCs are strongly influenced by the electronic properties and steric demands of the NHCs and also by the intrinsic reactivity of the metal carbonyls.[1]

When we started our work on the reactions of NHCs with ruthenium and osmium carbonyls,[2] very few reports dealing with carbonyl metal clusters and NHCs had been published. In 1977, as part of a study on the reactivity of tetraaminealkenes with group 8 metal carbonyls, Lappert and Pye reported the first trinuclear carbonyl cluster containing an NHC ligand, $[Ru_3(Et_2H_2Im)(CO)_{11}]$ ($Et_2H_2Im =$ 1,3-diethylimidazolin-2-ylidene).[3]

In 2002, we communicated the synthesis of some triruthenium clusters containing bifunctional NHC-thiolato ligands derived from levamisole hydrochloride[4] and later we extended this chemistry to triosmium clusters and methyl levamisolium salts.[5]

Very recently, in 2007, Cooke *et al.* have reported the reactions of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$,[6] $[Os_3(MeCN)_2(CO)_{10}]$[6] and $[Os_4(\mu\text{-}H)_4(CO)_{12}]$[7] with $[AgCl(Mes_2Im)]$. In the reactions of the triosmium clusters, the additional incorporation of the chlorine and/or the silver atoms of the silver reagent into the final clusters has been observed.[6] The normal (through C2) and abnormal[8] (through C4) coordinations of the Mes_2Im ligand have also been described for $[Os_4(\mu\text{-}H)_4(Mes_2Im)(CO)_{11}]$ clusters.[7] Whittlesey *et al.* have shown that the very bulky 1,3-di-*tert*-butylimidazol-2-ylidene ($^tBu_2Im$) reacts with $[Ru_3(CO)_{12}]$ to give a trinuclear CO-substitution product that contains an abnormal $^tBu_2Im$ ligand.[9]

In 2005, we communicated the thermal transformation of $[Ru_3(Me_2Im)(CO)_{11}]$ into $[Ru_3(\mu\text{-}H)_2(MeImCH)(CO)_9]$ *via* a process that involves the unusual cleavage of two C–H bonds of an N-methyl group.[2] We now report full details of this reaction, including the characterization of two minor pentanuclear products, and that this double NHC N-methyl C–H activation process is not unique for $[Ru_3(Me_2Im)(CO)_{11}]$. We have also observed it for other NHC trinuclear clusters containing N-methyl groups, such as $[Ru_3(MeOx)(CO)_{11}]$ ($MeOx =$ *N*-methyloxazol-2-ylidene) and the osmium cluster $[Os_3(Me_2Im)(CO)_{11}]$.

Recent publications have shown that the N–R arms of some NHC–ruthenium complexes may get involved in intramolecular C–H,[10–13] C–C,[12] and/or C–N[13] bond activation reactions. However, these reports refer to mononuclear ruthenium complexes and

---

[a] *Departamento de Química Orgánica e Inorgánica, Instituto de Química Organometálica "Enrique Moles", Universidad de Oviedo-CSIC, E-33071, Oviedo, Spain. E-mail: jac@fq.uniovi.es; Fax: 34 985103446*
[b] *Área de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-45071, Valladolid, Spain*
[c] *Departamento de Química Física y Analítica, Universidad de Oviedo, E-33071, Oviedo, Spain*

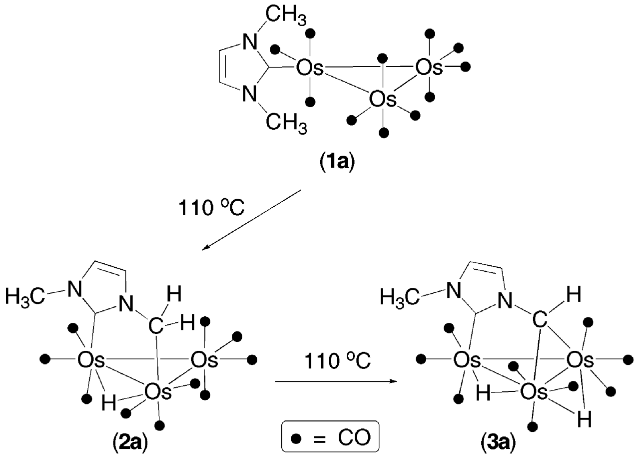
† Electronic supplementary information (ESI) available: Atomic coordinates for the DFT-optimized structures of **2a**, **3a** and **3c**. CCDC reference numbers 676043 (**4b**) and 676044 (**5b**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718770j

none of them describes the activation of two C–H bonds of an N-methyl group.

