

Reactivity of N-Heterocyclic Carbenes with [Ru₃(CO)₁₂] and [Os₃(CO)₁₂]. Influence of Ligand Volume and Electronic Effects

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The room-temperature reactions of [Ru₃(CO)₁₂] and [Os₃(CO)₁₂] with a variety of N-heterocyclic carbenes (NHCs) have been studied. [Ru₃(CO)₁₂] reacts easily with *N,N'*-dimethylimidazol-2-ylidene (Me₂Im), more slowly with *N*-methyloxazol-2-ylidene (MeOx), and very slowly with *N,N'*-dimesitylimidazol-2-ylidene (Mes₂Im) to give the corresponding CO substitution products [Ru₃(NHC)(CO)₁₁], but it does not react with the very bulky *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Dipp₂Im). DFT calculations have shown that [Ru₃(Dipp₂Im)(CO)₁₁] is a minimum in the corresponding potential energy surface; therefore, the absence of reaction between [Ru₃(CO)₁₂] and Dipp₂Im has a kinetic origin associated with the large volume of this NHC. [Os₃(CO)₁₂] reacts with Me₂Im to give [Os₃(Me₂Im)(CO)₁₁]. However, MeOx is not basic enough and Mes₂Im and Dipp₂Im are too bulky to react with [Os₃(CO)₁₂], which is less reactive than [Ru₃(CO)₁₂]. Therefore, the reactions of [Ru₃(CO)₁₂] and [Os₃(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.

Introduction

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 N-heterocyclic carbene (NHC) ligand (Scheme 1).¹ Since then, very few reports dealing with trinuclear carbonyl clusters and NHCs have been published. In 2002, we communicated the synthesis of some triruthenium clusters containing bifunctional NHC–thiolato ligands derived from levamisole hydrochloride,² and later we extended this chemistry to triosmium clusters and methyl levamisolium salts (Scheme 2).³

The increasing attention that NHCs have attracted in the past decade,^{4,5} particularly because many of their metal complexes are excellent homogeneous catalysts for alkene metathesis, C–C

bond-coupling reactions, and other important catalytic processes,⁵ and the lack of systematic studies on the reactivity of NHCs with transition metal–carbonyl clusters led us to investigate the reactivity of the simplest triruthenium and triosmium carbonyls, [M₃(CO)₁₂], with a variety of NHC ligands. Most of the NHCs we chose for this study are *N,N'*-disubstituted imidazol-2-ylidenes (R₂Im) because they are easily available, and their electronic and steric properties can be conveniently tuned by choosing the appropriate N-R groups.⁶

We now report that the reactivity of these NHCs with [M₃(CO)₁₂] (M = Ru, Os) strongly depends upon the nature of the N-R groups, since the more basic and less bulky the NHC ligand, the easier its reaction with the metal cluster. A small part of this work has been communicated in a preliminary form.⁷

While this work was underway, Cooke, Pomeroy, et al.⁸ reported the reactions of [Os₃(μ-H)₂(CO)₁₀] and [Os₃(MeCN)₂(CO)₁₀] with [AgCl(Mes₂Im)] (Mes₂Im = *N,N'*-dimesitylimidazol-2-ylidene). In these reactions, the additional incorporation of the chlorine and/or the silver atoms of the reagent into the final clusters was also observed. Very recently, when we were writing up this article, Whittlesey et al.⁹ showed that the very bulky *N,N'*-di-*tert*-butylimidazol-2-ylidene (tBu₂Im) reacts with [Ru₃(CO)₁₂] to give a CO substitution product in which the

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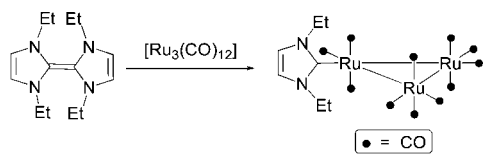
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Scheme 1. Synthesis of Lappert's NHC–Ru₃ Cluster

Scheme 2. NHC–Thiolate Clusters Derived from Levamisolium Salts

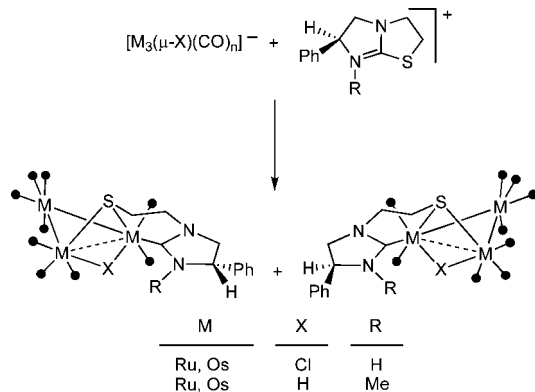


Table 1. Selected Interatomic Distances (Å) in Compounds 1, 2, 4, and 6

| | 1 ^a | 2 ^a | 4 ^a | 6 ^b |
|-----------|----------------|----------------|----------------|----------------|
| M(1)–M(2) | 2.917(1) | 2.845(2) | 2.8858(3) | 2.9333(9) |
| M(1)–M(3) | 2.884(2) | 2.850(2) | 2.8803(3) | 2.901(1) |
| M(2)–M(3) | 2.887(2) | 2.857(2) | 2.8307(4) | 2.908(1) |
| C(1)–M(1) | 2.115(4) | 2.071(8) | 2.144(3) | 2.116(9) |
| C(1)–N(1) | 1.360(5) | 1.30(1) | 1.365(4) | 1.35(1) |
| C(1)–N(2) | 1.360(5) | | 1.365(4) | 1.38(1) |
| C(1)–O(1) | | 1.36(1) | | |

^a M = Ru. ^b M = Os.

^bBu₂Im ligand is coordinated through the abnormal¹⁰ C4 position instead of the normal C2 position.

