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Reactivity of [Ru_4(*μ*-H)$_4$(CO)$_{12}$] with N-Heterocyclic Carbenes

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The tetraruthenium tetrahydrido cluster compound [Ru_4(*μ*-H)$_4$(CO)$_{12}$] (**1**) reacts at room temperature with N-heterocyclic carbenes of the 1,3-disubstituted imidazolin-2-ylidene type (R^1R^2Im) to give the carbonyl substitution products [Ru_4(*μ*-H)$_4$(CO)$_{11}$(R^1R^2Im)] (R^1R^2Im = 1,3-dimethylimidazolin-2-ylidene, **2**; 1-phenyl-3-methylimidazolin-2-ylidene, **3**; 1,3-diphenylimidazolin-2-ylidene, **4**; and 1,3-dimesitylimidazolin-2-ylidene, **5**). In solution, compounds **2**−**5** are fluxional in the NMR time scale and display the same pattern of *ν*(CO) IR absorptions. DFT calculations have shown that the C_S arrangement of the Ru_4H_4 cluster core of these clusters is 0.2−1.7 kcal mol^{-1} more stable than the D_{2d} cluster core, the smallest difference corresponding to the clusters with the very bulky 1,3-dimesitylimidazolin-2-ylidene ligand. Two conformers with C_S Ru_4H_4 cluster core have been found by X-ray crystallography in the crystals of compound **3**. The thermal stability of compounds **2**−**5** has also been studied. While the dimethyl derivative **2** is stable in refluxing toluene for 3 h, the dimesityl derivative **5** slowly decomposes in solution at room temperature. Two isostructural heptanuclear derivatives, [Ru_7(μ_3-H)(μ_4-CO)(*μ*-CO)$_2$(CO)$_{14}${*μ*-(η^1-η^6-C_6H_4)RIm}] (R = Me, **6**; Ph, **7**), which contain a quadruply bridging CO ligand and an orthometalated phenyl ring that is additionally coordinated as an η^6-arene ligand, are the major products of the thermolysis of compounds **3** and **4** in toluene at reflux temperature.

Introduction

After the pioneering work of Lappert and Pye, who reported the synthesis of [Ru_3(CO)$_{11}$(Et_2H_2Im)] (Et_2H_2Im = 1,3-diethylimidazolidin-2-ylidene) in 1977,[1] the N-heterocyclic carbene (NHC) chemistry of transition metal carbonyl clusters has remained dormant for nearly 30 years. However, the current interest of the chemical community in the coordination chemistry of NHCs[2] and in the catalytic properties of many of their complexes[3] has recently led to the renaissance of the transition metal cluster chemistry of NHCs.

In this field, the research groups of Cole,[4] Whittlesey,[5−7] and also ourselves[8−13] have recently reported studies on the reactivity of [Ru_3(CO)$_{12}$] and [Os_3(CO)$_{12}$] with various NHCs of the type 1,3-disubstituted imidazolin-2-ylidene[4−9] and also on the thermolysis of some of the products obtained from these reactions,[5,6,11−13] showing that 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, the stoichiometry of the reagents, the reaction temperature, and also by the intrinsic reactivity of the metal carbonyls.

Very recently, while the work reported in this paper was in progress, Clyburne, Cooke et al. communicated the reactions of [Os_3(*μ*-H)$_2$(CO)$_{10}$],[14] [Os_3(CO)$_{10}$(MeCN)$_2$],[14] and [Os_4(*μ*-H)$_4$(CO)$_{10}$(MeCN)$_2$][15] with [AgCl(Mes_2Im)] (Mes_2Im = 1,3-dimesitylimidazolin-2-ylidene). In the reactions of the triosmium clusters, the additional incorporation of the chlorine and/or the silver atoms of the [AgCl(Mes_2Im)] reagent into the final clusters has often been observed.[14] The normal (through C^2) and abnormal (through C^4) coordination of the Mes_2Im ligand have also been described for [Os_4(*μ*-H)$_4$(CO)$_{11}$(Mes_2Im)] clusters, which are also prone to undergo C−C and C−H bond activation processes at very high temperatures (200 °C).[15] In a subsequent full paper, which appeared when the writing of this manuscript was underway, they also described the synthesis of [Ru_4(*μ*-

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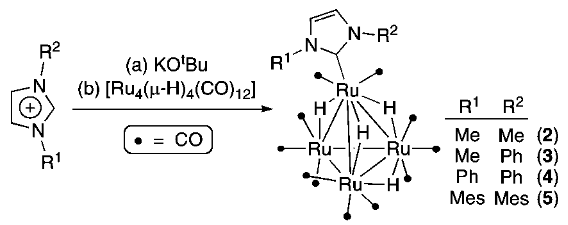
Scheme 1