While we were writing this manuscript, Cooke *et al.* have reported that the thermolysis of $[\mathrm{Os_4(\mu\text{-}H)_4(Mes_2Im)(CO)_{11}}]$ leads to the activation of the three C–H bonds of a methyl group of the $\mathrm{Mes_2Im}$ ligand.[7]

Results and discussion

A mixture of the edge-bridged cluster $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}MeImCH_2)(CO)_{10}}]$ (**2a**) and the face-capped derivative $[\mathrm{Os_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}MeImCH)(CO)_9}]$ (**3a**) was obtained when the NHC triosmium cluster $[\mathrm{Os_3(Me_2Im)(CO)_{11}}]$ (**1a**) was stirred in toluene at reflux temperature for 3.5 h (Scheme 1). Both complexes were satisfactorily separated by chromatographic methods. IR and TLC monitoring of the reaction revealed that compound **2a** is an intermediate in the synthesis of **3a**. In fact, in an independent experiment, compound **2a** was completely converted into **3a** after heating it for 5 h in refluxing toluene. No reaction was observed when **1a** was heated in THF at reflux temperature (2 h).



Scheme 1

Although the molecular structures of compounds **2a** and **3a** could not be established by X-ray diffraction methods, their structural parameters were theoretically obtained by DFT methods, using the B3LYP/LanL2DZ/6-31G level of theory (Fig. 1, Table 1).

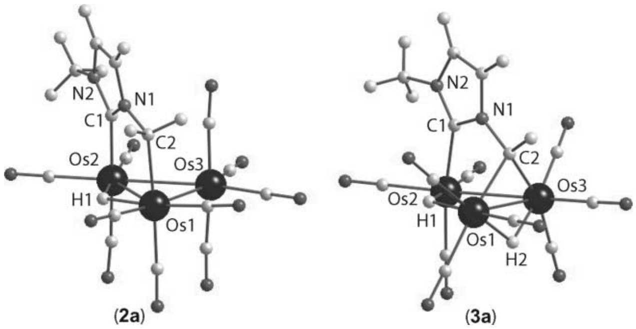


Fig. 1 DFT-optimized molecular structures of compounds **2a** and **3a**.

The structure of **2a** shows that an $\mathrm{MeImCH_2}$ ligand spans an edge of the triosmium triangle through the carbene carbon atom and through the $\mathrm{CH_2}$ fragment. A hydride ligand spans the same Os–Os edge. The cluster shell is completed by ten carbonyl ligands. The structure of **3a** shows that an MeImCH ligand caps a face of the triosmium triangle in such a way that the CH fragment spans an Os–Os edge, while the NHC carbene carbon atom is attached to the remaining Os atom. Two Os–Os edges are also spanned by hydride ligands. The cluster shell is completed by nine carbonyl ligands.

Table 1 Selected interatomic distances (Å) in compounds **2a** and **3a** (DFT data)

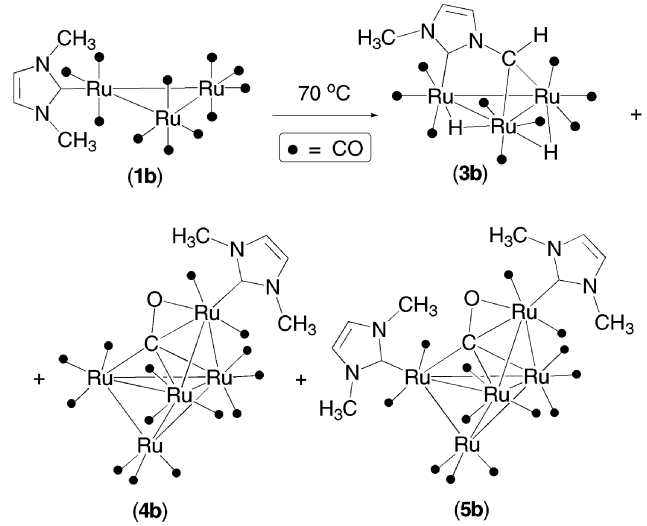
	2a	**3a**
Os(1)–Os(2)	3.021	3.130
Os(1)–Os(3)	3.004	2.890
Os(2)–Os(3)	2.981	2.919
H(1)–Os(1)	1.820	1.850
H(1)–Os(2)	1.820	1.794
H(2)–Os(1)	—	1.840
H(2)–Os(3)	—	1.832
C(1)–Os(2)	2.147	2.121
C(1)–N(1)	1.370	1.352
C(1)–N(2)	1.354	1.361
C(2)–Os(1)	2.214	2.170
C(2)–Os(3)	—	2.158
C(2)–N(2)	1.476	1.458

The optimized structures of **2a** and **3a** are in complete agreement with their spectroscopic IR and NMR data. Their IR spectra clearly show that these compounds only have terminal CO ligands. In addition to the resonances of the methyl and ring CH protons, the ^{1}H NMR spectrum of **2a** contains the typical resonances of a hydride (singlet at −16.13 ppm) and a $\mathrm{CH_2}$ group (doublets at 4.21 and 3.47, $J = 13.5$ Hz), whereas that of **3a** contains the resonances of two hydrides (doublets at −14.35 and −16.81, $J = 1.2$ Hz) and an aliphatic CH proton (singlet at 6.74 ppm). Both compounds give the correct molecular ion isotopomers in their +FAB mass spectra.

