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One-pot atmospheric pressure synthesis of $[H_3Ru_4(CO)_{12}]^-$

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One-Pot Atmospheric Pressure Synthesis of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$

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ABSTRACT:

Reductive carbonylation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ at CO-atmospheric pressure results in the $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**1**) polyhydride carbonyl cluster. This one-pot synthesis involves heating $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ at 80 °C in 2-ethoxyethanol for 2 h, addition of three equivalents of KOH, heating at 135 °C for 2 h, addition of a fourth equivalent of KOH and heating at 135 °C for 1 h. The resulting $\text{K}[\mathbf{1}]$ salt is transformed into $[\text{NEt}_4][\mathbf{1}]$ upon metathesis with $[\text{NEt}_4]\text{Br}$ in H_2O . The IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data are in agreement with those reported in the literature. $[\text{Ru}_8(\text{CO})_{16}(\text{X})_4(\text{CO}_3)_4]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; **2-X**) is formed as by-product during the synthesis of **1**, and the two compounds separated on the basis of their different solubility in organic solvents. The nature of the halide of **2-X** depends on the $[\text{NEt}_4]\text{X}$ salt used for metathesis. **2-Br** is transformed into $[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]^{2-}$ (**3**) upon reaction with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$. **1** is readily deprotonated by strong bases affording the previously known $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$ (**4**). The reaction of **1** with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ affords $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuMeCN})]$ (**7**), whereas $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**) is obtained from the reaction of **4** with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]/[\text{NEt}_4]\text{Br}$. All the compounds have been spectroscopically characterized, their molecular structures determined by single crystal X-ray diffraction (SC-XRD) and investigated by means of DFT methods in selected cases, in order to confirm the hydride positions and to study the relative stability of possible isomers.

Introduction

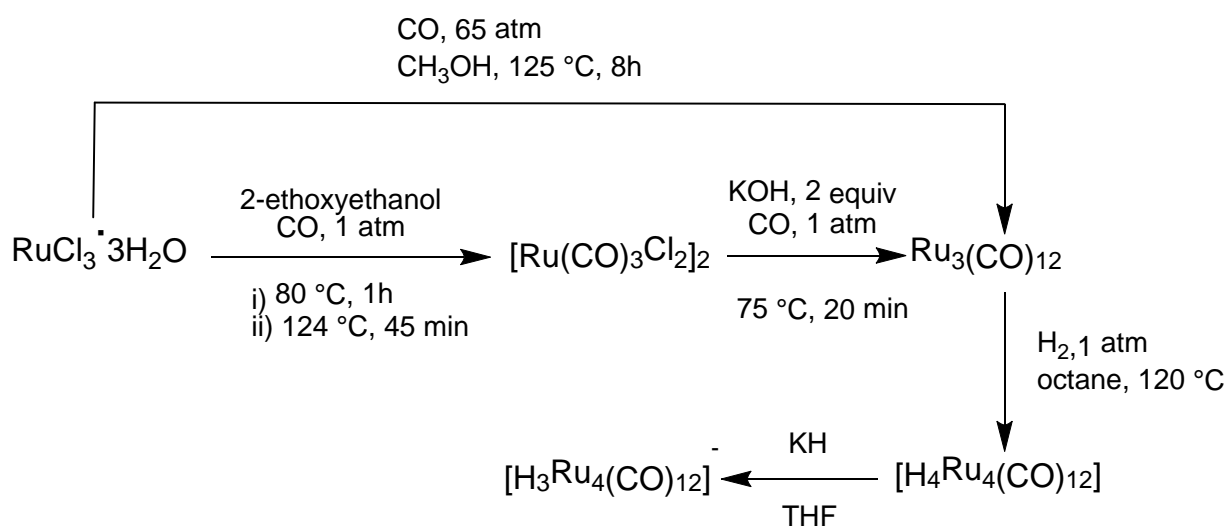
Metal hydrides play a fundamental role in chemistry,¹⁻⁷ and are widely investigated for applications in catalysis and hydrogen storage.⁸⁻¹⁰ In particular, ruthenium forms several hydride compounds, including coordination and organometallic complexes, molecular clusters and nanoclusters as well

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as Ru-H nanoparticles.¹¹⁻¹⁵ Ru hydride compounds are involved in several catalytic processes.¹⁵⁻²⁰ Moreover, molecular Ru-H complexes and clusters have been employed as models for the location of hydride ligands in Ru nanoparticles used in hydrogenation processes.^{21,22}