$H)_4(CO)_{11}(Mes_2Im)]$ by treatment of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with Me_3NO and $[AgCl(Mes_2Im)]$.[16]

We now report that it is not necessary to use NHC silver complexes to prepare 1,3-disubstituted imidazolin-2-ylidene derivatives of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$, since this tetraruthenium cluster reacts directly with the NHCs to give products of the type $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$. Although they are fluxional in solution, DFT calculations have shown that their most stable structures have a C_S Ru_4H_4 cluster core. We also report that the thermal stability of these clusters is strongly influenced by the nature of the NHC N-R arms, having identified the major products of the thermolysis of $[Ru_4(\mu\text{-}H)_4(CO)_{11}(PhMeIm)]$ and $[Ru_4(\mu\text{-}H)_4(CO)_{11}(Ph_2Im)]$ as two isostructural heptanuclear η^6-arene-NHC derivatives that contain a quadruply bridging CO ligand.

Results and Discussion

Synthesis and Characterization of Compounds of the type $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$. The cluster $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ (**1**) reacted readily with 1,3-disubstituted imidazolin-2-ylidenes, R^1R^2Im (prepared *in situ* from the corresponding imidazolium salts and potassium *tert*-butoxide), in THF at room temperature, to give the orange NHC tetranuclear derivatives $[Ru_4(\mu\text{-}H)_4(CO)_{11}(R^1R^2Im)]$ ($R^1R^2Im = Me_2Im$, **2**; MePhIm, **3**; Ph_2Im, **4**; Mes_2Im, **5**) (Scheme 1).

A single crystal of compound **3** was studied by X-ray diffraction. Two independent molecules (**A** and **B**) were found in the asymmetric unit (Figure 1). Their Ru_4H_4 cores have an approximate C_S symmetry and consist of a distorted tetrahedron of metal atoms with two short and four long edges, the former sharing a common Ru atom, Ru(4) in **A** and Ru(8) in **B**. Although the hydrides were not located in the Fourier maps, their positions were clearly assigned by the XHYDEX program[17] as bridging the four long edges of the metal polyhedron. In both molecules, the NHC ligand is attached to the Ru atom that is bonded to three hydrides. Eleven terminal CO ligands, two on the NHC-attached Ru atom and three on each of the remaining Ru atoms, complete the cluster shell. The main difference between molecules **A** and **B** is the orientation of the NHC ligand with respect to the cluster core. In Figure 1, the basal hydride ligand H(4) of **A** is below the NHC methyl group, while the basal hydride ligand H(8) of **B** is below the NHC phenyl group.

Previous investigations on the solid-state structures of the $[M_4(\mu\text{-}H)_4(CO)_{12\text{-}n}L_n]$ (M = Ru, Os; L = P-donor ligand, $n = 1-4$) cluster family have shown that the M_4H_4 cores of these clusters have either C_S or D_{2d} local symmetry (Figure 2), the latter being far more common.[18] In fact, as far as we are aware, all monosubstituted tetraruthenium derivatives of this family ($n = 1$) have D_{2d} Ru_4H_4 cores in the solid state,[18–20] although some have C_S Ru_4H_4 cores in solution at low temperature, e.g. $[Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OEt)_3\}]$.[20] Curiously, the tetraosmium cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$ has a D_{2d} Os_4H_4 core in the solid state, but the related cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(a\text{-}Mes_2Im)]$, which contains the abnormally bound NHC ligand 1,3-dimesitylimidazolin-4-ylidene, has a C_S Os_4H_4 core.[16]

The composition of compounds **2**–**5** was established by microanalysis. Their ESI mass spectra contained the appropriate cluster of molecular-ion isotopomers. IR solution studies on **2**–**5** afforded spectra that are nearly identical in the carbonyl stretching region. This fact strongly suggests that these complexes are isostructural, at least in solution.

The room temperature ^1H NMR spectra of **2**–**5** showed the resonances of the corresponding NHC ligand and a broad singlet at *ca.* −18.0 ppm, assignable to four hydrido ligands. The local symmetry of the NHC ligands is maintained in the spectra of their complexes. All these data indicate that compounds **2**–**5** are fluxional in solution at room temperature. This is a common feature of the members of the $[M_4(\mu\text{-}H)_4(CO)_{11}L]$ family of clusters.[16,18–20] Attempting to stop the motion of the hydrides and thus shed light on the most stable geometry of the Ru_4H_4 core of each cluster, ^1H NMR spectra were also run at −80 °C but, unfortunately, they indicated that compounds **2**–**5** maintain their nonrigidity in solution at that temperature.

