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Synthesis, molecular structure and fluxional behavior of the elusive $\left[\mathrm{HRu}_4(\mathrm{CO})_{12}\right]^{3-}$ carbonyl anion

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ABSTRACT:

The elusive mono-hydride tri-anion $[HRu_4(CO)_{12}]^{3-}$ (4) has been isolated and fully characterized for the first time. Cluster 4 can be obtained by deprotonation of $[H_3Ru_4(CO)_{12}]^-$ (2) with NaOH in DMSO. A more convenient synthesis is represented by the reaction of $[HRu_3(CO)_{11}]^-$ (6) with an excess of NaOH in DMSO. The molecular structure of 4 has been determined by single-crystal Xray diffraction (SC-XRD) as [NEt₄]₃[4] salt. It displays a tetrahedral structure of pseudo $C_{3\nu}$ symmetry with the unique hydride ligand capping a triangular Ru₃ face. Variable temperature (VT) ¹H and ¹³C{¹H} NMR experiments indicate that **4** is fluxional in solution and reveal an equilibrium between the $C_{3\nu}$ isomer found in the solid state and a second isomer with C_s symmetry. Protonationdeprotonation reactions inter-converting $H_4Ru_4(CO)_{12}$ (1), $[H_3Ru_4(CO)_{12}]^-$ (2), $[H_2Ru_4(CO)_{12}]^{2-}$ (3), $[HRu_4(CO)_{12}]^{3-}$ (4) and the purported $[Ru_4(CO)_{12}]^{4-}$ (5) have been monitored by IR and ¹H NMR spectroscopy. Whilst attempting the optimization of the synthesis of 4, crystals of $[NEt_4]_2[Ru_3(CO)_9(CO_3)]$ ($[NEt_4]_2[7]$) have been obtained. Anion 7 contains an unprecedented CO_3^{2-1} ion bonded to a zero-valent $Ru_3(CO)_9$ fragment. Finally, the reaction of 6 as $[N(PPh_3)_2]^+$ ([PPN]⁺) salt with NaOH in DMSO affords $[Ru_3(CO)_9(NPPh_3)]^-$ (9) instead of 4. Computational DFT studies have been carried out in order to support experimental evidence and location of the hydride ligands as well as to shed light on possible isomers.

Introduction

Hydridocarbonylates of Fe-Ru-Os triad played a fundamental role in the development of the chemistry of metal carbonyl clusters.¹⁻¹¹ The only species structurally characterized for the whole

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triad are $[HM_3(CO)_{11}]^{-,12-14}$ $[HM_4(CO)_{13}]^{-15-17}$ and $[H_2M_4(CO)_{12}]^{2-,10,18,19}$ In the case of iron, only low nuclearity species comprising 1-5 metal atoms have been structurally characterized, whereas nuclearities up to 10-11 metal atoms have been obtained with Ru and Os (Table 1).²⁰⁻²² This is mainly due to the fact that Ru-Ru and Os-Os bonds are stronger than Fe-Fe ones, favoring formation of larger clusters.^{1,2,23} Moreover, also the greater sizes of Ru and Os compared to Fe seem to play a role, allowing the coordination of more ligands to the same metal cage. In this respect, it is noteworthy that $[HRu_4(CO)_{13}]^-$ and $[HOs_4(CO)_{13}]^-$ display a tetrahedral metal cage, whereas $[HFe_4(CO)_{13}]^-$ adopts a more open butterfly structure in order to accommodate all the ligands.¹⁵⁻¹⁷

It must be remarked that most Ru and Os hydridocarbonylate clusters are neutral or show a low negative charge (charge/nuclearity ≤ 0.5). Conversely, all hydridocarbonylferrates characterized by single crystal X-ray diffraction (SC-XRD) are anionic reaching often high negative charges (charge/nuclearity = 0.25-1.00). This point is well exemplified by $[H_{4-n}M_4(CO)_{12}]^{n-}$ clusters (M = Fe, Ru, Os; n = 0-3). Iron clusters of this type have been obtained quite recently and only dihydride di-anion $[H_2Fe_4(CO)_{12}]^{2-}$ and mono-hydride tri-anion $[HFe_4(CO)_{12}]^{3-}$ are sufficiently stable in order to be isolated and characterized by SC-XRD.^{9,10} In contrast, Ru and Os congeners have been known since longtime, and neutral tetra-hydrides $H_4M_4(CO)_{12}$, tri-hydride mono-anions $[H_3M_4(CO)_{12}]^-$, and di-hydride di-anions $[H_2M_4(CO)_{12}]^{2-}$ (M = Ru, Os) have been structurally characterized.^{11,18,19,24,25} Even though there is spectroscopic evidence of their existence, monohydride tri-anions $[HM_4(CO)_{12}]^3$ (M = Ru, Os) seem to be rather elusive and they have not been characterized by SC-XRD so far.^{26,27}

Nuclearity	Fe	Ru	Os
1	[HFe(CO) ₄] ⁻		
2	[HFe ₂ (CO) ₈] ⁻		
	$[\mathrm{HFe}_{3}(\mathrm{CO})_{11}]^{-}$	$[HRu_3(CO)_{11}]^-$	$[HOs_3(CO)_{11}]^-$
3			$H_2Os_3(CO)_{11}$
			$H_2Os_3(CO)_{10}$
	$[HFe_4(CO)_{13}]^-$	$[HRu_4(CO)_{13}]^-$	$[HOs_4(CO)_{13}]^-$
4		$H_2Ru_4(CO)_{13}$	$H_2Os_4(CO)_{13}$
	$[HFe_4(CO)_{12}]^{3-}$	$[HRu_4(CO)_{12}]^{3-}$ (this work)	

Table 1 Structurally characterized hydridocarbonylates of Fe, Ru and Os (a complete list of references may be found in the Supporting Information, Table S1).