Therefore, the transformation of **1a** into **2a** and **3a** represents an unprecedented osmium cluster-promoted sequential activation of two N-methyl C–H bonds of an NHC ligand. The transformation of the acyclic aminocarbene cluster $[\mathrm{Os_3\{C(Et)NMe_2\}(CO)_{11}}]$ into $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}\{C(Et)N(Me)CH_2\}(CO)_{10}}]$ and $[\mathrm{Os_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}\{C(Et)N(Me)CH\}(CO)_9}]$, which also involves the sequential activation of two C–H bonds of an N-methyl group, has been previously reported.[14] These reactions can also be compared with that of $[\mathrm{Os_3(MeCN)_2(CO)_{10}}]$ with 2-amino-6-phenylpyridine ($\mathrm{H_2apyPh}$), that sequentially gives $[\mathrm{Os_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}HapyPh)(CO)_{10}}]$ and $[\mathrm{Os_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}apyPh)(CO)_9}]$,[15] which are structurally analogous to **2a** and **3a**, respectively. However, in the $\mathrm{H_2apyPh}$ case, the reaction involves the oxidative addition of N–H bonds. As commented in the Introduction, it has been reported that the thermolysis of $[\mathrm{Os_4(\mu\text{-}H)_4(Mes_2Im)(CO)_{11}}]$ in benzene at 200 °C leads to the activation of the three C–H bonds of a methyl group of the $\mathrm{Mes_2Im}$ ligand.[7] This is, as far as we are aware, the only previous example of C–H activation on an NHC N–R group promoted by an osmium complex.

The thermolysis of the NHC triruthenium cluster $[\mathrm{Ru_3(Me_2Im)(CO)_{11}}]$ (**1b**) in THF at reflux temperature for 3 h led to a mixture of the face-capped trinuclear cluster $[\mathrm{Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}MeImCH)(CO)_9}]$ (**3b**) and the pentanuclear derivatives $[\mathrm{Ru_5(Me_2Im)(\mu_4\text{-}\kappa^2\text{-}CO)(CO)_{14}}]$ (**4b**) and $[\mathrm{Ru_5(Me_2Im)_2(\mu_4\text{-}\kappa^2\text{-}CO)(CO)_{13}}]$ (**5b**)

(Scheme 2). These compounds were satisfactorily separated by column chromatography and were isolated in 63, 7 and 9% yield, respectively.



Scheme 2

Although an edge-bridged decacarbonyl ruthenium cluster analogous to **2a**, $[Ru_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}MeImCH_2)(CO)_{10}]$ (**2b**), should be an intermediate in the formation of **3b**, IR and TLC monitoring of the reaction gave no evidence of the presence of such a cluster at any reaction time. These data suggest that, under the reaction conditions, the transformation of **2b** into **3b** should be faster than the transformation of **1b** into **2b**.

The X-ray diffraction structure of **3b** revealed that this compound is isostructural with the osmium cluster **3a**. As this structure was described in the preliminary communication of this work,[2] its details will not be commented here. The IR and NMR spectroscopic data of **3b** are also consistent with its structure, being comparable with those of the osmium cluster **3a**.

Table 2 Selected interatomic distances (Å) in compounds **4b** and **5b** (X-ray diffraction data)

	4b	**5b**
Ru(1)–Ru(2)	2.8866(7)	2.8785(9)
Ru(1)–Ru(3)	2.8641(6)	2.8459(9)
Ru(2)–Ru(3)	2.7655(6)	2.7643(9)
Ru(2)–Ru(4)	2.7920(6)	2.8016(9)
Ru(2)–Ru(5)	2.8314(7)	2.8149(10)
Ru(3)–Ru(4)	2.8145(7)	2.8303(9)
Ru(3)–Ru(5)	2.8159(6)	2.8248(8)
Ru(4)–Ru(5)	2.7768(6)	2.7822(10)
Ru(1)–C(1)	2.072(4)	2.074(5)
Ru(1)–C(100)	2.342(4)	2.411(4)
Ru(1)–O(100)	2.123(3)	2.150(3)
Ru(2)–C(100)	2.181(4)	2.218(4)
Ru(3)–C(100)	2.176(4)	2.186(4)
Ru(5)–C(100)	2.010(4)	1.984(4)
Ru(5)–C(6)	—	2.106(5)
C(100)–O(100)	1.251(5)	1.274(5)

The structures of the pentanuclear derivatives **4b** and **5b** were unknown when we published the preliminary communication that described the thermolysis of compound **1b**; however we have recently obtained their X-ray structures (Fig. 2, Table 2). Both clusters have the same pentanuclear metallic skeleton, which can be described as an edge-bridged tetrahedron. While compound **4b** has one Me_2Im ligand, attached to Ru(1), compound **5b** has an additional Me_2Im ligand, attached to Ru(5). The most significant feature of these compounds is that they contain a quadruply-bridging CO ligand, C(100)–O(100), that is attached to the Ru(2)–Ru(3)–Ru(5) face through the carbon atom and to the edge-bridging Ru(1) metal atom through both the C and O atoms. The C(100)–O(100) distances, 1.251(5) Å in **4b** and 1.274(5) Å in **5b**, are considerably longer than the C–O distances found in the terminal CO ligands of these clusters (av. 1.137 Å). Quadruply-bridging CO ligands have only been observed in a few occasions[16–18] and they have been associated with early stages of metal cluster-mediated processes of activation of CO ligands.[18]