Results and Discussion

Reaction of [Ru₃(CO)₁₂] with *N,N'*-Dimethylimidazol-2-ylidene (Me₂Im). The cluster [Ru₃(CO)₁₂] reacted readily with Me₂Im in THF at room temperature to give the trinuclear NHC derivative [Ru₃(Me₂Im)(CO)₁₁] (1), which was isolated as an air-stable orange solid (Scheme 1).

The structure of compound 1 was determined by X-ray diffraction methods. Table 1 contains a selection of interatomic distances. Figure 1 shows that the NHC ligand occupies an equatorial position. The structure resembles those of some phosphane-monosubstituted derivatives of [Ru₃(CO)₁₂].¹¹ The Ru(1)–C(1) distance, 2.115(4) Å, is slightly shorter than the Ru–C_{NHC} distance found in the abnormal cluster [Ru₃(^bBu₂Im)(CO)₁₁], 2.151(2) Å, in which the NHC is attached to the cluster via the C4 carbon atom.⁹ The large volume of the Me₂Im ligand pushes away the adjacent equatorial CO ligand. This is clearly reflected by the Ru(2)–Ru(1)–C(102) angle, 147.6(1)°, which is more acute than the remaining Ru–Ru–CO_{trans-to-Ru} angles, which are in the range 152.9(1)–155.6(2)°. The plane defined by the atoms of the Me₂Im ligand forms an angle of 41.65(6)° with the Ru₃ plane. This also contributes to minimizing the steric interactions between the Me₂Im methyl

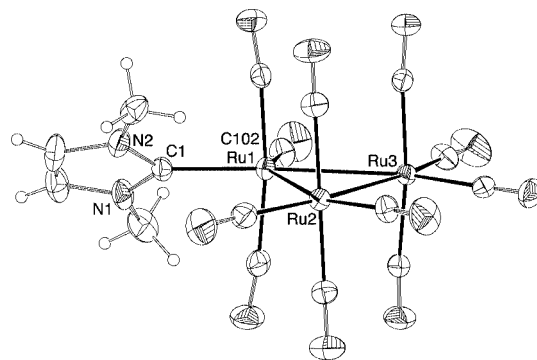
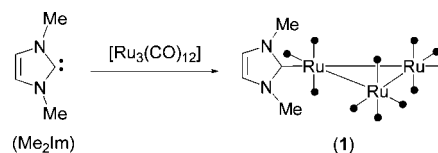
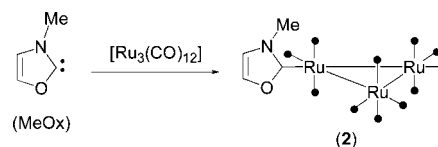


Figure 1. Molecular structure of compound 1. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 3



Scheme 4



groups and the CO ligands that are attached to the Ru(1) and Ru(2) metal atoms.

The room-temperature ¹H NMR spectrum of compound 1 is very simple, since it contains only two singlets, with integral ratio 1:3, assigned to the ring and methyl H atoms of the coordinated Me₂Im ligand. Therefore, although compound 1 has no symmetry in the solid state, a rotation process about the Ru(1)–C(1) axis, which creates a mirror plane that cuts the Me₂Im ligand into two equivalent halves, occurs in solution. No significant changes were observed in a spectrum run at –80 °C.

No simple di- or trisubstituted trinuclear products were observed in reactions of [Ru₃(CO)₁₂] with a 2-fold excess of Me₂Im at room or higher temperature. Although NHCs have often been compared with phosphane ligands,^{4,5} it is noteworthy that the latter do not react with [Ru₃(CO)₁₂] at room temperature and that trisubstituted derivatives of the type [Ru₃(PR₃)₃(CO)₉] are the usual products at higher temperatures, even without excess phosphane. This is because phosphine substitution enhances the rate of CO dissociation at the neighboring metal atoms.¹² This in turn is due to the fact that the phosphine ligand is a better π-acceptor ligand than the NHC ligand.

Reaction of [Ru₃(CO)₁₂] with *N*-Methyloxazol-2-ylidene (MeOx). The trinuclear NHC cluster [Ru₃(MeOx)(CO)₁₁] (2) was isolated as an air-stable orange solid after treating [Ru₃(CO)₁₂] with MeOx in THF at room temperature (Scheme 4). This reaction was slower than that of MeIm.

The CO-stretching region of its IR spectrum is very similar to that of compound 1. Its X-ray molecular structure (Figure 2, Table 1) is also comparable in many aspects to that of compound 1. However, there are some structural features that merit discussion: the Ru(1)–C(1) distance, 2.071(8) Å, is 0.04 Å shorter than that of compound 1 and the Ru(2)–Ru(1)–C(102)

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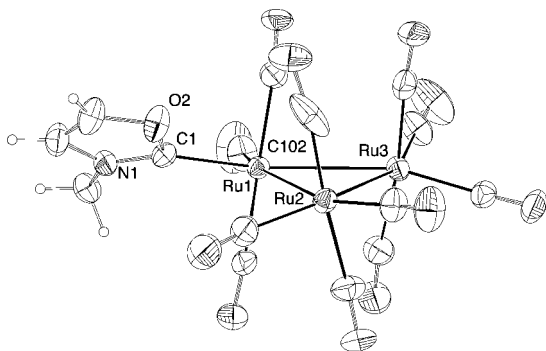
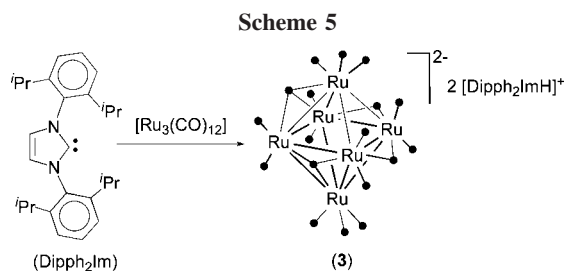


Figure 2. Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 30% probability level.



angle, 160.4(4)°, is 12.8° wider than that of **1**. The angle between the Ru₃ and the MeOx planes is 47.68°. These data clearly reflect that the MeOx ligand exerts a smaller steric hindrance over the adjacent CO ligands than the Me₂Im ligand.