Structurally characterized Ru hydride carbonyl clusters include $[\text{HRu}_3(\text{CO})_{11}]^-$,²³ $[\text{HRu}_4(\text{CO})_{13}]^-$,²⁴ $\text{H}_2\text{Ru}_4(\text{CO})_{13}$,²⁵ $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$,²⁶ $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$,²⁷ $\text{H}_4\text{Ru}_4(\text{CO})_{12}$,²⁸ $[\text{HRu}_6(\text{CO})_{18}]^-$,²⁹ $\text{H}_2\text{Ru}_6(\text{CO})_{18}$,³⁰ $\text{H}_2\text{Ru}_6(\text{CO})_{17}$,³¹ $[\text{HRu}_7(\text{CO})_{20}]^-$,³² $[\text{H}_2\text{Ru}_8(\text{CO})_{21}]^{2-}$,³³ $[\text{H}_2\text{Ru}_{10}(\text{CO})_{25}]^{2-}$,³⁴ and $[\text{HRu}_{11}(\text{CO})_{27}]^{3-}$.³⁴ All of these hydride clusters have been obtained starting from $\text{Ru}_3(\text{CO})_{12}$ or other preformed Ru carbonyls, except $[\text{HRu}_3(\text{CO})_{11}]^-$ which can be directly obtained by reductive carbonylation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ under CO pressure.³⁵ In particular, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**1**) was originally obtained in a multistep synthesis that involved (Scheme 1): (1) carbonylation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ to give $\text{Ru}_3(\text{CO})_{12}$;³⁶⁻³⁸ (2) hydrogenation of $\text{Ru}_3(\text{CO})_{12}$ to give $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$;^{39,40} (3) deprotonation of $[\text{H}_4\text{Ru}_4(\text{CO})_{12}]$ to give **1**.⁴¹ Step (1) could be achieved by carbonylation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ under CO at high pressure or at atmospheric pressure. In the latter synthesis, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was reduced under CO (1 bar), first, to Ru(II) carbonyls by heating in 2-ethoxyethanol (1 h at 80 °C, 1 h at 124 °C). Then, 2 equivalents of KOH per mole of Ru were added and the mixture heated at 75 °C affording $\text{Ru}_3(\text{CO})_{12}$.³⁸



Scheme 1. Current multistep synthesis of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**1**).

Herein, we report an one-step synthesis at CO-atmospheric pressure of **1** which employs $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as starting material. The readily availability of **1** prompted the study of some of its

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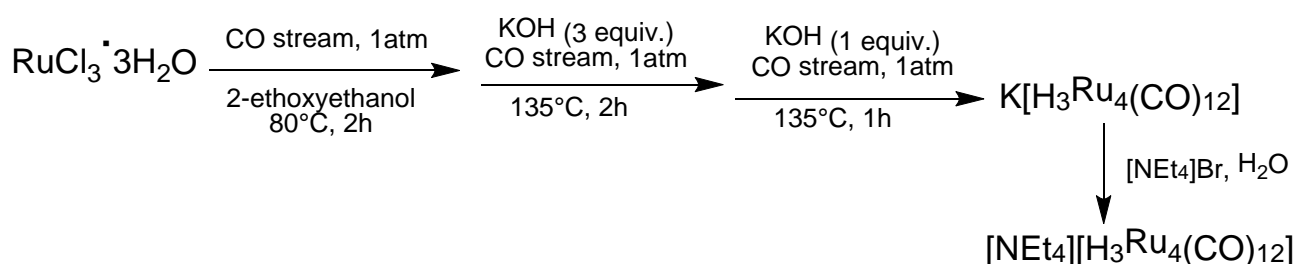
reactions, which resulted in the synthesis and structural characterization by single-crystal X-ray diffraction (SC-XRD) of the new hydride clusters $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuMeCN})]$ (**7**) and $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**).

Results and Discussion

One-pot synthesis of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**1**)

Seeking a direct synthesis of **1** from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ at atmospheric pressure, some modifications of the above mentioned synthesis of $\text{Ru}_3(\text{CO})_{12}$ were investigated.³⁸ In particular, the following parameters were systematically changed: 1) the amount of KOH added; 2) temperature; 3) reaction time. Several attempts were made in order to optimize these parameters, and the best conditions seemed to be the following (1 bar of CO, Scheme 2), which resulted in an overall yield of **1** based on $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ of 82%:

- 1) $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was heated at 80 °C in 2-ethoxyethanol for 2 h;
- 2) Three equivalents of KOH per mole of Ru were added and the temperature increased up to 135 °C (2 h);
- 3) An additional equivalent of KOH was added and the temperature maintained at 135 °C for 1 h resulting in the formation of a solution of $\text{K}[\mathbf{1}]$;
- 4) Upon filtration, $[\text{NEt}_4][\mathbf{1}]$ was precipitated by addition of a solution of $[\text{NEt}_4]\text{Br}$ in H_2O to the 2-ethoxyethanol solution of $\text{K}[\mathbf{1}]$.



Scheme 2. One-pot synthesis of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**1**).

As previously reported in the literature,^{38,42} during step (1) Ru(III) is reduced to Ru(II) carbonyls, which are further reduced to $\text{Ru}_3(\text{CO})_{12}$ upon addition of two equivalents of KOH. Addition of a total of four moles of KOH per mole of Ru in steps (2) and (3) results in the reduction of $\text{Ru}_3(\text{CO})_{12}$ to **1**. The reduction process is likely to occur through a well-known mechanism in organometallic chemistry, that is nucleophilic attack of OH^- to CO which is oxidized to CO_2 or

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CO_3^{2-} , depending on the total amount of base. Indeed, as reported in the next section, some carbonate-containing side products have been identified.