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	$[H_2Fe_4(CO)_{12}]^{2-}$	$[H_2Ru_4(CO)_{12}]^{2-}$	$[H_2Os_4(CO)_{12}]^{2-}$
		$[H_3Ru_4(CO)_{12}]^-$	$[H_3Os_4(CO)_{12}]^-$
		$H_4Ru_4(CO)_{12}$	$H_4Os_4(CO)_{12}$
			$H_2Os_5(CO)_{16}$
5			$[HOs_5(CO)_{15}]^-$
	$[HFe_5(CO)_{14}]^{3-}$		
			$H_2Os_6(CO)_{19}$
6		$[\mathrm{HRu}_6(\mathrm{CO})_{18}]^-$	$[HOs_6(CO)_{18}]^-$
U		$H_2Ru_6(CO)_{18}$	$H_2Os_6(CO)_{18}$
		$H_2Ru_6(CO)_{17}$	
			$H_2Os_7(CO)_{22}$
7			$H_2Os_7(CO)_{21}$
1		[HRu ₇ (CO) ₂₀] ⁻	
			$H_2Os_7(CO)_{20}$
8			$[\mathrm{HOs}_8(\mathrm{CO})_{22}]^-$
0		$[H_2Ru_8(CO)_{21}]^{2-}$	
9			$[HOs_9(CO)_{24}]^-$
		$[H_2Ru_{10}(CO)_{25}]^{2-}$	
10			$[H_4Os_{10}(CO)_{24}]^{2-}$
			$[H_5Os_{10}(CO)_{24}]^-$
11		$[HRu_{11}(CO)_{27}]^{3-}$	

Besides historical and fundamental aspects, Ru hydride carbonyl clusters are rather interesting from an application point of view.²⁸ Phosphine derivatives of $H_4Ru_4(CO)_{12}$ as well as other Ru-H-CO clusters are active in homogeneous catalysis.²⁹⁻³² For instance, $H_4Ru_4(CO)_{12-2x}(P-P)_x$ (x = 1, 2; P-P = chiral diphosphine) species catalyze several asymmetric isomerization, hydroformylation and hydrogenation reactions.³³⁻³⁶ Molecular Ru hydride carbonyl clusters may serve also as models in order to help the location of the hydride ligands within Ru nanoparticles employed for hydrogenation.^{37,38}

In view of this interest for Ru hydridocarbonylates, we have attempted to isolate and fully characterize the elusive mono-hydride tri-anion $[HRu_4(CO)_{12}]^{3-}$. Herein, we report its detailed synthesis as well as its first structural characterization by means of SC-XRD. In addition, the fluxional behavior of this cluster in solution has been investigated by variable temperature (VT) ¹H and ¹³C{¹H} NMR experiments. Protonation-deprotonation reactions inter-converting H₄Ru₄(CO)₁₂

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(1), $[H_3Ru_4(CO)_{12}]^-$ (2), $[H_2Ru_4(CO)_{12}]^{2-}$ (3), $[HRu_4(CO)_{12}]^{3-}$ (4) and the purported $[Ru_4(CO)_{12}]^{4-}$ (5) have been monitored by IR and ¹H NMR spectroscopy. Computational DFT studies have been carried out in order to support experimental evidence and location of the hydride ligands as well as to shed light on possible isomers.

Results and Discussion

Synthesis, molecular structure and dynamic behavior of $[HRu_4(CO)_{12}]^{3-}$ (4)

It was previously reported that **4** was not stable and decomposed into a mixture of **3** and **5**, when obtained by deprotonation of 1.²⁶ This was likely due to the experimental conditions employed, that is reaction of **1** with three equivalents of KH in THF, rather than an intrinsic instability of **4**. Indeed, it was later reported that **4** could be obtained by reaction of **5** with HBr in THF, even if it was not possible to isolate and structurally characterize it.²⁷

Seeking a way to isolate and fully characterize such an elusive species, we investigated the reaction of **2** with an excess of NaOH in a highly polar aprotic solvent such as DMSO. This approach was successful, allowing complete crystallographic and spectroscopic characterization of **4**. The same compound could be obtained even more conveniently from the reaction of $[HRu_3(CO)_{11}]^-$ (**6**) with an excess of NaOH in DMSO (Scheme 1). Both these syntheses were inspired by our previous findings on the synthesis of isostructural $[HFe_4(CO)_{12}]^{3-}$ as well as the highly reduced $[Fe_6C(CO)_{15}]^{4-.9,39}$ Formation of **4** from **2** was just a deprotonation reaction. Conversely, ruthenium was formally reduced from -2/3 to -1 passing from **6** to **4**. Electrons required for reduction were produced by oxidation of CO to CO₂ promoted by OH⁻ nucleophilic attack at a Ru-coordinated CO ligand. In the presence of an excess of base, CO₂ was converted into CO₃²⁻. Indeed, we were able to isolate the carbonate-cluster $[Ru_3(CO)_9(CO_3)]^{2-}$ (**7**) as side product (see experimental for details). After optimization of the synthetic procedure, we were able to isolate **4** as $[NEt_4]^+$ salt in 77% yields.

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Scheme 1 Synthesis of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ (n = 0-4).

The molecular structure of **4** was determined by SC-XRD (Figure 1 and Table 2). Moreover, **4** was spectroscopically characterized by IR and VT ¹H NMR techniques. In order to get further insights on its behavior in solution, VT ¹³C{¹H} NMR experiments were performed on a ¹³COenriched sample (*ca*. 50%) prepared from $[HRu_3(^{13}CO)_{11}]^-$ (**6**-¹³CO).

The structure of **4** closely resembles that of $[HFe_4(CO)_{12}]^{3-,9}$ and displays an idealized $C_{3\nu}$ symmetry. It consists of a tetrahedral Ru₄ cage and the unique hydride is μ_3 -coordinated to the triangular basal face. The apical Ru atom is bonded to three terminal carbonyls, whereas each of the three Ru atoms on the basal plane are bonded to two terminal CO ligands. The three remaining carbonyl ligands are in edge bridging positions on the basal triangle. The stereochemistry of the CO ligands of **4** is similar to that of **3**,^{11,18} which contains two edge bridging μ -H hydride ligands on two different Ru_{apical}-Ru_{basal} edges. In contrast, **2** exists in solution as well as in the solid state as two (C_2 and $C_{3\nu}$) isomers, and both contain only terminal carbonyls and edge bridging hydrides.^{11,24} In agreement with the solid state structure, the IR spectrum in CH₃CN solution of **4** (Figure S1 in the Supporting Information) displays three v_{CO} bands in the terminal region [1928(s), 1898(vs) and 1855(m) cm⁻¹] and one in the edge-bridging region [1714(m) cm⁻¹].

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Fig. 1 Molecular structure of $[HRu_4(CO)_{12}]^{3-}$ (4) (orange Ru; red O; grey C; white H).