The observation of clusters **4b** and **5b** as minor products of the thermolysis of **1b** indicates that this reaction not only proceeds toward the formation of **3b**, *via* concomitant CO elimination and C–H bond activation processes. Cluster fragmentation and metal

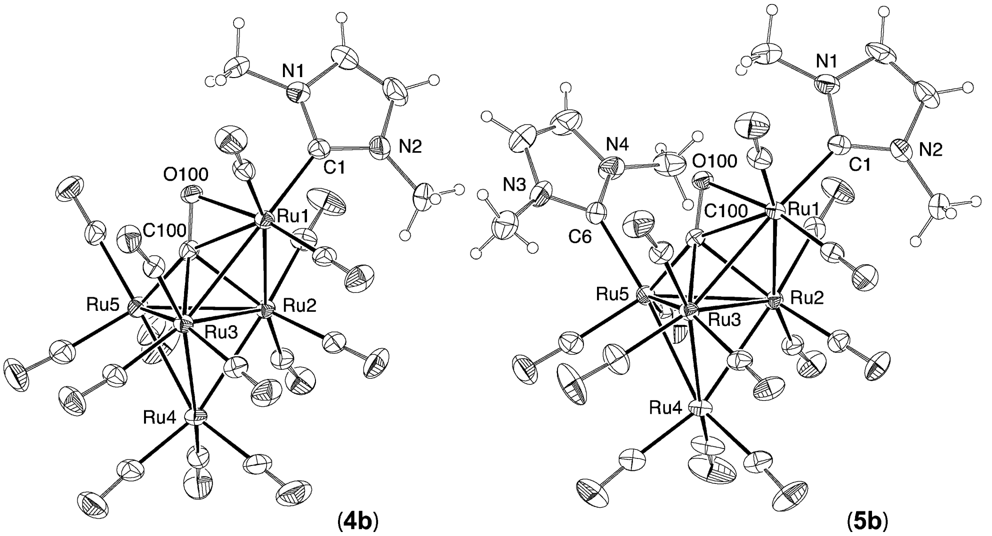
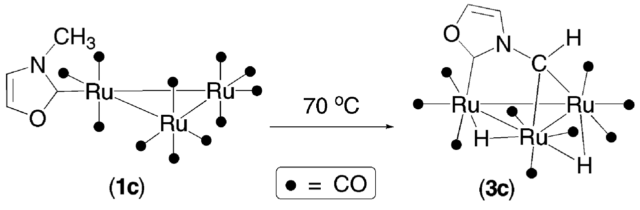


Fig. 2 Molecular structures of compounds **4b** and **5b** (X-ray diffraction data; 30% thermal ellipsoids).

fragment aggregation processes should also occur, as they account for the formation of **4b** and **5b**.

The thermolysis of the oxazole-derived NHC triruthenium cluster $[Ru_3(MeOx)(CO)_{11}]$ (**1c**) in THF at reflux temperature for 3 h allowed the isolation of the face-capped triruthenium derivative $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}\kappa^2\text{-}OxCH)(CO)_9]$ (**3c**) in 44% yield (Scheme 3). Again, IR and TLC monitoring of the reaction gave no evidence of the presence of an edge-bridged decacarbonyl triruthenium cluster analogous to **2a**, $[Ru_3(\mu\text{-}H)(\mu\text{-}\kappa^2\text{-}OxCH_2)(CO)_{10}]$ (**2c**), at any reaction time. In this case, compound **3c** was the only product that could be isolated.



Scheme 3

The molecular structure of **3c** was calculated by DFT methods (Fig. 3). It is analogous to those of **3a** and **3b**, the main difference being that the C(1)–Ru(2) distance in **3c** is ca. 0.05 Å shorter than the corresponding C(1)–M(2) distances in **3a** and **3b**. This is most probably due to the fact that the OxCH ligand of **3c** does not have a methyl group on the atom adjacent to the carbene carbon atom and therefore exerts less steric hindrance on the vicinal equatorial CO ligands than the MeImCH ligand of **3a** and **3b**. This fact has already been observed in the parent compounds **1a**, **1b** and **1c**, since the $C_{carbene}$–M distance in **1c** is shorter than in **1a** and **1b**.[1] The IR and NMR spectroscopic data of **3c** are also consistent with its structure, being comparable with those of **3b**.