The nature of **1** was confirmed by comparison of its IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra with those reported in the literature.^{27,41} Moreover, the structure of the new salt $[\text{NEt}_4][\mathbf{1}]$ was determined by SC-XRD (Figure 1 and Table 1). The unit cell of $[\text{NEt}_4][\mathbf{1}]$ contains two independent molecules which differ for the location of the three hydride ligands. One molecule possesses an idealized C_{3v} symmetry and the other idealized C_2 symmetry. Both these isomers of **1** have been previously structurally characterized, but always as separate salts.²⁷ The present findings confirm that the two isomers are in equilibrium in solution, as also demonstrated by VT ^1H NMR studies reported in the literature.⁴¹

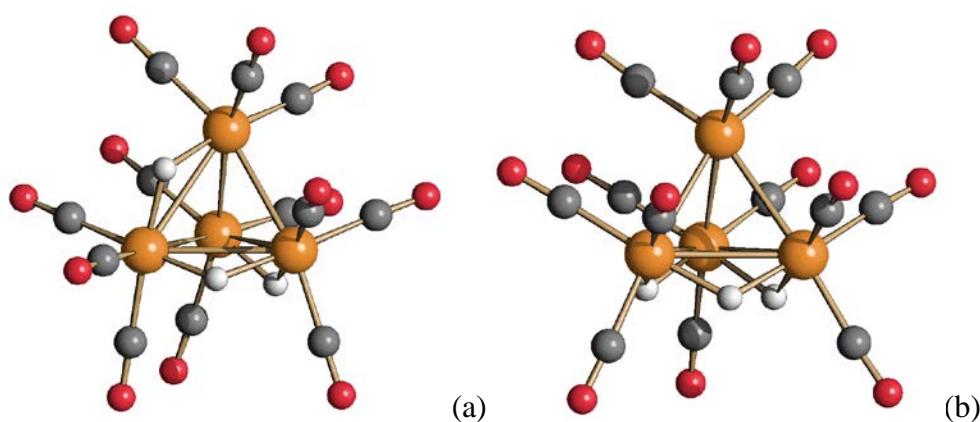


Fig. 1. Molecular structures of (a) the C_2 and (b) C_{3v} isomers of **1** as found in $[\text{NEt}_4][\mathbf{1}]$ (orange Ru; red O; grey C; white H).

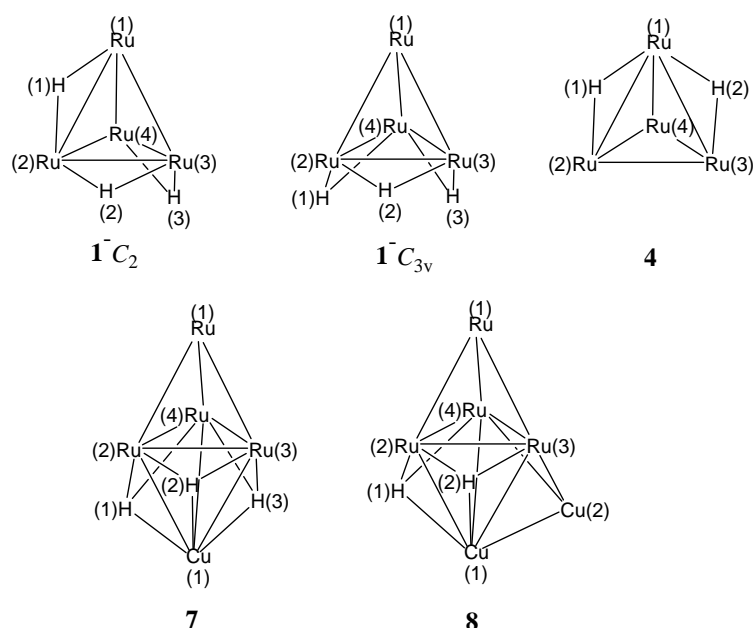
Table 1 Main bond distances (\AA) of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ (**1**) (C_2 and C_{3v} isomers), $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$ (**4**), $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuMeCN})]$ (**7**) and $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**). See Scheme 3 for labelling.

	1 (C_2 isomer)	1 (C_{3v} isomer)	4	7	8
Ru(1)-Ru(2)	2.9032(5)	2.7733(5)	2.9771(4)	2.7844(3)	2.776(4)
Ru(1)-Ru(3)	2.7871(5)	2.7753(5)	2.9558(4)	2.7938(3)	2.791(4)
Ru(1)-Ru(4)	2.7614(5)	2.7841(4)	2.8183(4)	2.7845(3)	2.777(4)
Ru(2)-Ru(3)	2.9423(4)	2.9380(5)	2.7735(4)	2.9469(3)	2.950(4)
Ru(2)-Ru(4)	2.7919(4)	2.9218(5)	2.7842(4)	2.9739(3)	2.958(4)
Ru(3)-Ru(4)	2.9167(5)	2.9191(4)	2.7526(4)	2.9489(3)	2.927(4)
Cu(1)-Ru(2)	-	-	-	2.7327(4)	2.781(5)
Cu(1)-Ru(3)	-	-	-	2.7421(4)	2.718(6)