As far as we are aware, no transition metal cluster complexes containing N,O-heterocyclic carbenes have been previously described. However, a few examples of tetranuclear iridium¹³ and trinuclear ruthenium¹⁴ and osmium¹⁵ carbonyl clusters having O-heterocyclic carbenes have been reported. They all contain 1,3-dioxacyclopentan-2-ylidene that arises from the coupling of ethylene oxide with a coordinated CO ligand.

Reaction of [Ru₃(CO)₁₂] with *N,N'*-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (DippH₂Im). This carbene was chosen because it is a very bulky NHC,⁶ and we wanted to compare the reactivity of [Ru₃(CO)₁₂] with NHCs with different steric demands.

The treatment of [Ru₃(CO)₁₂] with DippH₂Im in THF at room temperature resulted in a very slow reaction. After 4 h, a chromatographic workup allowed the isolation of the hexanuclear dianionic cluster [DippH₂ImH]₂[Ru₆(μ₃-CO)₂(μ-CO)₂(CO)₁₄] (**3**) in 36% yield (Scheme 5). This is the only product that could be isolated and characterized. No trinuclear derivatives analogous to compounds **1** and **2** were observed in the reacting solution when the reaction was monitored by IR spectroscopy, which showed that complex **3** was slowly formed prior to the chromatographic workup. Other attempts to make a cluster complex of formula [Ru₃(DippH₂Im)(CO)₁₁], using higher temperature or [Ru₃(MeCN)₂(CO)₁₀] as Ru₃ cluster precursor, were also unsuccessful.⁹

The analytical, IR, and ¹H NMR spectroscopic data of compound **3** were of little help to establish the nature of this product. Its crystal structure was determined by X-ray diffraction and consists of hexanuclear [Ru₆(μ₃-CO)₂(μ-CO)₂(CO)₁₄]²⁻

dianions and *N,N'*-bis(2,6-diisopropylphenyl)imidazolium cations.¹⁶ A literature search revealed that the structure of the [Ru₆(μ₃-CO)₂(μ-CO)₂(CO)₁₄]²⁻ dianion, as a [PMePh₃]⁺ salt, had been previously published.¹⁷

The original synthesis of [Ru₆(μ₃-CO)₂(μ-CO)₂(CO)₁₄]²⁻ involves the treatment of a THF solution [Ru₃(CO)₁₂] with a concentrated aqueous solution of KOH.¹⁸ In our case, the addition of a drop of water to a THF solution of [Ru₃(CO)₁₂] and DippH₂Im resulted in the immediate formation of compound **3** in quantitative yield. However, we always obtained some compound **3** as reaction product working under the “dry” conditions stated at the beginning of the Experimental Section, the yield depending on the reaction scale; the greater the scale, the lower the yield. Therefore, we propose that the formation of compound **3** in our “dry” reaction is associated with the ability of the very basic DippH₂Im carbene to react with adventitious moisture, most probably extracted from the glassware.¹⁹ Thus, deprotonation of water by the DippH₂Im carbene would give the corresponding imidazolium cation and the hydroxide anion required for the formation of [Ru₆(μ₃-CO)₂(μ-CO)₂(CO)₁₄]²⁻.

In order to know whether or not the large DippH₂Im ligand can be accommodated on the coordination shell of a trinuclear carbonyl cluster, the hypothetical species [Ru₃(DippH₂Im)(CO)₁₁] was theoretically studied by density functional theory (DFT) at the B3LYP/LANL2DZ/6-31G(d,p) level. A structure optimization process led to an energy minimum that corresponded to the structure shown in Figure 3. In this structure, the Ru–C(1) distance, 2.189 Å, is 0.074 Å longer than that of compound **1** and the Ru(2)–Ru(1)–C(102) angle, 129.2°, is 18.4° more acute than that of **1**. The angle between the Ru₃ and the DippH₂Im five-membered ring plane is 32.1°. Additionally, the axial CO ligands are not quite perpendicular to the Ru₃ plane. These particular features seem to minimize the steric hindrance exerted by the DippH₂Im ligand over the CO ligands attached to the Ru(1) and Ru(2) metal atoms.

As the electronic properties of DippH₂Im are comparable with those of *N,N'*-dialkylimidazol-2-ylidenes⁶ and as Me₂Im does react with [Ru₃(CO)₁₂], the absence of reaction between DippH₂Im and [Ru₃(CO)₁₂] should have a kinetic origin that has to be associated with the large volume of DippH₂Im. Their 2,6-diisopropylphenyl groups seem to impede the approach of the carbene C atom to the metal atoms of [Ru₃(CO)₁₂] and hence the replacement of one of the cluster CO ligands.

Reaction of [Ru₃(CO)₁₂] with *N,N'*-Dimesitylimidazol-2-ylidene (Mes₂Im). The reaction of [Ru₃(CO)₁₂] with Mes₂Im in THF at room temperature was also slow but gave a separable mixture of the trinuclear NHC derivative [Ru₃(Mes₂Im)(CO)₁₁] (**4**) and the hexanuclear salt [Mes₂ImH]₂[Ru₆(μ₃-CO)₂(μ-CO)₂(CO)₁₄] (**5**; Scheme 6).