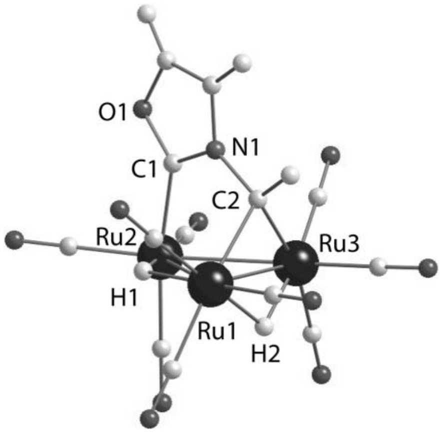


Fig. 3 DFT-optimized molecular structure of compound **3c**. Selected bond distances (Å): Ru(1)–Ru(2) 3.133, Ru(1)–Ru(3) 2.865, Ru(2)–Ru(3) 2.895, H(1)–Ru(1) 1.810, H(1)–Ru(2) 1.786, H(2)–Ru(1) 1.803, H(2)–Ru(3) 1.814, C(1)–Ru(2) 2.078, C(1)–N(1) 1.336, C(1)–O(1) 1.347, C(2)–Ru(1) 2.152, C(2)–Ru(3) 2.133, C(2)–N(1) 1.458.

The structures of the ruthenium clusters **3b** and **3c** remind those of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}\kappa^2\text{-}Hampy)(CO)_9]$ (H_2ampy = 2-amino-6-methylpyridine) and many of its derivatives,[19] although the Hampy ligand of the latter is bound to the Ru atoms through N atoms.

Therefore, the transformation of **1b** and **1c** into **3b** and **3c**, respectively, involves an uncommon oxidative addition of two C–H bonds of an N–Me group to ruthenium.[20] This process, is also rare for other metals.[14,21]

It is known that the reactions of $[Ru_3(CO)_{12}]$ with Me_2L (Me_2L = 6,6′-dimethyl-2,2′-bipyridine, 2,9-dimethyl-1,10-phenanthroline) give $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}MeLCH)(CO)_9]$ *via* the double C–H activation of a C–Me group.[22] However, in this case, the activated methyl group is not attached to a nitrogen atom and the chelating ability of the Me_2L ligands is the driving force of the C–H activation processes, since the chelation induces the interaction of one of the ligand methyl groups with the metal atoms.[23] In agreement with this, no reaction at all was observed when $[Ru_3(CO)_{12}]$ was treated with an excess of 2,6-dimethylpyridine under similar conditions.[22]

Interestingly, in the transformations described in this article, the metalation of one of the Me_2Im and MeOx methyl groups cannot be promoted by a previous chelation of these ligands. Therefore, the strong basicity of the NHC ligands has to be claimed as being responsible for the enhanced disposition of the metal atoms of NHC clusters to undergo the oxidative addition of $C(sp^3)$–H bonds.

Although the MeOx NHC ligand is basic enough to allow the transformation of **1c** into **3c**, its lower basicity, as compared with that of Me_2Im, is reflected in the slower rate of formation of **3c**, as compared with that of **3b** from **1b**.

Conclusions

The present work describes some examples of an unusual metal cluster-mediated reaction that involves the activation of two C–H bonds of a nitrogen-bound methyl group. Such a double C–H bond cleavage process represents a hitherto unprecedented example of degradation of a metal-coordinated NHC ligand that should be considered in future reactivity studies involving metal clusters and NHCs with N-methyl groups. The driving force of such a process is the strong basicity of the NHC ligands, which enhances the disposition of the metal atoms to get involved in oxidative addition reactions.

Experimental

General data

Compounds **1a**, **1b** and **1c** were prepared by published methods.[1] Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH_2 (dichloromethane) and distilled under nitrogen before use. The reactions were carried out under nitrogen, using Schlenk-vacuum line techniques, and were routinely monitored by solution IR spectroscopy (carbonyl stretching region) and spot TLC. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^1H NMR spectra were run on a Bruker DPX-300 instrument, using the dichloromethane solvent resonance as internal standard (δ = 5.30). Microanalyses were obtained from the University of Oviedo Analytical Service. FAB mass spectra were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

Reactivity studies

Thermolysis of compound 1a. A toluene solution (15 mL) of **1a** (60 mg, 0.060 mmol) was stirred at reflux temperature for 3.5 h. The original yellow color remained unchanged. The solution was evaporated to dryness under reduced pressure and the residue was dissolved in dichloromethane (1 mL). This solution was supported onto preparative silica gel TLC plates. Hexane–dichloromethane (3 : 1) eluted three yellow bands. The first one contained a trace amount of compound **1a**. The second and third bands were extracted into dichloromethane to give compounds **3a** (30 mg, 54%) and **2a** (14 mg, 24%), respectively, after solvent removal.

*Data for **2a***. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2102 (w), 2048 (s), 2021 (sh), 2011 (vs), 1978 (w), 1966 (w), 1942 (w, br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 6.80 (d, J = 1.9 Hz, 1 H, CH), 6.77 (d, J = 1.9 Hz, 1 H, CH), 4.21 (d, J = 13.5 Hz, 1 H, CH), 3.76 (s, 3 H, Me), 3.47 (d, J = 13.5 Hz, 1 H, CH), −16.13 (s, 1 H, μ-H). +FAB-MS: m/z = 948 [M$^+$]. Anal. Calcd for $C_{15}H_8N_2O_{10}Os_3$ (946.92): C, 19.03; H, 0.85; N, 2.96. Found: C, 18.98; H, 0.80; N, 2.91.