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Cu(1)-Ru(4)	-	-	-	2.7110(4)	2.698(5)
Cu(2)-Ru(3)	-	-	-	-	2.619(5)
Cu(2)-Ru(4)	-	-	-	-	2.630(5)
Cu(1)-Cu(2)	-	-	-	-	2.590(6)
H(1)-Ru(1)	1.73(4)	-	1.71(4)	-	-
H(1)-Ru(2)	1.77(4)	1.75(4)	1.86(4)	1.70(3)	1.82(2)
H(1)-Ru(4)	-	1.83(4)	-	1.84(3)	1.82(2)
H(1)-Cu(1)	-	-	-	1.86(3)	2.02(2)
H(2)-Ru(2)	1.79(4)	1.74(4)	-	1.87(3)	1.82(2)
H(2)-Ru(3)	1.72(4)	1.76(4)	1.87(4)	1.81(3)	1.82(2)
H(2)-Ru(1)	-	-	1.64(4)	-	-
H(2)-Cu(1)	-	-	-	1.95(3)	2.02(2)
H(3)-Ru(3)	1.72(4)	1.72(4)	-	1.79(3)	-
H(3)-Ru(4)	1.80(4)	1.76(4)	-	1.87(3)	-
H(3)-Cu(1)	-	-	-	1.79(3)	-



Scheme 3. Labelling of **1** (C_2 and C_{3v} isomers), **4**, **7** and **8** (CO omitted for clarity).

The geometries of the two isomers of **1**, indicated as C_2 and C_{3v} in Table 1, were optimized by means of DFT calculations. The energy difference between the two species is negligible ($0.3 \text{ kcal mol}^{-1}$), in agreement with the experimental outcomes. The search for other possible isomers indicated that one hydride can adopt μ_3 coordination mode, affording the isomer with approximate

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C_s symmetry depicted in Figure 2. The energy of such a species is closely comparable to the values obtained for the other two isomers. The experimentally observed hydride migration is perhaps related to the change of hydride coordination mode from μ_2 to μ_3 and *vice versa*.⁴¹ No stable stationary points were instead found for isomers with two μ_3 -H ligands, all the attempts affording the previously described species as stable minima. Finally, the inclusion of one hydride inside the $\{Ru_4\}$ tetrahedral cavity caused the rise of the relative energy by more than 18 kcal mol⁻¹, therefore isomers with interstitial hydrides can be ruled out. The DFT-optimized geometry of the most stable species optimized with μ_4 -H is reported in Figure S12 in the ESI.

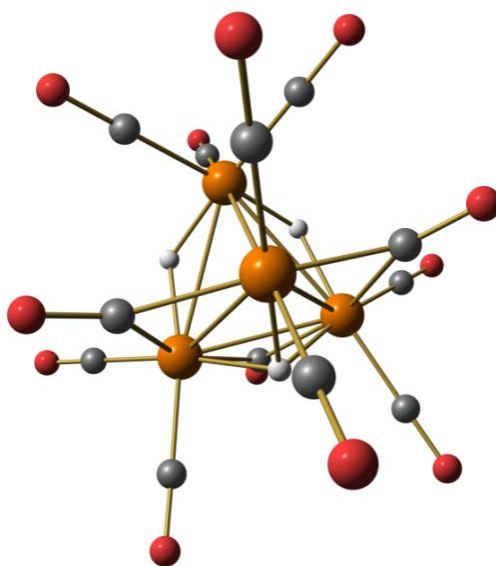


Fig. 2. DFT-optimized structure of the 1- C_s isomer with one μ_3 -H (orange Ru; red O; grey C; white H).

Synthesis and characterization of $[Ru_8(CO)_{16}(X)_4(CO_3)_4]^{4-}$ ($X = Cl, Br, I$) (2-X) and $[Ru_{10}(CO)_{20}(Br)_4(CO_3)_4]^{2-}$ (3)

The synthesis of $[NEt_4][1]$ was accompanied by the formation of a side-product, which was separated from $[NEt_4][1]$ on the basis of their different solubility in organic solvents. Thus, $[NEt_4][1]$ was extracted in CH_2Cl_2 , whereas the side-product was soluble in acetone. The amount of this side-product increased upon adding all the four equivalents of KOH just in one step, instead of two steps as for the optimized synthesis of $[NEt_4][1]$. Diffusion of n-hexane on the acetone solution afforded crystals of $K_2[NEt_4]_2[Ru_8(CO)_{16}(Br)_4(CO_3)_4] \cdot 5CH_3COCH_3$,

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$K_2[NEt_4]_3[Ru_8(CO)_{16}(Br)_4(CO_3)_4][Br] \cdot 4CH_3COCH_3$ or
 $[NEt_4]_4[Ru_8(CO)_{16}(Br)_4(CO_3)_4] \cdot 2CH_3COCH_3$ depending on the crystallization conditions. All these salts contain the same $[Ru_8(CO)_{16}(Br)_4(CO_3)_4]^{4-}$ (**2-Br**) anion, which closely resembles to $[Ru_8(CO)_{16}(Cl)_4(CO_3)_4]^{4-}$ (**2-Cl**), previously reported as $Na_2[NEt_4]_2[2-Cl] \cdot 2CH_3COCH_3 \cdot 0.5CH_3CH_2OH \cdot 1.5H_2O$ salt.⁴³ The presence of Br instead of Cl is due to the use of $[NEt_4]Br$ for precipitation. Indeed, by employing $[NEt_4]Cl$ or $[NEt_4]I$ instead of $[NEt_4]Br$, the salts $K_2[NEt_4]_2[2-Cl] \cdot 3MeCN$ and $[NEt_4]_4[2-I] \cdot 4CH_3COCH_3$ were obtained, respectively. Conversely, by using $[NBu_4]Br$ for precipitation, crystals of $K_2[NBu_4]_2[2-Br] \cdot 4CH_3COCH_3$ were obtained.