The easy formation of compounds **2**–**5** from $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ and NHCs of different volume and basicity contrasts with the reported reactivity of $[Ru_3(CO)_{12}]$ with these reagents. In the latter case, an adequate combination of the NHC volume and basicity is required to observe reaction with $[Ru_3(CO)_{12}]$ at room temperature, since Me_2Im (very basic and small) reacts quicky, Mes_2Im (very basic and bulky) reacts slowly, and Ph_2Im (less basic) does not react.[8] It seems that the NHC ligands can access the metal atoms of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ more easily that those of $[Ru_3(CO)_{12}]$.

As commented in the Introduction, while the present paper was being written, Clyburne, Cooke et al. reported the synthesis of $[Ru_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$ (**5**) by treatment of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ with Me_3NO and $[AgCl(Mes_2Im)]$.[16] While the IR spectrum they report for this cluster matches the IR spectrum of our compound (both run in hexane solvent), their room temperature ^1H NMR spectrum is slightly different from ours (they do not mention any NMR study at a lower temperature), since they report two broad hydride resonances (in CD_2Cl_2), while we observe only one (both in CD_2Cl_2 and $CDCl_3$). Their ^1H NMR spectrum of **5** and the X-ray structure of the related osmium cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$, which has a D_{2d} Os_4H_4 cluster core,[16] induced them to conclude that compound **5** has a D_{2d} Ru_4H_4 cluster core. Most probably, one of the two hydride peaks of the ^1H NMR spectrum recorded by Clyburne, Cooke et al. is due to an impurity. In fact, this compound is not very stable at room temperature and, to our knowledge, all clusters of the $[Ru_4(\mu\text{-}H)_4(CO)_{11}L]$ family display only one hydride signal in their room temperature ^1H NMR spectra.[20]

As we had proven (a) that compound **5** is highly fluxional in solution at room temperature, (b) that its nonrigidity is maintained at −80 °C, (c) that the solution IR spectra of compounds **2**–**5** are nearly identical, and (d) that both conformers (**A** and **B**) of **3** have C_S Ru_4H_4 cluster core (X-ray crystallography) in the solid state, we considered the possibility

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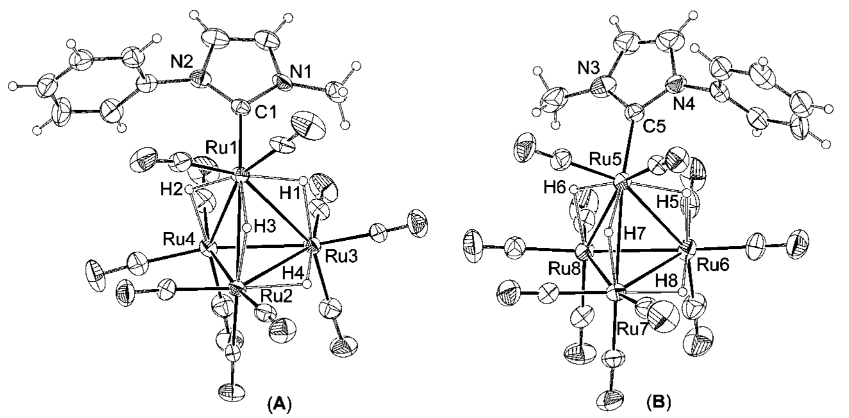


Figure 1. ORTEP views (30% thermal ellipsoids) of the two crystallographically independent molecules found in the crystals of compound **3**. Selected bond distances (Å): molecule **A**: Ru(1)−Ru(2) 2.980(1), Ru(1)−Ru(3) 3.043(1), Ru(1)−Ru(4) 2.992(1), Ru(2)−Ru(3) 2.923(1), Ru(2)−Ru(4) 2.790(1), Ru(3)−Ru(4) 2.778(1), Ru(1)−C(1) 2.08(1); molecule **B**: Ru(5)−Ru(6) 3.000(1), Ru(5)−Ru(7) 3.001(1), Ru(5)−Ru(8) 3.000(1), Ru(6)−Ru(7) 2.954(1), Ru(6)−Ru(8) 2.785(1), Ru(7)−Ru(8) 2.797(1), Ru(5)−C(5) 2.10(1).

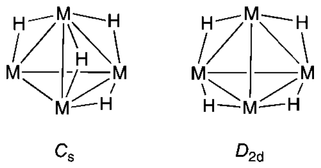
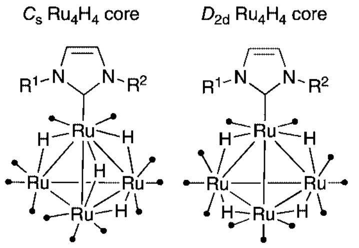


Figure 2. Two M_4H_4 cores of the $[M_4(\mu\text{-}H)_4(CO)_{12\text{-}n}L_n]$ (M = Ru, Os) group of clusters.