*Data for **3a***. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2095 (m), 2066 (vs), 2038 (vs), 2007 (s, br), 1994 (m, sh), 1978 (m, br), 1956 (w, br). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 6.90 (d, J = 1.6 Hz, 1 H, CH), 6.74 (s, 1 H, CH), 6.35 (d, J = 1.6 Hz, 1 H, CH), 3.59 (s, 3 H, Me), −14.35 (d, J = 1.2 Hz, 1 H, μ-H), −16.81 (d, J = 1.2 Hz, 1 H, μ-H). +FAB-MS: m/z = 920 [M$^+$]. Anal. Calcd for $C_{14}H_8N_2O_9Os_3$ (918.91): C, 18.30; H, 0.88; N, 3.05. Found: C, 18.25; H, 0.83; N, 3.01.

Thermolysis of compound 2a. A solution of **2a** (10 mg, 0.011 mmol) in toluene was stirred at reflux temperature for 5 h. An IR spectrum of the resulting solution revealed the complete conversion of **2a** into compound **3a**.

Thermolysis of compound 1b. A THF solution (60 mL) of **1b** (500 mg, 0.706 mmol) was stirred at reflux temperature for 3 h. The color changed from orange to garnet. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (2 × 2 mL). This solution was supported onto silica gel (*ca.* 4 g) and the resulting solid was transferred to the top of a silica gel chromatographic column (25 × 3 cm) packed in hexane. Hexane–dichloromethane (4 : 1) eluted three bands. The first (yellow) and third (yellow–orange) bands contained small amounts of [$Ru_3(CO)_{12}$] and compound **1b**, respectively. The second and major band (bright orange) gave compound **3b** after solvent removal (290 mg, 63%). Further elution of the column with hexane–dichloromethane (2 : 1) afforded two minor brown bands that gave compounds **4b** (31 mg, 7%) and **5b** (42 mg, 9%) after solvent removal.

*Data for **3b***. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2093 (m), 2063 (s), 2038 (vs), 2010 (m), 1998 (m), 1984 (m), 1965 (w, sh). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 6.88 (s, 1 H, CH), 6.86 (d, J = 1.8 Hz, 1 H, CH), 6.41 (d, J = 1.8 Hz, 1 H, CH), 3.55 (s, 3 H, Me), −12.64 (d, J = 2.6 Hz, 1 H, μ-H), −16.63 (d, J = 2.6 Hz, 1 H, μ-H). ^{13}C{^{1}H} NMR (75 MHz, 293 K, CD_2Cl_2): δ 170.3 (N*C*N), 119.9 (*C*H), 119.6 (*C*H), 104.7 (CH), 37.9 (Me). +FAB-MS: m/z = 653 [M$^+$]. Anal. Calcd for $C_{14}H_8N_2O_9Ru_3$ (651.53): C, 25.81; H, 1.24; N, 4.30. Found: C, 25.86; H, 1.27; N, 4.28.

*Data for **4b***. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2080 (m), 2038 (vs), 2024 (vs), 2010 (m), 1990 (w), 1558 (m). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.10 (s, br, 2 H, 2 CH), 4.13 (s, 3 H, Me), 3.93 (s, 3 H, Me). +FAB-MS: m/z = 1023 [M$^+$]. Anal. Calcd for $C_{20}H_8N_2O_{15}Ru_5$ (1021.63): C, 23.51; H, 0.79; N, 2.74. Found: C, 23.46; H, 0.74; N, 2.69.

*Data for **5b***. IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2061 (m), 2024 (vs), 2005 (vs), 1990 (w), 1558 (m). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 6.99 (m, 4 H, 4 CH), 3.89 (s, 3 H, Me), 3.85 (s, 3 H, Me), 3.51 (s, 6 H, Me). +FAB-MS: m/z = 1091 [M$^+$]. Anal. Calcd for $C_{24}H_{16}N_4O_{14}Ru_5$ (1089.75): C, 26.45; H, 1.48; N, 5.14. Found C, 26.40; H, 1.43; N, 5.09.

Thermolysis of compound 1c. A THF solution (10 mL) of **1c** (20 mg, 0.031 mmol) was stirred at reflux temperature for 3 h. The color changed from orange to garnet. The solvent was removed under reduced pressure and the residue was dissolved in dichloromethane (2 × 2 mL). This solution was supported onto silica gel (*ca.* 2 g) and the resulting solid was transferred to the top of a silica gel chromatographic column (25 × 3 cm) packed in hexane. Hexane–dichloromethane (3 : 1) eluted a small amount of the starting material **1c** and an orange band that gave compound **3c** after solvent removal (8 mg, 44%). IR (CH_2Cl_2, cm^{-1}): ν(CO) = 2098 (w), 2069 (s), 2044 (vs), 2026 (m), 2019 (m), 1997 (m), 1974 (w, sh). ^{1}H NMR (300 MHz, 293 K, $CDCl_3$): δ 7.39 (d, J = 1.2 Hz, 1 H, CH), 7.03 (d, J = 1.2 Hz, 1 H, CH), 6.52 (s, 1 H, CH), −12.56 (d, J = 2.3 Hz, 1 H, μ-H), −16.67 (d, J = 2.3 Hz, 1 H, μ-H). +FAB-MS: m/z = 640 [M^+]. Anal. Calcd for $C_{13}H_5NO_{10}Ru_3$ (638.39): C, 24.46; H, 0.79; N, 2.19. Found: C, 24.41; H, 0.74; N, 2.14.