Table 2 Main bond distances of $[HRu_4(CO)_{12}]^{3-}$ (**4**) compared to $[H_3Ru_4(CO)_{12}]^{-}$ (**2**) (C_2 and $C_{3\nu}$ isomers) and $[H_2Ru_4(CO)_{12}]^{2-}$ (**3**). See Scheme 2 for labelling.

	4	3*	2 (C ₂ isomer)**	2 ($C_{3\nu}$ isomer)**
Ru(1)-Ru(2)	2.8032(11)	2.9771(4)	2.9032(5)	2.7733(5)
Ru(1)-Ru(3)	2.8001(11)	2.9558(4)	2.7871(5)	2.7753(5)
Ru(1)-Ru(4)	2.8018(11)	2.8183(4)	2.7614(5)	2.7841(4)
Ru(2)-Ru(3)	2.8106(11)	2.7735(4)	2.9423(4)	2.9380(5)
Ru(2)-Ru(4)	2.8006(11)	2.7842(4)	2.7919(4)	2.9218(5)
Ru(3)-Ru(4)	2.8113(11)	2.7526(4)	2.9167(5)	2.9191(4)
H(1)-Ru(1)	-	1.71(4)	1.73(4)	-
H(1)-Ru(2)	1.78(4)	1.86(4)	1.77(4)	1.75(4)
H(1)-Ru(3)	1.77(4)			
H(1)-Ru(4)	1.78(4)	-	-	1.83(4)
H(2)-Ru(2)	-	-	1.79(4)	1.74(4)
H(2)-Ru(3)	-	1.87(4)	1.72(4)	1.76(4)
H(2)-Ru(1)	-	1.64(4)	-	-
H(3)-Ru(3)	-	-	1.72(4)	1.72(4)
H(3)-Ru(4)	-	-	1.80(4)	1.76(4)

* From ref. 11, 18. ** From ref. 11, 24.

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Scheme 2 Labelling of $[H_3Ru_4(CO)_{12}]^-$ (2) (C_2 and $C_{3\nu}$ isomers), $[H_2Ru_4(CO)_{12}]^{2-}$ (3), and $[HRu_4(CO)_{12}]^{3-}$ (4) (CO omitted for clarity).

The six Ru-Ru bonding contacts of **4** are comprised in a rather narrow range [2.8001(11)-2.8113(11) Å] even if they have different environments. Indeed, three of them [Ru(1)-Ru(2), Ru(1)-Ru(3) and Ru(1)-Ru(4), see Scheme 2 for labeling] are not bridged by any ligand, whereas the three Ru-Ru edges on the basal triangle [Ru(2)-Ru(3), Ru(3)-Ru(4), Ru(2)-Ru(4)] are bridged by three µ-CO ligands and the resulting triangular face is capped by a μ_3 -H. The shortening of the Ru-Ru distances expected because of the µ-CO ligands is compensated by the elongation due to the face capping hydride, making these three Ru-Ru contacts being similar to the not-bridged ones. Indeed, in the case of 3, where the two μ -H and three μ -CO ligands are located on different edges, it is possible to distinguish three sets of Ru-Ru distances.^{11,18} The two edges bridged by hydride ligands [2.9558(4) and 2.9771(4) Å] are considerably elongated as expected, whereas the three Ru-Ru edges supported by µ-CO ligands [2.7526(4)-2.7842(4) Å] are shortened. The unique Ru-Ru edge not bearing any bridging ligand displays an intermediate value [2.8183(4) Å], very similar to those found in 4. In the case of 2 (C_2 and $C_{3\nu}$ isomers), since all carbonyls are terminally coordinated, there are only two sets of Ru-Ru contacts: those bridged by μ -H ligands [2.9032(5)-2.9423(4) Å, C_2 isomer; 2.9191(4)-2.9380(5) Å, $C_{3\nu}$ isomer] are longer than the unbridged ones [2.7614(5)-2.7919(4) Å, C₂ isomer; 2.7735(5)-2.7841(4) Å, C_{3v} isomer].^{11,24}

The ¹H NMR spectrum of **4** recorded at 298 K (Figure 2 and Figure S8 in the Supporting Information) displays a broad resonance at -17.65 and -17.95 ppm in CD₃CN and DMF-d⁷ solutions, respectively. The sharp singlets at -15.56 and -19.06 ppm (in DMF-d⁷ solution) are due to an unknown impurity and **3**, respectively. The presence of **3** is due to the fact that **4** is easily protonated (see below for details). On lowering the temperature, complete coalescence of the resonance of **4** is observed at 273 K and, then, two resonances appear at lower temperatures. The

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slow exchange limit is reached at 223 K in DMF-d⁷ solution, where two singlets at -17.90 and - 15.16 ppm are present in a 1.2:1 ratio. The presence of two resonances in the hydride region can be explained assuming that two exchanging isomers of **4** are present in solution.



Fig. 2 Hydride region of the VT ¹H NMR spectra of $[NEt_4]_3[HRu_4(CO)_{12}]$ (4) in DMF-d⁷. * $[H_2Ru_4(CO)_{12}]^{2-}$ (3). # unknown impurity.

Kinetic constants for the exchange process in DMF-d⁷ solution at different temperatures (Table 3) have been obtained by line-shape analysis using the program gNMR 5.0.6.0 for simulation of VT ¹H NMR spectra.⁴⁰ The Eyring plot yields the following values for the activation parameters: $\Delta H^{\neq} = +43\pm6$ kJ mol⁻¹ and $\Delta S^{\neq} = -14\pm24$ J K⁻¹ mol⁻¹. The precision on the entropy term does not allow to determine if it is zero, positive or negative. In all cases, we could expect a value close to zero. These activation parameters are comparable to those reported for the rapid interconversion of the C_2 and $C_{3\nu}$ isomers of **2**, that is $\Delta H^{\neq} = +46$ kJ mol⁻¹ and $\Delta S^{\neq} = 0.2$ -8 J K⁻¹ mol⁻¹.⁴¹

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Т	k
298 K	$6.0 \times 10^4 \text{ s}^{-1}$
273 K	$3.5 \times 10^3 \text{ s}^{-1}$
248 K	$8.0 \times 10^3 \text{ s}^{-1}$
223 K	$1.0 \times 10^2 \text{ s}^{-1}$

Table 3 Kinetic constants at different temperatures for the exchange between the two isomers of $[HRu_4(CO)_{12}]^{3-}$ (4) in DMF-d⁷ solution as obtained from line-shape analysis of VT ¹H NMR spectra.