The X-ray molecular structure of compound **4** (Figure 4, Table 1) is similar to that calculated for [Ru₃(DippH₂Im)(CO)₁₁] in that the axial CO ligands are not perpendicular to the Ru₃ plane. However, in compound **4**, the Ru(1)–C(1) distance, 2.144(3) Å, the Ru(2)–Ru(1)–C(102) angle, 140.8(1)°, and the

(16) A figure showing the dianion and cations of compound **3** is given as Supporting Information.

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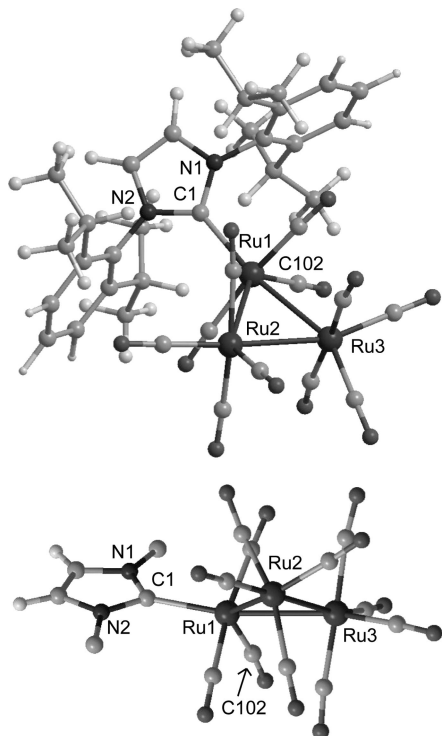
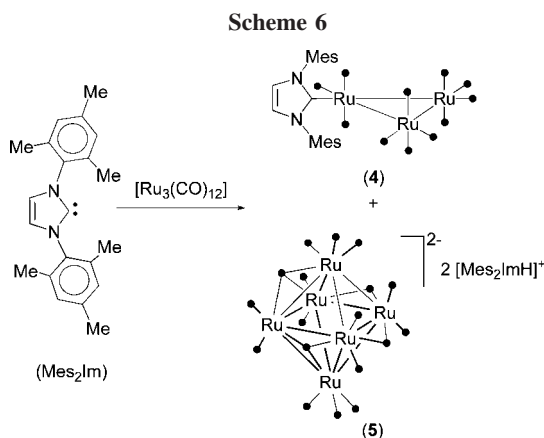


Figure 3. Two views of the DFT-optimized structure of $[\text{Ru}_3(\text{Diph}_2\text{Im})(\text{CO})_{11}]$. For clarity, only the ipso carbon atoms of the 2,6-diisopropylphenyl groups are shown in the bottom view. Selected bond distances (Å) and angles (deg): Ru(1)–Ru(2) 3.070, Ru(1)–Ru(3) 2.869, Ru(2)–Ru(3) 2.891, Ru(1)–C(1) 2.189, Ru(2)–Ru(1)–C(102) 129.2.



angle between the Ru_3 and the Mes_2Im five-membered ring plane, $35.68(1)^\circ$, lie between those of compounds **1** and $[\text{Ru}_3(\text{Diph}_2\text{Im})(\text{CO})_{11}]$. These data are in accordance with the fact that Mes_2Im is much bigger than Me_2Im but smaller than Diph_2Im .⁶

The ^1H NMR spectrum of **4** shows equivalence of both imidazolic CH atoms and both mesityl groups, indicating that, as also occurs with compound **1**, this cluster is nonrigid in solution.

Compound **5** was characterized by microanalysis and spectroscopic techniques. The CO stretching region of its IR spectrum is comparable to that of compound **3**. Its ^1H NMR spectrum only shows the signals expected for the $[\text{Mes}_2\text{ImH}]^+$ cation. In addition, the highest molecular weight peaks of its negative and positive FAB mass spectra correspond to those of $\{[\text{Ru}_6(\mu_3\text{-CO})_2(\mu\text{-CO})_2(\text{CO})_{14}]^{2-} + \text{H}^+\}^-$ and $[\text{Mes}_2\text{ImH}]^+$, respectively. Therefore, compound **5** is a salt that contains

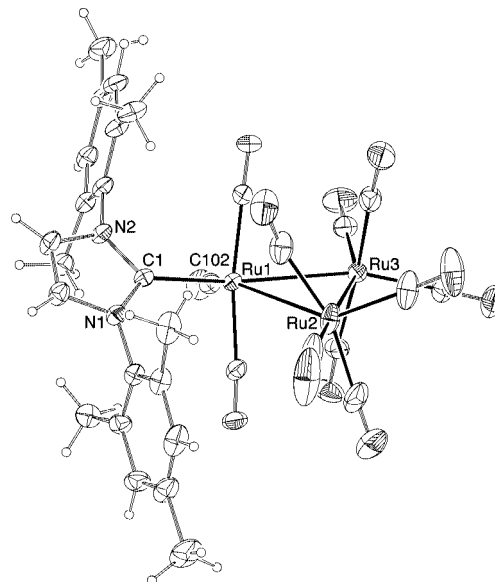
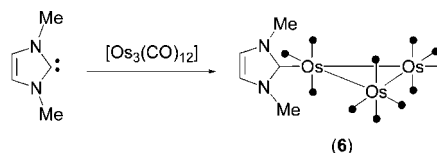


Figure 4. Molecular structure of compound **4**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 7



N,N' -dimesitylimidazolium cations and the same dianion as compound **3**.

The result of this reaction can be rationalized taking into account that Diph_2Im does not react with $[\text{Ru}_3(\text{CO})_{12}]$ and that Mes_2Im is a bulky NHC but smaller than Diph_2Im , while both have similar electronic properties.⁶ The electronic and steric properties of Mes_2Im permit the reaction of this NHC with $[\text{Ru}_3(\text{CO})_{12}]$, but its large volume makes this reaction slow enough to allow its competitive reaction with the small amount of water present in solution or in the glassware, thus giving a mixture of compounds **4** and **5**.