R^1	R^2	Relative energy (kcal mol^{-1})	
Me	Me	0.0	1.7
Me	Ph	0.0	1.5
Ph	Me	0.0	1.5
Ph	Ph	0.0	1.6
Mes	Mes	0.0	0.2

Figure 3. Relative energies of pairs of clusters of the $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$ family with C_S and D_{2d} Ru_4H_4 cluster cores.

that the structural assignment made by Clyburne, Cooke et al. for compound **5** (D_{2d} Ru_4H_4 cluster core) might be incorrect. To check this, as we had no crystals of cluster **5** suitable for an X-ray diffraction study, we calculated the absolute energies of clusters of the $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$ family with C_S and D_{2d} Ru_4H_4 cluster cores. The results, obtained from DFT calculations at the B3LYP/LanL2DZ/6−31G(d,p) level, are displayed in Figure 3. In all cases, the structures with C_S Ru_4H_4 core are slightly more stable than the structures with D_{2d} Ru_4H_4 core. It seems that the energy difference between each pair is related to the volume of the NHC ligand. While the smallest difference (0.2 kcal mol^{-1}) corresponds to the species with the very bulky Mes_2Im ligand, the differences between the species with the remaining NHC ligands are very similar (1.5−1.7 kcal mol^{-1}) because the phenyl groups of MePhIm and Ph_2Im are perpendicular to the five-membered carbene ring and, consequently, the steric hindrance of the Me_2Im, MePhIm, and Ph_2Im ligands is very similar. It should also be noted that both conformers (**A** and **B**) of compound **3** (which contains an asymmetric NHC ligand) have approximately the same energy (their computed energies differ by less than 0.01 kcal mol^{-1}); therefore, in the solid state, they coexist in 1:1 ratio.

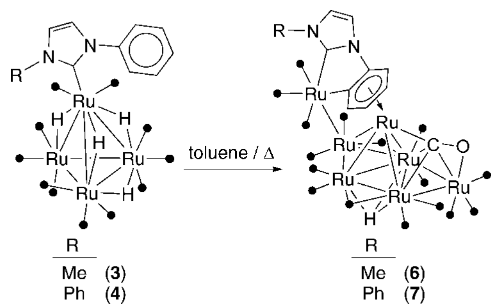
Therefore, these calculations indicate that, in the solid state, all studied members of the $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$ family of clusters, including the Mes_2Im derivative **5**, should have a C_S Ru_4H_4 core. However, the related osmium cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$ has a D_{2d} Os_4H_4 cluster core.[16] To shed light on this apparent contradiction, we also calculated the energies of the C_S and D_{2d} structures of this osmium cluster and also of the Me_2Im derivative $[Os_4(\mu\text{-}H)_4(CO)_{11}(Me_2Im)]$. It resulted that, for the Mes_2Im derivative, the D_{2d} cluster core is 0.6 kcal mol^{-1} more stable than the C_S cluster core. On the contrary, for the Me_2Im derivative, the D_{2d} cluster core is 1.6 kcal mol^{-1} less stable than the C_S cluster core. These results not only indicate that $[Os_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$ should have a D_{2d} Os_4H_4 cluster core in the solid state, as it actually has,[16] but also justify that the Os_4H_4 cluster core of $[Os_4(\mu\text{-}H)_4(CO)_{11}(a\text{-}Mes_2Im)]$ is of C_S symmetry,[16] because the steric hindrance of the abnormally bound (through C^4) *a*-Mes_2Im ligand is much smaller than that of the normally bound (through C^2) Mes_2Im ligand.

Thermolysis of the $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$ Clusters. We[11−13] and others[5,6] have recently reported that NHC-containing triruthenium clusters are prone undergo intramolecular bond activation processes upon heating. In fact, the cluster $[Ru_3(CO)_{11}(Me_2Im)]$ undergoes facile methyl C−H[11−13] and C−N[13] bond activation processes upon mild heating, while similar treatments of the clusters $[Ru_3(CO)_{11}(a\text{-}R_2Im)]$[5,6] (R = *tert*-butyl, adamantyl), which contain abnormally bound NHCs, provoke facile intramolecular C(sp^2)-H bond activation processes.[5,6] These interesting results prompted us to study the thermal stability of compounds **2**−**5**.