In order to get further insight on the structures of the two isomers of **4**, VT ¹³C{¹H} NMR experiments have been performed on a ¹³CO-enriched (*ca.* 50%) sample prepared starting from **6**-¹³CO (Figure 3). The ¹³C{¹H} NMR spectrum recorded at 298 K displays, in the carbonyl region, a broad resonance at *ca.* 226 ppm in agreement with the fluxional behavior observed in the VT ¹H NMR experiments. Some sharp resonances are also observed, due to the above mentioned impurities. Moreover, the broad resonance at *ca.* 220 ppm is attributable to **3**. On lowering the temperature to 223 K, the broad resonance of **4** is split into several resonances. Four sharp resonances are clearly visible at 268.7, 213.4, 213.0, 201.7 ppm in a 1:1:1:1 ratio, the first resonance corresponding to μ -CO ligands and the other three resonances to terminal carbonyls. These NMR features are in agreement with the *C*_{3v} symmetry of the major isomer found also in the solid state structure of **4**. A similar low temperature ¹³C{¹H} NMR spectrum was previously reported for [HFe₄(CO)₁₂]^{3-.9}

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Fig. 3 Carbonyl region of the ${}^{13}C{}^{1}H$ NMR spectra of [NEt₄]₃[HRu₄(CO)₁₂] (4) in DMF-d⁷ at 298 K and 223 K. The sample has been enriched with ${}^{13}CO$.

Regarding the second isomer, it must be remarked that, in the ¹³C{¹H} NMR spectrum recorded at 223 K, two further resonances in the μ -CO region are present at 277.8 and 276.7 in a 1:2 ratio. Thus, it can be supposed that the second isomer retains the same stereochemistry of the CO ligands (9 terminal and 3 edge-bridging), whereas the unique hydride is now bridging one Ru_{apical}-Ru_{basal} edge lowering the symmetry from C_{3v} to C_s . Because of C_s symmetry, the three μ -CO ligands are not equivalent but split into two sets composed of one and two carbonyls, respectively, as spectroscopically observed. The same should apply also to the terminal CO ligands resulting in six resonances with relative intensities 1:2:1:2:1:2. Indeed, several resonances are present at low temperature in the 195-220 ppm region but, because of the presence of **3** as well as other impurities, it is not possible to fully assign them.

The location of the hydride in the $C_{3\nu}$ isomer of **4** was confirmed by DFT calculations (Figure 4). Moreover, the computational simulations allowed to optimize a second isomer of **4** with roughly C_s symmetry (R = 0.019), in agreement with the NMR data. The coordination mode of the

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hydride in the C_s isomer is μ -H, bridging the apical and one of the basal Ru centers. The energies of the two isomers are comparable in the limits of the computational model applied, accordingly to the NMR integration of the hydride resonances (Figure 2). It is worth noting that in the absence of intermolecular interactions the C_s isomer is predicted to be slightly more stable than the $C_{3\nu}$ one.



Fig. 4 DFT-optimized isomers of cluster **4** and relative energy values (orange Ru; red O; grey C; white H).

The stepwise protonation of **4** with HBF₄·Et₂O affords the previously reported **3**, **2**, and **1**. The reaction has been monitored by IR and ¹H NMR spectroscopy (Figures 5 and 6; Figures S1-S5 and S9 in the Supporting Information). As mentioned above, **4** is a strong base and is readily protonated. Indeed, its ¹H NMR spectrum is always contaminated by significant amounts of **3**. After the addition of one mole equivalent of acid, **4** has completely reacted, and the ¹H NMR spectrum displays the presence of **3** accompanied by a small amount of **2**. Addition of a second mole equivalent of HBF₄·Et₂O, quantitatively converts **3** into **2** with a small amount of **1**. The latter becomes the unique species in solution after addition of a third mole equivalent of acid. Because of the strong basicity of **4**, all attempts to deprotonate it and isolate the tetra-anion **5** failed.

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Fig. 5 IR spectra in the v_{CO} region of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ (n = 0-3) obtained from the stepwise protonation of $[HRu_4(CO)_{12}]^{3-}$ (4) with HBF₄·Et₂O in CH₃CN.



Fig. 6 Hydride region of the ¹H NMR spectra of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ (n = 0-3) obtained from the stepwise protonation of $[HRu_4(CO)_{12}]^{3-}$ (4) with HBF₄·Et₂O in CD₃CN at 298 K

In order to shed light on the different stability of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ compared to $[H_{4-n}Fe_4(CO)_{12}]^{n-}$, the energy variation associated to the reaction $[H_{4-n}Ru_4(CO)_{12}]^{n-} + [H_{4-n}Ru_4(CO)_{12}]^{n-}$

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 ${}_{m}Fe_{4}(CO)_{12}]^{m-} \rightarrow [H_{4-m}Ru_{4}(CO)_{12}]^{m-} + [H_{4-n}Fe_{4}(CO)_{12}]^{n-}$ (n = 1, 2, 3; m = n-1) was studied. Negative energy variations indicate higher basicity of ruthenium cluster with respect to related iron species. For sake of comparison, the same isomer was considered on changing the metal centre (see Figure 7). As reported in Figure 7, ruthenium clusters were in all cases more basic than related iron species, and the relative basicity increased with the number of coordinated hydrides.



Fig. 7 Energy variations for the reactions $[H_{4-n}Ru_4(CO)_{12}]^{n-} + [H_{4-m}Fe_4(CO)_{12}]^{m-} \rightarrow [H_{4-m}Ru_4(CO)_{12}]^{m-} + [H_{4-n}Fe_4(CO)_{12}]^{n-}$ (m = n -1) and DFT-optimized structures of the isomers considered (green Fe; orange Ru; red O; grey C; white H).

As mentioned at the begin of this section, **7** was obtained as side product during the synthesis of **4** starting from **6**. Its formation is likely due to partial decomposition of **6** which formally results in a zero-valent unsaturated "Ru₃(CO)₉" fragment. The latter can bind a CO_3^{2-} ion which, in turn, is formed from the oxidation of CO to CO_2 and subsequent reaction with OH⁻. This

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may be viewed as an indirect proof of the fact that **6** is reduced to **4** by oxidation of CO in the presence of OH^- ions.