Reactions of $[\text{Os}_3(\text{CO})_{12}]$ with NHCs. As no previous reaction of $[\text{Os}_3(\text{CO})_{12}]$ with an NHC has been published, we became interested in knowing whether or not $[\text{Os}_3(\text{CO})_{12}]$ would react with NHCs in a similar way as $[\text{Ru}_3(\text{CO})_{12}]$.

The carbene Me_2Im reacted with $[\text{Os}_3(\text{CO})_{12}]$ in THF at room temperature to give $[\text{Os}_3(\text{Me}_2\text{Im})(\text{CO})_{11}]$ (**6**) as a yellow solid (Scheme 7).

The molecular structure of the osmium compound **6** was determined by X-ray diffraction (Figure 5, Table 1). It is very similar to that of the related ruthenium cluster **1**. Moreover, both compounds crystallize in the same crystallographic space group with similar cell parameters. The $\text{Os}(1)\text{--C}(1)$ distance, 2.116(9) Å, is slightly shorter than that of $[\text{Os}_3(\mu\text{-Cl})(\mu\text{-H})(\text{Mes}_2\text{Im})(\text{CO})_9]$, 2.121(6) Å,⁸ and longer than those of $[\text{Os}_3(\text{Dox})_2(\text{CO})_{10}]$ ($\text{Dox} = 1,3\text{-dioxacyclopentan-2-ylidene}$), 1.88(6) and 1.91(5) Å,¹⁵ and $[\text{Os}_3\{\text{C}(\text{Et})\text{NMe}_2\}(\text{CO})_{11}]$, 2.09(1) Å.²⁰ These distances correlate well with the volume of the corresponding carbene ligands.

Interestingly, except for Me_2Im , no reaction was observed between $[\text{Os}_3(\text{CO})_{12}]$ and the NHCs used in the above-described reactions with $[\text{Ru}_3(\text{CO})_{12}]$, even at temperatures as high as 70

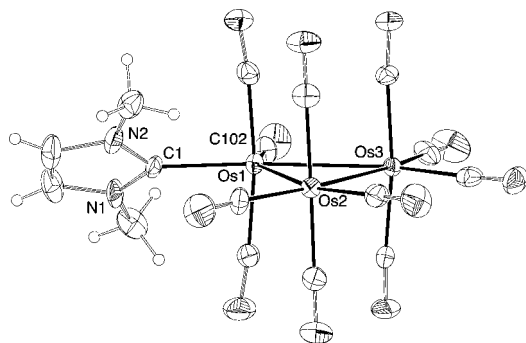


Figure 5. Molecular structure of compound **6**. Thermal ellipsoids are drawn at the 30% probability level.

°C. This result can be rationalized considering the electronic and steric properties of each NHC and also the different stability of the M–CO bonds (M = Ru, Os).

The NHCs Me₂Im, DippH₂Im, and Mes₂Im have similar electronic properties, being strong σ -donors, but Me₂Im is smaller than the other two.⁶ The N,O-heterocyclic carbene MeOx is smaller than Me₂Im, but it is also less basic. The experimental results indicate that Me₂Im is the only NHC, out of those we have used, that has an appropriate combination of steric demand and electronic properties to react with [Os₃(CO)₁₂]. The unusual room-temperature substitution of the osmium carbonyl by the Me₂Im is due to the fact that this ligand is very nucleophilic relative to other ligands and so the reaction proceeds via an appreciable associative component.

The lower tendency of [Os₃(CO)₁₂] to undergo CO substitution reactions under mild conditions, as compared with that of [Ru₃(CO)₁₂], is well documented in the chemical literature.²¹ Thermal reactions of [Ru₃(CO)₁₂] and [Os₃(CO)₁₂], especially those involving loss of CO, require high temperatures, typically above 60 °C for ruthenium and 100 °C for osmium. This prevents the isolation of any but thermally robust products. We are not aware of any CO substitution reaction carried out directly on [Os₃(CO)₁₂] at room temperature.

Alternative methods for obtaining CO substitution products of these clusters are UV irradiation, activation with Me₃NO, catalysis, or previous derivatization.²¹ However, as this work was aimed to compare the reactivity of [Ru₃(CO)₁₂] and [Os₃(CO)₁₂] with NHC, and not to make many members of a family of compounds, we have made no effort to prepare more NHC-containing triosmium clusters by alternative synthetic methods.

Concluding Remarks

The room-temperature reactions of [Ru₃(CO)₁₂] with the NHCs Me₂Im, Mes₂Im, and DippH₂Im proceed at very different rates. Since these NHCs have similar electronic properties, the different reaction rates must be associated with their different steric demands. In fact, while Me₂Im reacts fast to give the monosubstitution product **1**, the bigger Mes₂Im reacts slowly to give **4**, but the biggest DippH₂Im does not react at all. The reason for the absence of reaction between [Ru₃(CO)₁₂] and DippH₂Im is of kinetic nature, since the release of CO would drive the reaction toward the monosubstituted product and DFT calculations have revealed that [Ru₃(DippH₂Im)(CO)₁₁] is a minimum on the corresponding potential energy surface.

When their reaction with [Ru₃(CO)₁₂] is slow or does not proceed, the bulky NHCs react slowly with adventitious water to give small amounts of imidazolium cations and OH[−] anions. The latter are responsible for the observation of the hexanuclear dianion [Ru₆(μ -CO)₂(μ -CO)₂(CO)₁₄]^{2−} when [Ru₃(CO)₁₂] is treated with DippH₂Im and Mes₂Im (compounds **3** and **5**, respectively).