As described in the previous Section, Ru(III) is initially reduced to Ru(II), and, then, Ru(II) is reduced to Ru(0) after the addition of KOH. Further increasing the amount of the base, eventually results in **1**, which formally contains Ru(-1). It may be that part of Ru(II) is reduced to Ru(I) and, in the presence of an excess of CO_3^{2-} ions, this is transformed into **2-Cl**, as reported in the literature.⁴³ Because of the stability of this complex, the Ru(I) ions trapped in such compound are not further reduced. CO_3^{2-} ions are formed by the reaction of the CO_2 molecules produced by CO oxidation, and the OH^- ions. Thus, adding all the KOH at once favours the formation of CO_3^{2-} and, as a consequence, more **2-Cl** is obtained as side product. Then, metathesis of the halide ions takes place during precipitation resulting in **2-X**.

The anions **2-X** display the same structure composed of four $\{Ru_2(CO)_4\}^{2+}$ units which are joined by four $\mu-X^-$ ligands and four CO_3^{2-} anions (Figure 3). Each CO_3^{2-} anion is bonded to two $\{Ru_2(CO)_4\}^{2+}$ units *via* its three O-atoms. Among these, one O-atom is bonded to two Ru-atoms, whereas the other two oxygens of each CO_3^{2-} are bonded to a single Ru each. These two O-atoms can be, then, used to further coordinate K^+ ions, as found in the structures of $K_2[NEt_4]_2[2-Br] \cdot 5CH_3COCH_3$, $K_2[NEt_4]_3[2-Br][Br] \cdot CH_3COCH_3$, $K_2[NBu_4]_2[2-Br] \cdot 4CH_3COCH_3$ and $K_2[NEt_4]_2[2-Br] \cdot 6MeCN \cdot solv.$

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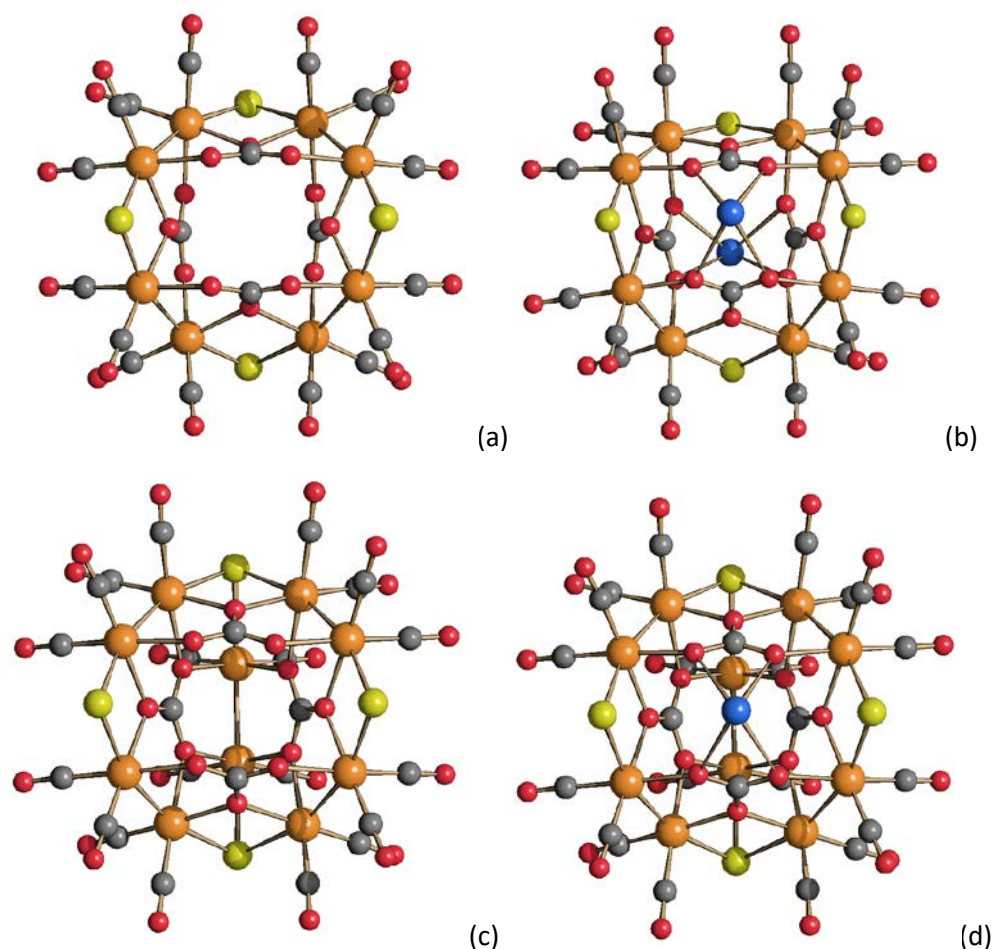
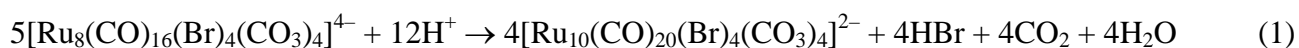