The molecular structure of **7** (Figure 8) is rather unique, since it contains the first example of a CO_3^{2-} ion bonded to (formally) zero-valent metal atoms. Indeed, the carbonate ion is usually found bonded, also as a multidentate ligand, to metals in a formal positive oxidation state.^{11,42} In particular, the CO_3^{2-} ion of **7** is bonded to one Ru atom *via* one O-atom and to two further Ru atoms through a second (edge bridging) O-atom, whereas the third oxygen is not bonded to any metal atom. Three CO ligands are edge bridging on the Ru₃ triangle and, in addition, there are two terminal carbonyls on each Ru atom.



Fig. 8 (a) Molecular structure of $[Ru_3(CO)_9(CO_3)]^{2-}$ (**7**) (orange Ru; red O; grey C) with a labeling scheme. Main bond distances (Å) and angles (°): Ru(1)-Ru(2) 2.790(3), Ru(1)-Ru(3) 2.800(2), Ru(2)-Ru(3) 2.634(2), Ru(1)-O(1) 2.147(14), Ru(2)-O(2) 2.149(13), Ru(3)-O(12) 2.174(13), C(1)-O(1) 1.34(3), C(1)-O(2) 1.28(3), C(1)-O(3) 1.22(3), Ru(1)-O(1)-C(1) 117.9(14), Ru(2)-O(2)-Ru(3) 75.1(4), O(1)-C(1)-O(2) 118(2), O(1)-C(1)-O(3) 114(2), O(2)-C(1)-O(3) 128(2). (b) DFT-optimized

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structure of **7** (orange Ru; red O; grey C) and selected (3,-1) b.c.p. (green) with density values at b.c.p. (potential energy density values in parenthesis). Data in a.u.

The coordination mode of the carbonate ion was confirmed by DFT calculations. The rootmean-square deviation (RMSD) between X-ray and DFT-optimized structures is only 0.019 Å. Three Ru-O (3,-1) bond critical points (b.c.p.) were obtained from the atom-in-molecule (AIM) analysis of the cluster (Figure 8). The computed Mayer bond order for the Ru-(κ^1 -O) bond is 0.575, while the bond order for the two Ru-(μ -O) bonds is lower (0.437). In agreement with this result, the electron density (ρ) at b.c.p. is higher and the potential energy density (V) is more negative for the Ru-(κ^1 -O) interaction with respect to the Ru-(μ -O) ones. AIM data are reported in Figure 8.

The Hirshfeld partial charges on the Ru atoms are strictly comparable, and the average value is 0.105 a.u. The average value for the separated neutral {Ru₃(CO)₉} fragment is similar, 0.078 a.u., but surprisingly slightly less positive. Charge decomposition analysis (CDA) indicates that CO_3^{2-} behaves as donor towards {Ru₃(CO)₉} by about 0.51 a.u., without back-donation. The increase of electron density is drained by carbonyl ligands, as confirmed by population analyses. The average CO Hirshfeld charge in **7** is -0.122 a.u., while it is -0.020 a.u. in the related {Ru₃(CO)₁₂} fragment. Overall, the computed data do not suggest any change of the formal oxidation state of the Ru atoms upon coordination of CO_3^{2-} .

Synthesis and molecular structure of [Ru₃(CO)₉(NPPh₃)]⁻ (9)

The reaction of **6** with an excess of NaOH in DMSO under CO atmosphere affords $[Ru_2(CO)_8]^{2-}$ (**8**) rather than **4**. Both the compounds contain Ru in the formal oxidation state -1, but **8** has a higher CO/Ru ratio (4) compared to **4** (CO/Ru = 3) in accordance to equation (1). Compound **8** has been identified by IR spectroscopy and, moreover, its structure has been supported by SC-XRD on the new [NEt₄]₂[Ru₂(CO)₈] salt (Figure S12 in the Supporting Information).

$$[HRu_4(CO)_{12}]^{3-} + 4CO \leftrightarrow 2[Ru_2(CO)_8]^{2-} + H^+$$
(1)

Interestingly, performing the reaction of **6** with NaOH ion DMSO in the presence of $[PPN]^+$ ions $([PPN]^+ = [N(PPh_3)_2]^+)$ afforded the new $[Ru_3(CO)_9(NPPh_3)]^-$ (**9**) cluster.

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Compound **9** has been previously identified by IR and ³¹P{¹H} NMR spectroscopy during deprotonation of [HRu₃(CO)₉(NPPh₃)] (**10**) which, in turn, was obtained from the reaction of Ru₃(CO)₁₂ with Ph₃P=NSiMe₃.⁴³ The molecular structure of **9** has been determined by SC-XRD as its [NEt₄][Ru₃(CO)₉(NPPh₃)] salt (Figure 9). It consists of a triangular Ru₃ cluster with a μ_3 -NPPh₃ ligand, six terminal carbonyls (two per each Ru atom) and three μ -CO ligands on three edges of the Ru₃ triangle. In agreement with the solid state structure, its FT-IR spectrum in solution and in the solid state shows v_{CO} bands due to both terminal and edge bridging carbonyls. It must be remarked that two isomers of **10** have been structurally characterized, one displaying the same stereochemistry of the CO ligands as found in **9**, whereas the second isomer possesses only terminal carbonyls. It is well known that increasing the anionic charge of a carbonyl cluster favours the bridging mode of the CO ligands.^{44,45} For instance, **1** and **2** contain only terminal CO's, whereas **3** and **4** contain three μ -CO ligands.

Cluster **9** is electron precise since it possesses 48 cluster valence electrons (CVE) [3×8 (3Ru) + 9×2 (9CO) + 1×5 (μ_3 -NPPh_3) + 1 (charge)] as expected for a triangular cluster. The μ_3 -NPPh₃ contributes 5 CVE if considered as a neutral ligand, and 6 CVE if considered as a monoanion. A computational analysis of **9** is included in the Supporting Information.

The ³¹P{¹H} NMR spectrum of **9** in CD₂Cl₂ at 298 K displays a sharp singlet at δ_P 57.03 ppm, considerably deshielded compared to the starting [PPN]⁺ ions (δ_P 21 ppm).