[Ru₃(CO)₁₂] also reacts with the oxazole-derived NHC MeOx, which is less basic and smaller than Me₂Im, to give compound **2**.

While Mes₂Im and DippH₂Im are too big to substitute a CO of [Os₃(CO)₁₂] at room temperature, the smaller MeOx is not basic enough for this process. Only Me₂Im has an appropriate combination of steric and electronic properties to react with [Os₃(CO)₁₂] under similar conditions. This has allowed the isolation of compound **6**. In [Os₃(CO)₁₂] chemistry, this is the first example of a CO substitution reaction that proceeds at room temperature without UV light, catalysis, or previous transformation of [Os₃(CO)₁₂] into other derivatives.

Experimental Section

General Data. The imidazolium salts [Me₂ImH]I,²² [MeOxH]-OTf,²² [Mes₂ImH]Cl,²³ and the NHC DippH₂Im²³ were prepared by published methods. The remaining reagents were purchased from commercial suppliers. Glassware was oven-dried at 100 °C overnight and allowed to cool to room temperature under a nitrogen atmosphere. Solvents were dried over sodium diphenyl ketyl (hydrocarbons, diethyl ether, THF) or CaH₂ (dichloromethane) and distilled under nitrogen prior to use. Free carbenes, imidazolium salts, and KO^tBu were stored and handled under nitrogen in an M-Braun drybox. 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-MS were obtained from the University of Santiago de Compostela Mass Spectrometric Service; data given refer to the most abundant molecular ion isotopomer.

[Ru₃(Me₂Im)(CO)₁₁] (1). THF (50 mL) was added to a Schlenk tube containing KO^tBu (176 mg, 1.564 mmol) and [Me₂ImH]I (350 mg, 1.564 mmol). The mixture was stirred for 30 min. Finely ground [Ru₃(CO)₁₂] (1.000 g, 1.564 mmol) was added, and the resulting solution was stirred for 1 h. The color changed from orange to garnet. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (50 mL). The filtered solution was concentrated to ca. 3 mL, and this solution was transferred onto a silica gel chromatographic column (20 × 3 cm) packed in hexane. Hexane–dichloromethane (4:1) eluted two bands. The first one, yellow, contained some unreacted [Ru₃(CO)₁₂]. The second band, red-orange, contained compound **1** (578 mg, 55%). Anal. Calcd for C₁₆H₈N₂O₁₁Ru₃ (707.73): C, 27.16; H, 1.14; N, 3.96. Found: C, 27.20; H, 1.17; N 3.90. (+)-FAB MS: *m/z* 709 [M]⁺. IR (CH₂Cl₂): δ_{CO} 2093 (m), 2038 (s), 2019 (s), 2005 (vs), 1975 (w), 1949 (w). ¹H NMR (CDCl₃, 293 K): δ 7.02 (s, 1 H, CH), 3.80 (s, 3 H, Me).

[Ru₃(MeOx)(CO)₁₁] (2). A solution of K[(Me₃Si)₂N] in toluene (0.6 mL, 0.5 M, 0.300 mmol) was added to a mixture of [MeOxH]OTf (70 mg, 0.313 mmol) and [Ru₃(CO)₁₂] (200 mg,

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0.313 mmol) in THF (20 mL). The resulting solution was stirred for 1.5 h. The color changed from orange to garnet. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (10 mL). The filtered solution was concentrated to ca. 2 mL, and this solution was transferred onto a silica gel chromatographic column (20 × 3 cm) packed in hexane. Hexane–dichloromethane (4:1) eluted two bands. The first one, yellow, contained some unreacted $[\text{Ru}_3(\text{CO})_{12}]$. The second band, dark orange, contained compound **2** (81 mg, 38%). Anal. Calcd for $\text{C}_{15}\text{H}_5\text{NO}_{12}\text{Ru}_3$ (694.41): C, 25.94; H, 0.73; N, 2.02. Found: C, 25.89; H, 0.68; N 1.97. (+)-FAB MS: m/z 696 $[\text{M}]^+$. IR (CH_2Cl_2): ν_{CO} 2094 (m), 2039 (s), 2025 (s), 2006 (s), 1976 (w), 1948 (vw). ^1H NMR (CDCl_3 , 293 K): δ 7.80 (d, $J = 0.7$ Hz, 1 H, CH), 7.06 (d, $J = 0.7$ Hz, 1 H, CH), 3.88 (s, 3 H, Me).

[Diph₂ImH]₂[Ru₆(μ_3 -CO)₂(μ -CO)₂(CO)₁₄] (3). Finely ground $[\text{Ru}_3(\text{CO})_{12}]$ (80 mg, 0.125 mmol) was added into a solution of Diph₂Im (48 mg, 0.125 mmol) in THF (15 mL). The mixture was stirred for 4 h. The color changed from orange to orange-brown. The filtered solution was concentrated to ca. 2 mL, and this solution was supported on TLC silica gel chromatographic plates. Dichloromethane–acetone–hexane (1:1:2) eluted several bands. The major band (fourth, orange-brown) contained compound **3** (43 mg, 36%). Anal. Calcd for $\text{C}_{72}\text{H}_{74}\text{N}_4\text{O}_{18}\text{Ru}_6$ (1889.79): C, 45.76; H, 3.95; N, 2.96. Found: C, 45.71; H, 3.90; N 2.91. (+)-FAB MS: m/z 389 $[\text{Diph}_2\text{ImH}]^+$. (–)-FAB MS: m/z 1112 $[\text{3} - 2(\text{Diph}_2\text{ImH})^+ + \text{H}^+]$. IR (CH_2Cl_2): ν_{CO} 2044 (w), 1998 (s), 1981 (vs), 1928 (w), 1758 (w, br). ^1H NMR (CDCl_3 , 293 K): δ 8.38 (s, br, 1 H, CH), 7.83 (d, $J = 1.5$ Hz, 2 H, 2 CH), 7.63 (t, $J = 7.5$ Hz, 2 H, 2 CH), 7.40 (d, $J = 7.5$ Hz, 4 H, 4 CH), 2.44 (sep, $J = 7.5$ Hz, 4 H, 4 CH), 1.36 (d, $J = 7.5$ Hz, 12 H, 4 Me), 1.23 (d, $J = 7.5$ Hz, 12 H, 4 Me).