Computational studies

Optimized structures were calculated by hybrid DFT, within the GAUSSIAN-03 program suite,[24] using the Becke's three-parameter hybrid exchange–correlation functional[25] and the B3LYP non-local gradient correction.[26] The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.[27] The basis set used for the remaining atoms was the standard 6-31G, with addition of (d,p)-polarization. For each calculation, the input model molecule was based on the X-ray-determined structure of compound **3b**, conveniently modified by manually changing, adding or removing the appropriate atoms. Each optimized structure was confirmed as an energy minimum by calculation of analytical frequencies. Molecular drawings from DFT data were made with CrystalMaker.[28]

X-Ray crystallography

A selection of crystal, measurement, and refinement data is given in Table 3. Diffraction data for **4b** and **5b** were collected with a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo-Kα X-radiation and a CCD area detector. Raw frame data were integrated with the SAINT program.[29] The structure was solved by direct methods with SHELXTL.[30] A semi-empirical absorption correction was applied with the program SADABS.[31] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. All refinements were made with SHELXTL. Molecular plots were made with the PLATON[32] program package. The WINGX program system[33] was used throughout the structure determination.

CCDC reference numbers 676043 (**4b**) and 676044 (**5b**).

Table 3 Selected crystal, measurement and refinement data for compounds **4b** and **5b**

	4b	**5b**
Formula	$C_{20}H_8N_2O_{15}Ru_5$	$C_{24}H_{16}N_4O_{14}Ru_5$
Formula weight	1021.63	1089.76
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	11.474(3)	11.016(4)
b/Å	16.127(4)	11.274(4)
c/Å	15.209(3)	14.241(5)
α/°	90	81.390(7)
β/°	96.326(4)	82.044(7)
γ/°	90	67.424(6)
V/Å^3	2796.9(10)	1608.4(10)
Z	4	2
F(000)	1928	1040
D_c/g cm^{-3}	2.426	2.250
λ(Mo-Kα)/Å	0.71073	0.71073
μ/mm^{-1}	2.712	2.365
Crystal size/mm	0.26 × 0.22 × 0.20	0.15 × 0.13 × 0.10
T/K	296(2)	296(2)
θ limits/°	1.79 to 23.29	1.97 to 23.39
Min./max. h	−8/12	−12/11
Min./max. k	−17/17	−12/10
Min./max. l	−16/16	−15/14
Collected reflections	12031	7191
Unique reflections	4010	4588
Reflections with $I > 2\sigma(I)$	3620	3931
Parameters/restraints	382/0	428/0
GOF on F^2	1.110	0.992
R_1 (on F, $I > 2\sigma(I)$)	0.0221	0.0272
wR_2 (on F^2, all data)	0.0522	0.0703
Max./min. $\Delta\rho$/e Å^{-3}	0.374/−0.333	0.538/−0.695

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718770j

Acknowledgements

This work was supported by the Principado de Asturias Government (grant IB05–014), the European Union (FEDER grants) and the Spanish Ministerio de Educación y Ciencia (grants MAT2006–01997 and CTQ2007–60865). M. G. S.-V is also grateful to the University of Carabobo (Venezuela) for providing her a fellowship to do her PhD thesis in Oviedo.

References

1 J. A. Cabeza, I. del Río, D. Miguel, E. Pérez-Carreño and M. G. Sánchez-Vega, *Organometallics*, 2008, **27**, 211.

2 J. A. Cabeza, I. del Río, D. Miguel and M. G. Sánchez-Vega, *Chem. Commun.*, 2005, 3956.

3 M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 1977, 2172.

4 J. A. Cabeza, I. del Río, S. García-Granda, V. Riera and M. G. Sánchez-Vega, *Eur. J. Inorg. Chem.*, 2002, 2561.

5 J. A. Cabeza, I. da Silva, I. del Río and M. G. Sánchez-Vega, *Dalton Trans.*, 2006, 3966.

6 C. E. Cooke, T. Ramnial, M. C. Jennings, R. K. Pomeroy and J. A. C. Clyburne, *Dalton Trans.*, 2007, 1755.

7 C. E. Cooke, M. C. Jennings, R. K. Pomeroy and J. A. C. Clyburne, *Organometallics*, 2007, **26**, 6059.

8 P. L. Arnold and S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596.

9 C. E. Ellul, M. F. Mahon, O. Saker and M. K. Whittlesey, *Angew. Chem., Int. Ed.*, 2007, **46**, 6343.

10 (*a*) F. E. Hahn, D. Le Van, M. C. Moyes, T. von Fehren, R. Fröhlich and E. U. Würthwein, *Angew. Chem., Int. Ed.*, 2001, **40**, 3144; (*b*) A. J. Arduengo III, J. C. Calabrese, F. Davidson, H. V. Rasika-Dias, J. R. Goerlich, R. Krafczyk, W. J. Marshall, M. Tamm and R. Schmutzler, *Helv. Chim. Acta.*, 1999, **82**, 2348.