Fig. 9 Molecular structure of $[Ru_3(CO)_9(NPPh_3)]^-$ (9) (orange Ru; purple P; blue N; red O; grey C; white H). Main bond distances (Å): Ru-Ru 2.7297(7), 2.7455(7) and 2.7471(7); Ru-N 2.125(5), 2.129(5) and 2.141(5); N-P 1.597(5).

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Conclusions

Synthesis, spectroscopic characterization and structural determination of $H_4Ru_4(CO)_{12}$ (1), $[H_3Ru_4(CO)_{12}]^-$ (2) and $[H_2Ru_4(CO)_{12}]^{2-}$ (3) hydride carbonyl clusters represented a milestone in cluster chemistry.^{1,11,18,24,25} Spectroscopic evidence that they can be further deprotonated affording $[HRu_4(CO)_{12}]^{3-}$ (4) mono-hydride tri-anion has been reported more than 40 years ago.^{26,27} Nonetheless, **4** escaped up to now any effort devoted to its isolation and structural characterization. This is likely due to the experimental conditions employed during these attempts, rather than an intrinsic instability of **4**. Indeed, by carefully choosing the operational conditions and, in particular, by working in a highly polar aprotic solvent such as DMSO and using a strong base such as NaOH, it has been possible to convert **2** as well as $[HRu_3(CO)_{11}]^-$ (6) into **4**. This allowed its isolation and the determination of its structure by SC-XRD. Similar approaches have been recently adopted for the isolation of $[HFe_4(CO)_{12}]^{3-}$ starting from $[Fe_4(CO)_{13}]^{2-}$ or $[HFe_3(CO)_{11}]^{-9,10}$ as well as the synthesis of $[Fe_6C(CO)_{15}]^{4-}$ from $[Fe_6C(CO)_{16}]^{2-.39}$ Thus it seems that the use of strong bases in polar solvents such as DMSO or CH₃OH may be a general synthetic pathway towards highly reduced carbonylate clusters.

Two isomers of **4** rapidly exchange in solution, whereas a single isomer has been reported for $[HFe_4(CO)_{12}]^{3-.9}$ The latter possesses the same $C_{3\nu}$ structure with a μ_3 -H found in the solid state structure of **4**. This might be due to the fact that, due to the larger size of Ru compared to Fe, there is more space on a Ru₄(CO)₁₂ tetrahedron rather than Fe₄(CO)₁₂ in order to accommodate the hydride ligand on different sites. Indeed, it is well know that both $[Ru_4(CO)_{13}]^{2-}$ and $[Fe_4(CO)_{13}]^{2-}$ have a tetrahedral structure, which is retained in $[HRu_4(CO)_{13}]^{-}$, whereas $[HFe_4(CO)_{13}]^{-}$ shows a more open butterfly structure.¹⁵⁻¹⁷ Nonetheless, it must be remarked that **3** and $[H_2Fe_4(CO)_{12}]^{2-}$ are isostructural.¹⁰

Comparison of $[H_{4-n}Ru_4(CO)_{12}]^{n-}$ (n = 0-3) and $[H_{4-n}Fe_4(CO)_{12}]^{n-}$ (n = 2-3) indicates that Ru prefers less charged poly-hydride species, whereas more charged anions are favored in the case of Fe. This may be explained assuming a higher basicity of Ru cluster anions compared to related Fe species. Indeed, **4** is easily protonated to **3**, whereas protonation of $[HFe_4(CO)_{12}]^{3-}$ to $[H_2Fe_4(CO)_{12}]^{2-}$ requires strictly controlled conditions. Moreover, there is no evidence of less charged Fe poly-hydrides of the type $[H_3Fe_4(CO)_{12}]^{-}$ and $H_4Fe_4(CO)_{12}$.

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These findings further corroborate the tendency of Ru toward the formation of poly-hydride clusters. Somehow this is correlated to the involvement of Ru-H complexes, molecular carbonyl clusters and nanoparticles in catalytic processes using hydrogen.²⁸⁻³⁸

Experimental

General procedures.

All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Analyses of C, H and N were obtained with a Thermo Quest Flash EA 1112NC instrument. IR spectra were recorded on a Perkin Elmer Spectrum One interferometer in CaF₂ cells. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR measurements were performed on a Varian Mercury Plus 400 MHz instrument. The proton and carbon chemical shifts were referenced to the non-deuterated aliquot of the solvent. The phosphorus chemical shifts were referenced to external H₃PO₄ (85% in D₂O). Structure drawings have been performed with SCHAKAL99.⁴⁶

Synthesis of [NEt₄][HRu₃(CO)₁₁] (6) ⁴⁷

RuCl₃•3H₂O $\xrightarrow{NaOMe}_{[NEt_4]Br}$ [NEt₄][HRu₃(CO)₁₁] CH₃OH p(CO): 60atm 120°C, 14h

In a 100-mL autoclave, RuCl₃·3H₂O (1.57 g, 6 mmol), NaOMe (1.92g, 35.6 mmol) and [NEt₄]Br (0.630 g, 3 mmol) were dissolved in CH₃OH (40 mL). The autoclave was pressurized with CO (60 bar) and heated at 120°C for 14 h. After cooling and venting, the deep red solution, containing already solid product was moved to a 250 mL Schlenck tube, filtered under nitrogen atmosphere and the residue washed with methanol (30 mL). Then, the solvent was removed from the filtrate under vacuum and the residue extracted in CH₂Cl₂ (40 mL). The solvent was removed from the CH₂Cl₂ solution under reduced pressure. The residue washed with water (2×30 mL) and toluene (2×20 mL), and then extracted with CH₂Cl₂ (30 mL). The product [NEt₄][HRu₃(CO)₁₁] was obtained as a red solid with a yield of 75% after removal of the solvent under reduced pressure. Crystals of [NEt₄][HRu₃(CO)₁₁] suitable for SC-XRD can be obtained by slow diffusion of n-hexane on the CH₂Cl₂ solution (yield 1.48 g, 85%).

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 $C_{19}H_{21}NO_{11}Ru_3$ (742.583): calcd. (%): C 30.73, H 2.85, N 1.89; found: C 30.91, H 2.62, N 2.05. IR (CH₂Cl₂, 298 K) v_{CO}: 2016(vs), 1987(s), 1952(m) cm⁻¹. ¹H NMR (acetone-d⁶, 298 K) δ (hydride region): -12.51 ppm.