[Ru₃(Mes₂Im)(CO)₁₁] (4) and [Mes₂ImH]₂[Ru₆(μ_3 -CO)₂(μ -CO)₂(CO)₁₄] (5). THF (50 mL) was added to a Schlenk tube containing KO^tBu (37 mg, 0.313 mmol) and $[\text{Mes}_2\text{ImH}]\text{Cl}$ (107 mg, 0.313 mmol). The mixture was stirred for 30 min. Finely ground $[\text{Ru}_3(\text{CO})_{12}]$ (200 mg, 0.313 mmol) was added, and the resulting solution was stirred for 3 h. The color changed from orange to garnet. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (20 mL). The filtered solution was concentrated to ca. 3 mL, and this solution was transferred onto a silica gel chromatographic column (20 × 3 cm) packed in hexane. Hexane–dichloromethane (4:1) eluted two bands. The first one, yellow, contained some unreacted $[\text{Ru}_3(\text{CO})_{12}]$. The second band, red-orange, contained compound **4** (152 mg, 43%). Further elution of the column with dichloromethane–THF (4:1) eluted a yellowish-brown band that contained compound **5** (109 mg, 31%). Data for **4**: Anal. Calcd for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_{11}\text{Ru}_3$ (915.75): C, 41.97; H, 2.64; N, 3.06. Found: C, 41.91; H, 2.59; N 3.01. (+)-FAB MS: m/z 917 $[\text{M}]^+$. IR (CH_2Cl_2): ν_{CO} 2090 (m), 2035 (s), 2020 (s), 2008 (s), 1971 (w). ^1H NMR (CDCl_3 , 293 K): δ 7.02 (s, 2 H, 2 CH), 6.97 (s, 1 H, CH), 2.37 (s, 3 H, Me), 2.09 (s, 6 H, 2 Me). Data for **5**: Anal. Calcd for $\text{C}_{60}\text{H}_{50}\text{N}_4\text{O}_{18}\text{Ru}_6$ (1721.47): C, 41.86; H, 2.93; N, 3.25. Found: C, 41.81; H, 2.88; N 3.20. (+)-FAB MS: m/z 305 $[\text{Mes}_2\text{ImH}]^+$. (–)-FAB MS: m/z 111 $[\text{5} - 2(\text{Mes}_2\text{ImH})^+ + \text{H}^+]$. IR (CH_2Cl_2): ν_{CO} 2046 (w), 1998 (s), 1981 (vs), 1930 (w), 1754 (w, br). ^1H NMR (CDCl_3 , 293 K): δ 8.61 (s, br, 1 H, CH), 7.58 (d, $J = 1.2$ Hz, 2 H, 2 CH), 7.05 (s, 4 H, 4 CH), 2.37 (s, 6 H, 2 Me), 2.13 (s, 12 H, 4 Me).

[Os₃(Me₂Im)(CO)₁₁] (6). THF (50 mL) was added to a Schlenk tube containing KO^tBu (35 mg, 0.312 mmol) and $[\text{Me}_2\text{ImH}]\text{I}$ (70 mg, 0.312 mmol). The mixture was stirred for 30 min. Finely ground $[\text{Os}_3(\text{CO})_{12}]$ (200 mg, 0.221 mmol) was added, and the resulting solution was stirred for 4 h. The color changed from yellow to orange-yellow. The solvent was removed in vacuo, and the residue was extracted into dichloromethane (25 mL). The filtered solution was concentrated to ca. 3 mL, and this solution was transferred onto a silica gel chromatographic column (20 × 3 cm) packed in

hexane. Hexane–dichloromethane (2:1) eluted two yellow bands. The first one contained some unreacted $[\text{Os}_3(\text{CO})_{12}]$. The second band contained compound **6** (160 mg, 74%). Anal. Calcd for $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_{11}\text{Os}_3$ (974.94): C, 19.59; H, 0.82; N, 2.85. Found: C, 19.54; H, 0.77; N 2.80. (+)-FAB MS: m/z 976 $[\text{M}]^+$. IR (CH_2Cl_2): ν_{CO} 2102 (w), 2068 (s), 2048 (s), 2011 (vs), 1979 (w), 1941 (w). ^1H NMR (CDCl_3 , 293 K): δ 7.00 (s, 1 H, CH), 3.96 (s, 3 H, Me).

Computational Details. The optimized structure of $[\text{Ru}_3(\text{Diph}_2\text{Im})(\text{CO})_{11}]$ was calculated by hybrid DFT, within the GAUSSIAN-03 program suite,²⁴ using the Becke's three-parameter hybrid exchange–correlation functional²⁵ and the B3LYP nonlocal 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. The structure shown in Figure 3 was confirmed as an energy minimum by calculation of analytical frequencies. The input model molecule was based on the X-ray structure of compound **4**, conveniently modified by manually adding or removing the appropriate atoms.