11 (*a*) S. Burling, B. M. Paine, D. Nama, V. S. Brown, M. F. Mahon, T. J. Prior, P. S. Pregosin, M. K. Whittlesey and J. M. J. Williams, *J. Am. Chem. Soc.*, 2007, **129**, 1987; (*b*) C. Fischmeister, L. Toupet and P. H. Dixneuf, *Organometallics*, 2006, **25**, 2126; (*c*) K. Abdur-Rashid, T. Fedorkiw, A. J. Lough and R. H. Morris, *Organometallics*, 2004, **23**, 86; (*d*) S. Burling, M. F. Mahon, B. M. Paine, M. K. Whittlesey and J. M. J. Williams, *Organometallics*, 2004, **23**, 4537.

12 R. F. R. Jazzar, S. A. MacGregor, M. F. Mahon, S. P. Richards and M. K. Whittlesey, *J. Am. Chem. Soc.*, 2002, **124**, 4944.

13 S. Burling, R. E. Powell, M. K. Whittlesey and J. M. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 13702.

14 R. D. Adams and G. Chen, *J. Cluster Sci.*, 1991, **2**, 29.

15 J. A. Cabeza, I. del Río, V. Riera, M. Suárez and S. García-Granda, *Organometallics*, 2004, **23**, 1107.

16 (*a*) R. D. Adams, J. E. Babin and M. Tasi, *Polyhedron*, 1988, **7**, 2263; (*b*) R. D. Adams, J. E. Babin and M. Tasi, *Inorg. Chem*, 1988, **27**, 2618; (*c*) R. D. Adams, B. Captain, P. J. Pellechia and J. L. Smith Jr., *Inorg. Chem.*, 2004, **43**, 2695.

17 (*a*) Y. Chi, F. J. Wu, B. J. Liu, C. C. Wang and S. L. Wang, *J. Chem. Soc., Chem. Commun.*, 1989, 873; (*b*) Y. Chi, S. H. Chuang, L. K. Liu and Y. S. Wen, *Organometallics*, 1991, **10**, 2485; (*c*) Y. Chi, C. J. Su, L. J. Farrugia, S. M. Peng and G. H. Lee, *Organometallics*, 1994, **13**, 4167; (*d*) C. Yun, C. J. Su, W. C. Tseng, S. M. Peng and G. H. Lee, *J. Cluster Sci.*, 1997, **8**, 507; (*e*) C. Yun, C. J. Su, S. M. Peng and G. H. Lee, *J. Am. Chem. Soc.*, 1997, **119**, 11114; (*f*) P. C. Su, Y. Chi, C. J. Su, S. M. Peng and G. H. Lee, *Organometallics*, 1997, **16**, 1870.

18 P. J. Bailey, B. F. G. Johnson and J. Lewis, *Inorg. Chim. Acta*, 1994, **227**, 197, and references cited therein.

19 J. A. Cabeza, *Eur. J. Inorg. Chem.*, 2002, 1559.

20 M. Day, S. Hajela, S. E. Kabir, M. Irving, T. McPhillips, E. Wolf, K. I. Hardcastle, E. Rosenberg, L. Milone, R. Gobetto and D. Osella, *Organometallics*, 1991, **10**, 2743.

21 C. J. C. Tazelaar, S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2004, **23**, 936.

22 (*a*) J. A. Cabeza, I. da Silva, I. del Río, L. Martínez-Méndez, D. Miguel and V. Riera, *Angew. Chem., Int. Ed.*, 2004, **43**, 3464; (*b*) J. A. Cabeza, I. del Río, L. Martínez-Méndez and D. Miguel, *Chem.–Eur. J.*, 2006, **12**, 1529.

23 M. Gandelman, L. J. W. Shimon and D. Milstein, *Chem.–Eur. J.*, 2003, **9**, 4295, and references therein.

24 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, 2004.

25 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

26 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

27 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.

28 *CrystalMaker*, version 7.2.4, CrystalMaker Software Ltd., Yarnton, Oxfordshire, UK, 2007.

29 *SAINT+. SAX area detector integration program*, version 6.02, Bruker AXS, Inc., Madison, WI, 1999.

30 G. M. Sheldrick, *SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data*, version 5.1, Bruker AXS, Inc., Madison, WI, 1998.

31 G. M. Sheldrick, *SADABS, Empirical absorption correction program*, University of Göttingen, Göttingen, Germany, 1997.

32 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, University of Göttingen, Göttingen, Germany, 1997.

33 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.