The thermal stability of the Me_2Im compound **2** is high, since it remained unaltered when it was heated in toluene at reflux temperature for 3 h. After 4 h, an incipient decomposition to an untractable black solid was observed. On the other hand, as noted by Clyburne, Cooke et al.,[16] the Mes_2Im cluster **5** has a limited thermal stability, since it decomposes slowly to an uncharacterized mixture of products even at room temperature. Most probably, the large volume of the mesityl groups provokes their interaction with the neighboring hydride and carbonyl ligands, thus reducing the stability of the cluster.[16]

The thermolysis of clusters **3** and **4** in toluene at reflux temperature led to mixtures of products. The major products of

Scheme 2



these mixtures were separated and characterized as the heptanuclear derivatives $[Ru_7(\mu_3\text{-}H)(\mu_4\text{-}CO)(\mu\text{-}CO)_2(CO)_{14}\{\mu\text{-}(\eta^1\text{-}\eta^6\text{-}C_6H_4)MeIm\}]$ (**6**) and $[Ru_7(\mu_3\text{-}H)(\mu_4\text{-}CO)(\mu\text{-}CO)_2(CO)_{14}\{\mu\text{-}(\eta^1\text{-}\eta^6\text{-}C_6H_4)PhIm\}]$ (**7**) (Scheme 2).

The molecular structure of compound **6** was established by X-ray diffraction (Figure 4). Its cluster core can be described as a trigonal bipyramid of Ru atoms, Ru(2) to Ru(6), expanded in one edge, Ru(4)−Ru(6), and one vertex, Ru(2), by two additional Ru atoms, Ru(7) and Ru(1), respectively. The carbene carbon atom of the original MePhIm ligand, C(1), is attached to Ru(1), while the phenyl group is now orthometalated to Ru(1) and η^6-bonded to Ru(3). A hydrido ligand caps the Ru(4)−Ru(5)−Ru(6) face. The cluster shell is completed by 17 CO ligands, 14 of which are terminal, two are edge-bridging, and one is quadruply bridging, C(400)−O(400).

The solution IR spectra of compounds **6** and **7** indicate that both compounds have the same arrangement of CO ligands, since they are nearly identical in the CO stretching region. In addition, both show the absorption of the μ_4-CO ligand at 1560 cm^{-1}. The composition of **6** and **7** was confirmed by their microanalysis and ESI mass spectra, which gave the corresponding molecular ion peaks. ^1H NMR spectrometry established the presence in each complex of a hydride and the corresponding metalated NHC ligand. The η^6-coordination of the metalated phenyl ring was suggested by the low chemical shifts of its four protons, which are observed as two doublets and two triplets in the 5.9−5.0 ppm range. All these data strongly suggest that compounds **6** and **7** are isostructural.

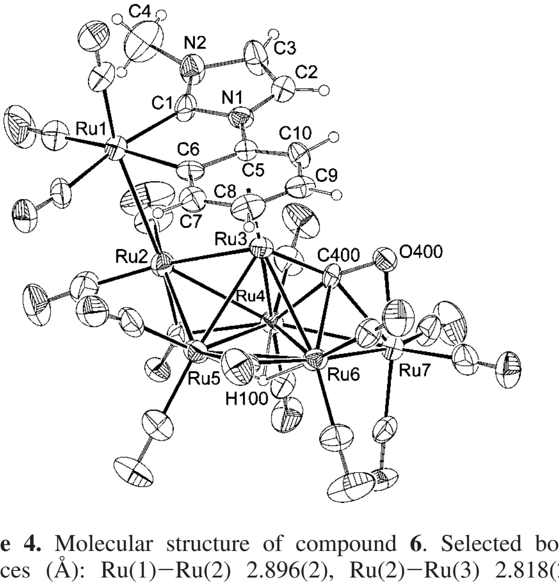


Figure 4. Molecular structure of compound **6**. Selected bond distances (Å): Ru(1)−Ru(2) 2.896(2), Ru(2)−Ru(3) 2.818(2), Ru(2)−Ru(4) 2.832(2), Ru(2)−Ru(5) 2.756(2), Ru(3)−Ru(4) 2.781(2), Ru(3)−Ru(5) 2.755(2), Ru(3)−Ru(6) 2.821(2), Ru(4)−Ru(5) 2.926(2), Ru(4)−Ru(6) 2.863(2), Ru(4)−Ru(7) 2.802(2), Ru(5)−Ru(6) 2.694(2), Ru(6)−Ru(7) 2.755(2), C(1)−Ru(1) 2.07(2), C(6)−Ru(1) 2.08(2), C(5)−Ru(3) 2.24(2), C(6)−Ru(3) 2.35(2), C(7)−Ru(3) 2.34(2), C(8)−Ru(3) 2.26 (2), C(9)−Ru(3) 2.20(2), C(10)−Ru(3) 2.27(2), C(400)−Ru(3) 1.87(2), C(400)−Ru(4) 2.22(2), C(400)−Ru(6) 2.22(2), C(400)−Ru(7) 2.34(2), O(400)−Ru(7) 2.11(1), C(400)−O(400) 1.29(2).