X-Ray Diffraction Analyses. Diffraction data for **1** and **6** were measured at room temperature on a Bruker AXS SMART 1000 diffractometer, using graphite-monochromated Mo K α radiation. Raw frame data were integrated with SAINT.²⁸ Absorption corrections were applied with SADABS,²⁹ and the structures were solved by direct methods and refined by full matrix least-squares against F^2 with SHELXL.³⁰ Diffraction data for **2**, **3**, and **4** were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated Cu K α radiation. Absorption corrections were performed using XABS2.³¹ Structures were solved by Patterson interpretation using the program DIRDIF-96.³² Isotropic and full matrix anisotropic least-squares refinements were carried out using SHELXL-97.³³ All non-H atoms of all structures were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms. In compound **2**, we found that, due to disorder or twinning, the molecule was situated in the crystal in two independent positions with different site occupancies. For the main molecule, the Ru atoms were refined with a site occupancy factor of 0.9, whereas

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Table 2. Crystal, Measurement, and Refinement Data for the Compounds Studied by X-Ray Diffraction

| | 1 | 2 | 3 | 4 | 6 |
|--|---|---|---|--|---|
| formula | C ₁₆ H ₈ N ₂ O ₁₁ Ru ₃ | C ₁₅ H ₅ NO ₁₂ Ru ₃ | C ₁₈ O ₁₈ Ru ₆ ·2(C ₂₇ H ₃₇ N ₂) | C ₃₂ H ₂₄ N ₂ O ₁₁ Ru ₃ | C ₁₆ H ₈ N ₂ O ₁₁ Os ₃ |
| fw | 707.45 | 694.41 | 1889.77 | 915.76 | 974.84 |
| cryst syst | monoclinic | triclinic | triclinic | monoclinic | monoclinic |
| space group | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> -1 | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>n</i> | <i>P</i> 2 ₁ / <i>n</i> |
| <i>a</i> , Å | 8.512(5) | 8.332(4) | 10.5169(2) | 13.6171(1) | 8.472(3) |
| <i>b</i> , Å | 22.951(12) | 11.889(7) | 14.0030(2) | 15.1982(9) | 22.858(8) |
| <i>c</i> , Å | 11.753(6) | 11.904(7) | 27.2135(4) | 16.7505(1) | 11.767(4) |
| α, deg | 90 | 84.78(5) | 87.424(1) | 90 | 90 |
| β, deg | 110.20(1) | 73.10(5) | 87.675(1) | 90.604(1) | 110.195(7) |
| γ, deg | 90 | 70.62(5) | 86.000(1) | 90 | 90 |
| <i>V</i> , Å ³ | 2155(2) | 1064.3(1) | 3991.1(1) | 3466.41(4) | 2139(2) |
| <i>Z</i> | 4 | 2 | 2 | 4 | 4 |
| <i>F</i> (000) | 1352 | 660 | 1884 | 1800 | 1736 |
| <i>D</i> _{calcd} , g cm ⁻³ | 2.181 | 2.167 | 1.573 | 1.755 | 3.028 |
| μ (radiation), mm ⁻¹ | 2.136 (Mo Kα) | 17.602 (Cu Kα) | 9.506 (Cu Kα) | 10.972 (Cu Kα) | 17.840 (Mo Kα) |
| cryst size, mm | 0.23 × 0.14 × 0.12 | 0.10 × 0.03 × 0.02 | 0.27 × 0.17 × 0.07 | 0.10 × 0.05 × 0.05 | 0.12 × 0.06 × 0.04 |
| temp, K | 296(2) | 293(2) | 293(2) | 293(2) | 296(2) |
| θ limits, deg | 1.77 to 23.33 | 3.88 to 74.49 | 3.17 to 70.04 | 3.93 to 74.58 | 1.78 to 23.29 |
| min/max <i>h</i> | -9/8 | -8/10 | 0/12 | -16/16 | -9/8 |
| min/max <i>k</i> | -25/25 | -13/14 | -16/16 | -15/18 | -25/21 |
| min/max <i>l</i> | -9/13 | -14/14 | -32/33 | -20/20 | -12/13 |
| no. of collected rflns | 9508 | 32216 | 38005 | 21074 | 9429 |
| no. of unique rflns | 3108 | 8476 | 14793 | 6887 | 3073 |
| no. of reflns with <i>I</i> > 2σ(<i>I</i>) | 2888 | 3765 | 12419 | 6048 | 2844 |
| no. of params/restraints | 292/0 | 307/0 | 901/0 | 433/0 | 292/0 |
| GOF on <i>F</i> ² | 1.111 | 1.002 | 1.032 | 1.075 | 1.083 |
| <i>R</i> 1 (on <i>F</i> , <i>I</i> > 2σ(<i>I</i>)) | 0.0230 | 0.0500 | 0.0560 | 0.0343 | 0.0293 |
| <i>wR</i> 2 (on <i>F</i> ² , all data) | 0.0552 | 0.1627 | 0.1819 | 0.1061 | 0.0774 |
| max/min Δρ, e Å ⁻³ | 0.378/-0.408 | 1.687/-0.907 | 2.451/-1.273 | 0.398/-1.794 | 1.961/-1.051 |

the remaining atoms of this molecule were refined with a site occupancy factor of 1. The three main residual peaks in the final model were assigned as the Ru atoms of the minor molecule and were refined with a site occupancy factor of 0.1. This treatment resulted in good final discrepancy indexes. This crystallographic problem has previously been observed on a few occasions.³⁴ Molecular plots were made with the PLATON program package.³⁵ The WINGX program system³⁶ was used throughout the structure determinations. A selection of crystal, measurement, and refinement data is given in Table 2. CCDC

deposition numbers: 265383 (1), 662383 (2), 662384 (3), 662385 (4), and 662386 (6).

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Supporting Information Available: Atomic coordinates for the DFT-optimized structure of [Ru₃(Dipp₂Im)(CO)₁₁], a figure showing the X-ray structure of compound 3, 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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