Synthesis of $[NEt_4]_3[HRu_4(CO)_{12}]$ (4) and $[NEt_4]_2[Ru_3(CO)_9(CO_3)]$ (7)

 $[NEt4][HRu_3(CO)_{11}] \xrightarrow{NaOH} [HRu_4(CO)_{12}]^3 \xrightarrow{} [NEt4]_3[HRu_4(CO)_{12}]$

NaOH (0.800 g, 200 mmol) was added as a solid to a solution of $[NEt_4][HRu_3(CO)_{11}]$ (0.550 g, 0.741 mmol) in DMSO (10 mL). The resulting mixture was stirred at room temperature for 3 days. The crude product was precipitated by addition of *i*PrOH (100 mL) and the solid recovered by filtration, washed with *i*PrOH (30 mL), and dried under reduced pressure. The orange solid was further washed with toluene (15 mL), THF (15 mL), and extracted in acetone (15 mL). The acetone solution was layered with *n*-hexane affording crystals of $[NEt_4]_2[Ru_3(CO)_9(CO_3)]$ suitable for SC-XRD (yield 0.175 g, 27%). Then, the residue was extracted in acetonitrile (15 mL) and layered with *n*-hexane and diisopropyl ether affording crystals of $[NEt_4]_3[HRu_4(CO)_{12}]$ suitable for SC-XRD (yield 0.349 g, 58%).

[NEt₄]₂[Ru₃(CO)₉(CO₃)] (4) IR (CH₃CN, 298 K) ν_{CO} : 1938(vs), 1907(s), 1757(m) cm⁻¹. IR (Nujol, 298 K) ν_{CO} : 1984(m), 1957(vs) (m), 1931(m), 1912(s), 1761(s) cm⁻¹. ¹³C{¹H} NMR (Acetone-d⁶, 298 K) δ (carbonyl region): 223.2 (CO), 217.7 (CO), 166.9 (CO₃) ppm.

[NEt₄]₃[HRu₄(CO)₁₂] (7) IR (CH₃CN, 298 K) v_{CO}: 1928(s), 1898(vs), 1855(m), 1714(m) cm⁻¹. IR (Nujol, 298 K) v_{CO}: 1934(m), 1860(s) (m), 1744(w) cm⁻¹. ¹H NMR (CD₃CN, 298 K) δ (hydride region): -17.65 (br) ppm. ¹H NMR (CD₃CN, 273 K) δ (hydride region): -18.00 (coalescence) ppm. ¹H NMR (CD₃CN, 248 K) δ (hydride region): -18.43, -15.75 ppm. ¹H NMR (DMF-d⁷, 298 K) δ (hydride region): -17.95 (br) ppm. ¹H NMR (DMF-d⁷, 273 K) δ (hydride region): (coalescence). ¹H NMR (DMF-d⁷, 248 K) δ (hydride region): -18.04, -15.32 ppm. ¹H NMR (DMF-d⁷, 223 K) δ (hydride region): -17.90, -15.16 ppm. ¹³C{¹H} NMR (CD₃CN, 298 K) δ (carbonyl region): 226 (br) ppm. ¹³C{¹H} NMR (CD₃CN, 273 K) δ (carbonyl region): 225.0 (coalescence) ppm. ¹³C{¹H} NMR (DMF-d⁷, 273 K) δ (carbonyl region): 225.1 (br) ppm. ¹³C{¹H} NMR (DMF-d⁷, 273 K) δ (carbonyl region): 226.0 (coalescence) ppm. ¹³C{¹H} NMR (DMF-d⁷, 273 K) δ (carbonyl region): 225.2 (br) ppm. ¹³C{¹H} NMR (DMF-d⁷, 273 K) δ (carbonyl region): 268.7, 213.4, 213.0, 201.7 (C_{3v} isomer), 277.8, 276.7 (C_s isomer; the resonances of the terminal CO ligands could not be resolved) ppm.

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Optimized synthesis of [NEt₄]₃[HRu₄(CO)₁₂] (4)

[NEt₄][HRu₃(CO)₁₁] (0.700 g, 0.943 mmol) was stirred at room temperature with 1.50 g of freshly powdered KOH suspended in 10 mL of DMSO for 16 h. The orange solution decanted from KOH powder was added dropwise to a stirred solution of [NEt₄]Br (2.00 g) in H₂O (15 mL) and *i*PrOH (150 mL). The crude compound precipitated immediately as an orange powder. The solid was collected by filtration and vacuum dried. Then, the solid was washed with acetone (10 mL) and the product extracted in CH₃CN was identified as [NEt₄]₃[HRu₄(CO)₁₂] by means NMR and IR spectroscopy (yield 0.616 g, 77%).

C₃₆H₆₁N₃O₁₂Ru₄ (1132.15): calcd. (%): C 38.19, H 5.43, N 3.71; found: C 38.31, H 5.07, N 3.49.

Synthesis of [NEt₄][Ru₃(CO)₉(NPPh₃)] (9)

[PPN][HRu₃(CO)₁₁] NaOH DMSO [NEt4]Br [NEt4][Ru₃(CO)₉(NPPh₃)]

NaOH (0.950 g, 23.8 mmol) was added as a solid to a solution of [PPN][HRu₃(CO)₁₁] (0.670 g, 0.582 mmol) in DMSO (10 mL), and the resulting mixture was stirred at room temperature overnight. The crude product was filtered and the solution precipitated by addition of a saturated solution of [NEt₄]Br in H₂O. The solid obtained was recovered by filtration, washed with H₂O (40 mL), toluene (20 mL) and 2-propanol (20 mL), then extracted with CH₂Cl₂ (15 mL). Crystals of [NEt₄][Ru₃(CO)₉(NPPh₃)] suitable for SC-XRD were obtained by layering n-pentane on the CH₂Cl₂ solution (yield 0.352 g, 63%).

C₃₅H₃₅N₂O₉PRu₃ (961.83): calcd. (%): C 43.71, H 3.67, N 2.91; found: C 43.56, H 3.38, N 3.11.

IR (CH₂Cl₂, 298 K) ν_{CO} : 2016(w), 1990(s), 1959(vs), 1926(m), 1750(m) cm⁻¹.

IR (Nujol, 298 K) v_{CO} : 2018(w), 1979(ms), 1961(s), 1941(m), 1907(mw), 1890(mw), 1772(m), 1746(s) cm⁻¹.