Fig. 3. Molecular structures of (a) $[\text{Ru}_8(\text{CO})_{16}(\text{X})_4(\text{CO}_3)_4]^{4-}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (**2-X**), (b) the $\{\text{K}_2[\text{Ru}_8(\text{CO})_{16}(\text{Br})_4(\text{CO}_3)_4]\}^{2-}$ unit present in the structure of $\text{K}_2[\text{NEt}_4]_2[\text{2-Br}] \cdot 5\text{CH}_3\text{COCH}_3$, (c) $[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]^{2-}$ (**3**) and (d) the $\{\text{K}[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]\}^-$ unit present in the structure of $\text{K}[\text{NEt}_4]_3\{[\text{3}]_2\}$ (orange Ru; yellow X; blue K; red O; grey C).

2-Br is transformed into $[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]^{2-}$ (**3**) upon reaction with an excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ (equation 1):



3 has been structurally characterized by SC-XRD as $\text{K}[\text{NEt}_4]_3\{[\text{3}]_2\}$ salt. The **3** anion is composed of five $\{\text{Ru}_2(\text{CO})_4\}^{2+}$ units which are joined by two $\mu\text{-Br}^-$, two $\mu_3\text{-Br}^-$ ligands and four CO_3^{2-} anions (Figure 3). Within the crystal structure of $\text{K}[\text{NEt}_4]_3\{[\text{3}]_2\}$, two **3** anions are coordinated to a K^+ cation resulting in a $\{\text{K}[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]_2\}^{3-}$ unit (Figure 4).

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The structure of **3** formally arises from that of **2-Br** by adding a fifth $\{\text{Ru}_2(\text{CO})_4\}^{2+}$ unit *via* four O-atoms of two CO_3^{2-} ligands. The other two CO_3^{2-} ligands are, then, employed to bind the K^+ cation. Overall, the **2-X** anions can be viewed as multidentate ligands, due to the presence of eight O-atoms, four on each side of the molecule, belonging to the four CO_3^{2-} anions, which can be used to coordinate K^+ ions or $\{\text{Ru}_2(\text{CO})_4\}^{2+}$ units. The addition of two of the latter units would eventually result in a purported neutral $[\text{Ru}_{12}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]$ species.

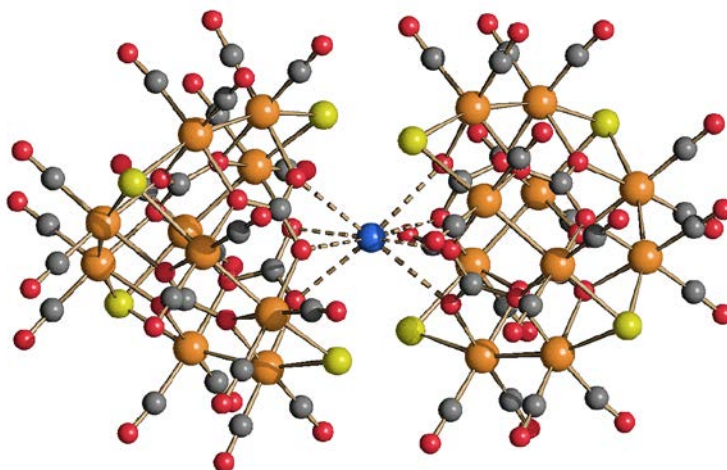


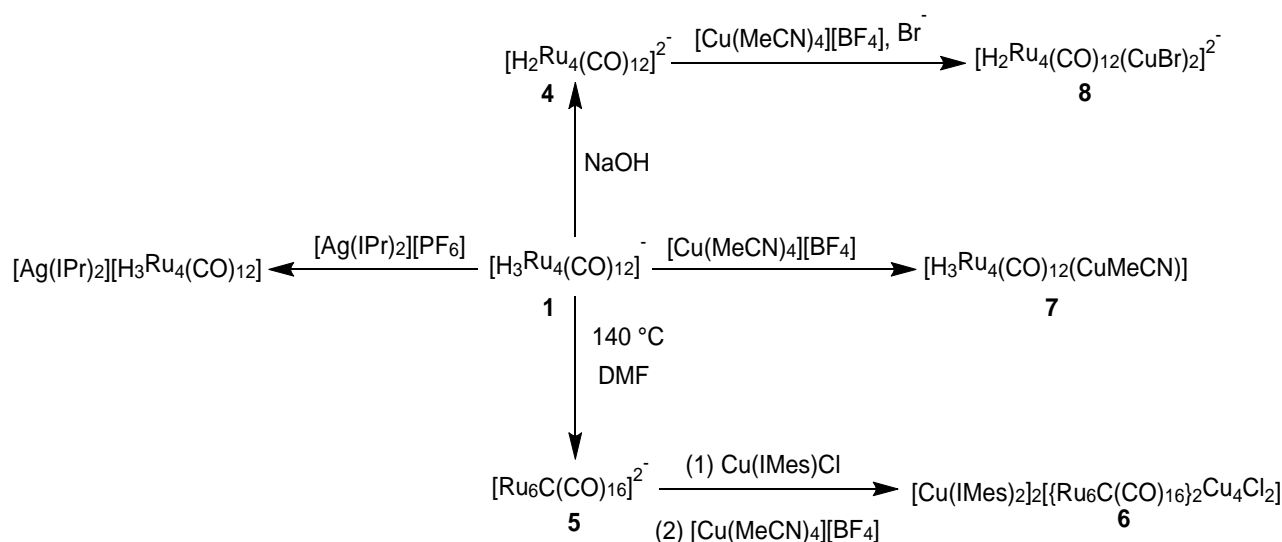
Fig. 4. Molecular structure of the $\{\text{K}[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]_2\}^{3-}$ unit present in $\text{K}[\text{NEt}_4]_3\{\mathbf{3}\}_2$ (orange Ru; yellow Br; blue K; red O; grey C).