Therefore, the thermolysis of compounds **3** and **4** leads to cluster aggregation accompanied by orthometalation of a phenyl group of the NHC ligand and its additional coordination as an η^6-arene fragment. The orthometalation of NHC N-phenyl groups has been previously observed in mononuclear complexes,[21] but their coordination as η^6-arene ligands is unprecedented.

An additional interesting feature of compounds **6** and **7** is that they contain a quadruply bridging carbonyl ligand. Such ligands have been previously observed only in a few occasions[11,22−24] and they have been associated with early stages of metal cluster-mediated CO activation processes.[24]

Concluding Remarks

The substitution of an NHC for a CO ligand of $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ proceeds smoothly at room temperature, even with very bulky carbenes such as 1,3-dimesitylimidazolin-2-ylidene, to give the corresponding $[Ru_4(\mu\text{-}H)_4(CO)_{11}(NHC)]$ derivative (compounds **2**−**5**). Such substitution reactions are easier for $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ than for $[Ru_3(CO)_{12}]$.

DFT calculations have shown that the C_S arrangement of the Ru_4H_4 cluster core of clusters **2**−**5** is 0.2−1.7 kcal mol^{-1} more stable than the D_{2d} cluster core and that the difference between the energies of these two structures decreases as the steric hindrance of the NHC ligand increases. These DFT calculations, accompanied by additional calculations on the related osmium cluster $[Os_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$, have helped us to fix and rationalize the results published by Clyburne, Cooke et al. on the structures of compounds $[M_4(\mu\text{-}H)_4(CO)_{11}(Mes_2Im)]$ (M = Ru, Os).[16]

Two isostructural heptanuclear derivatives, compounds **6** and **7**, which contain a quadruply bridging CO ligand and an orthometalated phenyl ring that is additionally coordinated as an η^6-arene ligand, are the major products of the thermolysis of compounds **3** and **4** in toluene at reflux temperature.

Experimental Section

General Data. The cluster $[Ru_4(\mu\text{-}H)_4(CO)_{12}]$ was prepared by a published method.[25] The remaining reagents were purchased from commercial suppliers. 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 stretch-

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ing region) and spot TLC. IR spectra were recorded in solution on a Perkin-Elmer Paragon 1000 FT spectrophotometer. ^{1}H NMR spectra were run on a Bruker DPX-300 instrument, using the dichloromethane solvent resonance as internal standard ($\delta = 5.30$). Microanalyses were obtained from the University of Oviedo Analytical Service. ESI mass spectra were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

[Ru$_4$(μ-H)$_4$(CO)$_{11}$(Me$_2$Im)] (2). Solid potassium *tert*-butoxide (9 mg, 0.067 mmol) was added to a solution of 1,3-dimethylimidazolium iodide (16 mg, 0.067 mmol) in THF (10 mL). After stirring at room temperature for 30 min, compound **1** (50 mg, 0.067 mmol) was added and the mixture was stirred for 2 h. The color changed from yellow to orange. The solvent was removed under reduced pressure and the resulting residue was redissolved in dichloromethane (10 mL). The filtered solution was concentrated to ca. 1 mL and was supported on preparative silica gel TLC plates. Dichloromethane−hexane (1:1) eluted several bands. The first one, yellow, contained a small amount of the starting material **1**. The second band, orange, contained compound **2** (34 mg, 60%). Anal. Calcd for $C_{16}H_{12}N_2O_{11}Ru_4$ (812.55): C, 23.53; H, 1.48; N, 3.43. Found: C, 23.58; H, 1.52; N, 3.38. (+)-ESI MS: *m/z* 814 [M]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2082 (w), 2049 (vs), 2025 (s), 1999 (m), 1984 (sh), 1957 (sh). ^{1}H NMR (CDCl$_3$, 293 K): δ 6.97 (s, 2 H, CH), 3.80 (s, 6 H, Me), −17.88 (s, br, 4 H, μ-H).