 ${}^{31}P{}^{1}H$ NMR (CD₂Cl₂, 298 K) δ : 57.03 ppm.

 $^{13}C\{^1H\}$ NMR (CD₂Cl₂, 298 K) δ (carbonyl region): 221.5 ppm.

X-ray Crystallographic Study.

Crystal data and collection details for and $[NEt_4][HRu_3(CO)_{11}]$, $[NEt_4][Ru_3(CO)_9(NPPh_3)]$, $[NEt_4]_2[Ru_2(CO)_8]$, $[NEt_4]_3[HRu_4(CO)_{12}]$ and $[NEt_4]_2[Ru_3(CO)_9(CO_3)]$ are reported in Table 5. The

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diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo–K α radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).⁴⁸ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using $F^{2,49}$ Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters, unless otherwise stated.

CCDC 2115041-2115045 contain the supplementary crystallographic data for this paper.

Table 5

Crystal data and experimental details for [NEt₄][HRu₃(CO)₁₁], [NEt₄]₂[Ru₂(CO)₈],

$[NEt_4][Ru_3(CO)_9(NPPh_3)]$, [NEt ₄] ₃ [HRu ₄ (CO) ₁₂] a	and $[NEt_4]_2[Ru_3(CO)_9(CO_3)].$
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	[NEt ₄][HRu ₃ (CO) ₁₁]	[NEt ₄] ₂ [Ru ₂ (CO) ₈]	[NEt ₄][Ru ₃ (CO) ₉ (NPPh ₃)]
Formula	$C_{19}H_{21}NO_{11}Ru_3$	$C_{24}H_{40}N_2O_8Ru_2$	$C_{35}H_{35}N_2O_9PRu_3$
Fw	742.58	686.72	961.83
Т, К	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space Group	$P2_{1}/c$	$P2_1/n$	PĪ
a, Å	12.3458(10)	9.5198(6)	11.1727(11)
b, Å	11.7217(9)	13.7870(8)	11.9062(12)
c, Å	17.4163(15)	11.8620(7)	14.3383(14)
α, °	90	90	90.095(3)
β, °	97.810(3)	113.085(2)	99.075(3)
γ, °	90	90	100.292(3)
Cell Volume, Å ³	2497.0(4)	1432.21(15)	1852.3(3)
Z	4	2	2
$D_c, g cm^{-3}$	1.975	1.592	1.725
μ , mm ⁻¹	1.847	1.100	1.305
F(000)	1448	700	956
Crystal size, mm	0.22×0.18×0.14	0.24×0.21×0.19	0.18×0.12×0.11
θ limits, °	1.665-26.996	2.380-27.994	1.439–25.099
Index ranges	$-15 \le h \le 15$	$-12 \le h \le 12$	$-13 \le h \le 13$
muex ranges	$-14 \le k \le 14$	$-18 \le k \le 18$	$-14 \le k \le 14$

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	$-22 \le 1 \le 22$	-15 ≤ 1 ≤ 15	-17 ≤ l ≤ 17
Reflections collected	30401	31227	23609
Independent reflections	5447 [$\mathbf{R}_{int} = 0.0938$]	3453 [$\mathbf{R}_{int} = 0.0377$]	$6537 [R_{int} = 0.0604]$
Completeness to θ max	100.0%	100.0%	99.2%
Data / restraints / parameters	5447 / 0 / 314	3453 / 0/ 167	6537 / 414 / 482
Goodness on fit on F ²	1.042	1.084	1.172
$R_1 (I > 2\sigma(I))$	0.0403	0.0145	0.0521
wR_2 (all data)	0.0837	0.0355	0.0993
Largest diff. peak and hole, e Å ⁻³	1.156 / -1.005	0.292 / -0.355	1.438 / -2.126

	[NEt ₄] ₃ [HRu ₄ (CO) ₁₂]	[NEt ₄] ₂ [Ru ₃ (CO) ₉ (CO ₃)]
Formula	$C_{36}H_{61}N_3O_{12}Ru_4$	$C_{26}H_{40}N_2O_{12}Ru_3$
Fw	1132.15	875.81
Т, К	293(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space Group	$P2_{1}/n$	$P2_1/c$
a, Å	12.9763(8)	16.5638(16)
b, Å	19.4012(12)	10.2807(10)
c, Å	18.0370(11)	19.8070(19)
α, °	90	90
β, °	97.884(2)	105.465(3)
γ, °	90	90
Cell Volume, Å ³	4498.0(5)	3250.8(5)
Z	4	4
D_c , g cm ⁻³	1.672	1.790
μ , mm ⁻¹	1.375	1.436
F(000)	2280	1752
Crystal size, mm	0.14×0.12×0.11	0.16×0.14×0.10

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θ limits, °	1.549-26.036	2.134-25.074	
	$-15 \le h \le 15$	$-19 \le h \le 19$	
Index ranges	$-23 \le k \le 23$	$-12 \le k \le 12$	
	$-22 \le 1 \le 22$	$-23 \le 1 \le 23$	
Reflections	56877	40201	
collected	50877	49201	
Independent	8833 [R 0.0815]	5706 [R 0 1011]	
reflections	$10000 [R_{int} - 0.0010]$	$5700 [R_{int} - 0.1011]$	
Completeness to	100.0%	99.1%	
θ max	100.070	///.1/U	
Data / restraints	8833 / 825 / 647	5706 / 252 / 380	
/ parameters	00557 0257 047	570072527500	
Goodness on fit	1 157	1 330	
on F ²	1.10 /	1.550	
$R_1 (I > 2\sigma(I))$	0.0879	0.1398	
wR_2 (all data)	0.1983	0.3260	
Largest diff.			
peak and hole, e	2.194 / -1.663	2.880 / -2.865	
Å-3			

Computational details

Geometry optimizations of the clusters were performed in the gas phase using the range-separated hybrid DFT functional ωB97X.⁵⁰ The basis set used was Ahlrichs'def2 split-valence, with relativistic ECP for Ru.⁵¹ The "restricted" approach was used in all the cases. The software used was Gaussian 09.⁵² The output was used for AIM and Mayer analyses,⁵³ performed using software Multiwfn, version 3.5.⁵⁴ Cartesian coordinates of the DFT-optimized structures are collected in a separated.xyz file.

ACKNOWLEDGMENTS

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