Synthesis and molecular structures of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuMeCN})]$ (**7**) and $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**)

As previously reported, **1** can be deprotonated to $[\text{H}_2\text{Ru}_4(\text{CO})_{12}]^{2-}$ (**4**) by Na/naphtalene in DMF or NaOH in DMSO (Scheme 4).²⁶ The nature of **4** has been further confirmed by SC-XRD analyses of the new $[\text{NEt}_4]_2[\mathbf{4}]$ salt (Figure S11 in ESI).

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Scheme 4. Reactions of **1**.

Moreover, **1** is transformed into $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ (**5**) upon thermal treatment at 140 °C in DMF. **5** does not react with Cu(IMes)Cl, whereas the salt $[\text{Cu}(\text{IMes})_2]_2[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_4\text{Cl}_2] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{solv}$ ($[\text{Cu}(\text{IMes})_2]_2[\mathbf{6}] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{solv}$) is obtained upon treatment with Cu(IMes)Cl and $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$. The molecular structures of these products have been determined as their $[\text{NEt}_4]_2[\mathbf{5}] \cdot \text{CH}_2\text{Cl}_2$ and $[\text{Cu}(\text{IMes})_2]_2[\mathbf{6}] \cdot \text{CH}_2\text{Cl}_2 \cdot \text{solv}$ salts (Figure 5). The cluster anions **5** and $[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_4\text{Cl}_2]^{2-}$ (**6**) have been previously reported and, therefore, they will not be discussed any further.^{44,45}

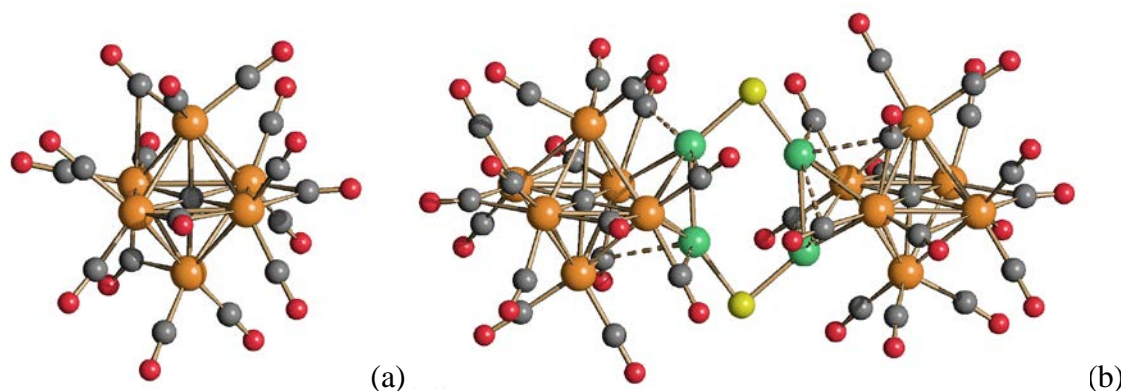


Fig. 5. Molecular structures of (a) $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ (**5**) and (b) $[\{\text{Ru}_6\text{C}(\text{CO})_{16}\}_2\text{Cu}_4\text{Cl}_2]^{2-}$ (**6**) (orange Ru; green Cu; yellow Cl; red O; grey C).

The neutral $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuMeCN})]$ (**7**) cluster was obtained from the reaction of **1** with $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$. Performing a similar reaction starting from **4** in the presence of Br^- ions

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resulted in the dianion $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**). Conversely, the reaction of **1** with $[\text{Ag}(\text{IPr})_2][\text{PF}_6]$ resulted simply in a metathesis reaction which afforded the salt $[\text{Ag}(\text{IPr})_2][\text{1}]\cdot\text{solv}$. All the new compounds have been spectroscopically characterized and their molecular structures determined by SC-XRD as their **7**, $[\text{NEt}_4]_2[\text{8}]$, and $[\text{Ag}(\text{IPr})_2][\text{1}]\cdot\text{solv}$ salts. In addition, crystals of $[\text{NEt}_4]_2[\text{H}_2\text{Ru}_{12}(\text{CO})_{34}\text{Cu}_6\text{Br}_2]\cdot\text{solv}$ ($[\text{NEt}_4]_2[\text{9}]\cdot\text{solv}$) were obtained as side product during the synthesis of **7**. The two compounds were separated owing to their different solubility in organic solvents. Thus, **7** was extracted in toluene, whereas $[\text{NEt}_4]_2[\text{9}]\cdot\text{solv}$ was extracted in acetone. $[\text{Ag}(\text{IPr})_2][\text{1}]\cdot\text{solv}$ and $[\text{NEt}_4]_2[\text{9}]\cdot\text{solv}$ contain the clusters **1** and $[\text{H}_2\text{Ru}_{12}(\text{CO})_{34}\text{Cu}_6\text{Br}_2]^{2-}$ (**9**) (Figure 6) which were previously described in the literature and, thus, they will not be discussed any further.^{27,46} The position of the hydrides inside $\{\text{Ru}_6\}$ cages was corroborated by DFT calculations on the **9** anion, carried out on a model with imposed C_2 symmetry, the axis crossing the two bromine atoms. The RMSD between experimental and computed geometries is only 0.076 Å.