[Ru$_4$(μ-H)$_4$(CO)$_{11}$(MePhIm)] (3). This compound was prepared as described above for cluster **2**, using potassium *tert*-butoxide (9 mg, 0.067 mmol), 1-phenyl-3-methylimidazolium chloride (14 mg, 0.067 mmol) and compound **1** (50 mg, 0.067 mmol) as starting materials, and dichloromethane−hexane (2:1) as eluant. Orange solid (32 mg, 52%). Anal. Calcd for $C_{21}H_{14}N_2O_{11}Ru_4$ (874.72): C, 28.84; H, 1.61; N, 3.20. Found: C, 28.69; H, 1.56; N, 3.15. (+)-ESI MS: *m/z* 876 [M]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2082 (w), 2050 (vs), 2025 (s), 2000 (m), 1982 (sh), 1949 (sh). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.54 (m, 3 H, CH), 7.38 (m, 2 H, CH), 7.10 (d, $J = 1.9$ Hz, 1 H, CH), 7.07 (d, $J = 1.9$ Hz, 1 H, CH), 3.80 (s, 3 H, Me), −17.99 (s, br, 4 H, μ-H).

[Ru$_4$(μ-H)$_4$(CO)$_{11}$(Ph$_2$Im)] (4). This compound was prepared as described above for cluster **2**, using potassium *tert*-butoxide (9 mg, 0.067 mmol), 1,3-diphenylimidazolium chloride (18 mg, 0.067 mmol) and compound **1** (50 mg, 0.067 mmol) as starting materials, and dichloromethane−hexane (2:1) as eluant. Orange solid (62 mg, 64%). Anal. Calcd for $C_{26}H_{16}N_2O_{11}Ru_4$ (936.69): C, 33.34; H, 1.72; N, 2.99. Found: C, 33.29; H, 1.76; N, 2.94. (+)-ESI MS: *m/z* 938 [M]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2081 (w), 2050 (vs), 2024 (s), 1999 (m), 1980 (sh), 1948 (sh). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.59 (m, 6 H, CH), 7.49 (m, 4 H, CH), 7.18 (s, 2 H, CH), −18.10 (s, br, 4 H, μ-H).

[Ru$_4$(μ-H)$_4$(CO)$_{11}$(Mes$_2$Im)] (5). This compound was prepared as described above for cluster **2**, using potassium *tert*-butoxide (13 mg, 0.114 mmol), 1,3-dimesitylimidazolium chloride (39 mg, 0.114 mmol), and compound **1** (85 mg, 0.114 mmol) as starting materials. The reaction mixture was separated by column chromatography (silica gel, 2 × 8 cm). Hexane eluted a small amount of the starting material **1**, followed by compound **5**, which was completely eluted with dichloromethane−hexane (1:4). Orange solid (60 mg, 52%). Anal. Calcd for $C_{32}H_{28}N_2O_{11}Ru_4$ (1020.86): C, 37.65; H, 2.76; N 2.74. Found: C, 37.72; H, 2.79; N, 2.70. (+)-ESI MS: *m/z* 1022 [M]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2081 (w), 2047 (vs), 2024 (s), 1997 (m), 1984 (sh), 1956 (sh). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.07 (s, 2 H, CH), 7.05 (s, 4 H, CH), 2.37 (s, 6 H, Me), 2.11 (s, 12 H, Me), −17.88 (s, br, 4 H, μ-H).

[Ru$_7$(μ_3-H)(μ_4-CO)(μ-CO)$_2$(CO)$_{14}${μ-(η^1-η^6-C$_6$H$_4$)MeIm}] (6). A solution of compound **3** (10 mg, 0.012 mmol) in toluene (10 mL) was stirred at reflux temperature for 2 h. The color changed from orange to garnet. The solvent was removed under reduced pressure, the resulting residue was dissolved in dichloromethane, and this solution was supported on preparative silica gel TLC plates. Dichloromethane−diethyl ether (2:1) eluted several bands. The first and major one, garnet, contained compound **6** (4 mg, 43%). Anal. Calcd for $C_{27}H_{10}N_2O_{17}Ru_7$ (1341.86): C, 24.17; H, 0.75; N, 2.09. Found: C, 24.12; H, 0.82; N, 2.04. (+)-ESI MS: *m/z* 1343 [M]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2091 (w), 2074 (vs), 2023 (vs), 1998 (m), 1962 (w), 1938 (w), 1814 (w), 1560 (m). ^{1}H NMR (CDCl$_3$, 293 K): δ 6.96 (d, $J = 2.1$ Hz, 1 H, CH), 6.75 (d, $J = 2.1$ Hz, 1 H, CH), 5.91 (d, $J = 5.3$ Hz, 1 H, CH), 5.60 (d, $J = 5.3$ Hz, 1 H, CH), 5.47 (t, $J = 5.3$ Hz, 1 H, CH), 4.98 (t, $J = 5.3$ Hz, 1 H, CH), 3.88 (s, 3 H, Me), −18.56 (s, 1 H, μ_3-H).

[Ru$_7$(μ_3-H)(μ_4-CO)(μ-CO)$_2$(CO)$_{14}${μ-(η^1-η^6-C$_6$H$_4$)PhIm}] (7). This compound was prepared as described above for cluster **6**, using compound **4** (10 mg, 0.011 mmol) as starting material. Garnet solid (4 mg, 42%). Anal. Calcd for $C_{32}H_{12}N_2O_{17}Ru_7$ (1403.93): C, 27.38; H, 0.86; N, 2.00. Found: C, 27.33; H, 0.81; N, 1.95. (+)-ESI MS: *m/z* 1405 [M]$^+$. IR (CH$_2$Cl$_2$): ν_{CO} 2091 (w), 2074 (vs), 2023 (vs), 1997 (m), 1964 (w), 1953 (w), 1815 (w), 1560 (m). ^{1}H NMR (CDCl$_3$, 293 K): δ 7.60 (m, 3 H, CH), 7.37 (m, 2 H, CH), 7.10 (d, $J = 2.2$ Hz, 1 H, CH), 6.97 (d, $J = 2.2$ Hz, 1 H, CH), 5.88 (d, $J = 5.3$ Hz, 1 H, CH), 5.66 (d, $J = 5.3$ Hz, 1 H, CH), 5.50 (t, $J = 5.3$ Hz, 1 H, CH), 5.01 (t, $J = 5.3$ Hz, 1 H, CH), −18.60 (s, 1 H, μ_3-H).

Computational Details. All optimized structures were calculated by hybrid DFT, within the GAUSSIAN-03 program suite,[26] using the Becke's three-parameter hybrid exchange-correlation functional[27] and the B3LYP nonlocal gradient correction.[28] The LanL2DZ basis set, with relativistic effective core potentials, was used for the Ru atoms.[29] The basis set used for the remaining atoms was the standard 6−31G with addition of (d,p)-polarization. Each structure was confirmed as an energy minimum by calculation of analytical frequencies. For each calculation, the input model molecule was based on a structure determined X-ray diffraction, conveniently modified, if necessary, by manually changing, adding, or removing the appropriate atoms.

X-Ray Diffraction Analyses. Diffraction data for **3** were collected on a Nonius Kappa-CCD diffractometer, using graphite-monochromated Mo Kα radiation. A semiempirical absorption correction was performed with SORTAV.[30] Diffraction data for **6** were collected on an Oxford Diffraction Xcalibur-Nova diffractometer, using Cu Kα radiation. An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in CrysAlisPro RED.[31] Both structures were solved by Patterson interpretation using the program DIRDIF-96.[32] Isotropic and full matrix anisotropic least-squares refinements were carried

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out with SHELXL-97.[33] All non-H atoms of all structures were refined anisotropically. Hydride atom positions were calculated using the program XHYDEX.[17] The remaining hydrogen atoms were set in calculated positions and refined riding on their parent atoms. Two independent cluster molecules were found in the asymmetric unit of **3**. The molecular plots were made with the PLATON program package.[34] The WINGX program system[35] was used throughout the structure determinations. Selected crystal data for **3**: $C_{21}H_{14}N_2O_{11}Ru_4$, $M_r = 874.62$, crystal dimensions: 0.27 × 0.22 × 0.17, monoclinic, space group $P2_1/c$, $a = 30.6398(2)$, $b = 11.2946(1)$, $c = 16.2455(1)$ Å, $\beta = 102.018(1)°$, $V = 5498.77(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 2.113$ g cm^{-3}, $F(000) = 3344$, $\mu = 2.212$ mm^{-1}, 10419 independent reflections, $R_1 = 0.0667$, $wR_2 = 0.2015$ (all data). Selected crystal data for **6**: $C_{27}H_{10}N_2O_{17}Ru_7$, $M_r = 1341.86$, crystal dimensions: 0.17 × 0.07 × 0.03, monoclinic, space group $P2_1/c$, $a = 16.8183(5)$, $b = 13.2795(5)$, $c = 19.0421(6)$ Å, $\beta = 108.590(3)°$, $V = 4030.9(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.211$ g cm^{-3}, $F(000) = 2520$, $\mu = 21.280$ mm^{-1}, 22498 independent reflections, $R_1 = 0.0836$, $wR_2 = 0.2478$ (all data). CCDC deposition numbers: 713127 (**3**) and 713128 (**6**).

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Supporting Information Available: Images and atomic coordinates of the structures optimized by DFT calculations, and crystallographic data in CIF format for the compounds studied by X-ray diffraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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