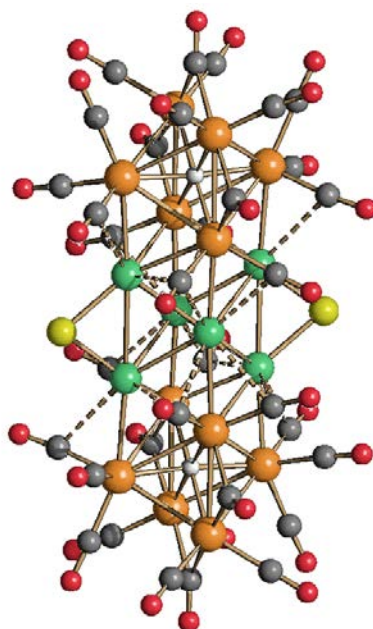


Fig. 6. Molecular structure of $[\text{H}_2\text{Ru}_{12}(\text{CO})_{34}\text{Cu}_6\text{Br}_2]^{2-}$ (**9**) (orange Ru; green Cu; yellow Br; red O; grey C; white H).

The molecular structure of **7** (Figure 7 and Table 1) closely resembles those previously reported for $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuPMePh}_2)]$ ⁴⁷ and $[\{\text{H}_3\text{Ru}_4(\text{CO})_{12}\}_2\text{Cu}_2(\text{dppe})]$.⁴⁸ It consists of a Ru_4 tetrahedron capped on a triangular face by a $\mu_3\text{-}\{\text{CuMeCN}\}^+$ fragment. Each Ru atoms is bonded to three terminal CO ligands, and the three hydrides are μ_3 -coordinated on the CuRu_2 triangular faces

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of the CuRu₃ tetrahedron. Alternatively, **7** may be viewed as a trigonal bipyramid with Cu in an apical position. The Ru-Ru bonding contacts involving the unique apical Ru atom [2.7844(3)-2.7938(3) Å] are significantly shorter than those of the equatorial Ru₃ triangle [2.9469(3)-2.9739(3) Å]. This is in keeping with the presence of three bridging hydride ligands on the equatorial Ru₃ triangle.

In agreement with the solid state structure, the ¹H NMR spectrum of **7** shows one singlet in the hydride region at -17.58 ppm, and a singlet at 2.32 ppm due to the MeCN ligand.

7 possesses 72 cluster valence electrons (CVE) [3×1 (3H) + 4×8 (4Ru) + 12×2 (12CO) + 1×11 (1Cu) + 2×1 (MeCN)] in agreement with the Effective Atomic Number rule (EAN) for a TBP cluster.⁴⁹⁻⁵¹

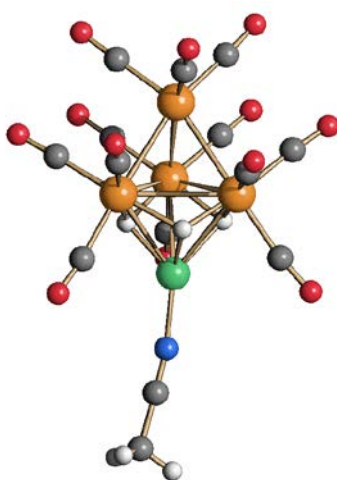


Fig. 7. Molecular structure of [H₃Ru₄(CO)₁₂(CuMeCN)] (**7**) (orange Ru; green Cu; blue N; red O; grey C; white H).

The molecular structure of **8** (Figure 8) can be formally originated from that of **7** by replacing {CuMeCN}⁺ with one CuBr unit, and one hydride with the second CuBr unit without altering the stereochemistry of the other ligands. Alternatively, **8** may be viewed as composed of a trigonal bipyramidal Ru₄Cu core with the two hydrides and the second Cu capping the three CuRu₂ triangular faces of the CuRu₃ tetrahedron. As a consequence, a cuprophilic Cu...Cu contact is present [2.590(6) Å].⁵² Several neutral clusters of the type [H₂Ru₄(CO)₁₂(ML)₂] (M = Cu, Ag, Au; L = PPh₃, PCy₃, P(CH₂Ph)₃, P(o-C₆H₄CH₃)₃) and [H₂Ru₄(CO)₁₂(M)₂(LL)] (M = Cu, Ag, Au; LL = Ph₂PCH₂PPh₂, Ph₂PCH₂CH₂PPh₂, Ph₂P(CH₂)₃PPh₂, Ph₂P(CH₂)₅PPh₂, Ph₂PCH₂CH₂AsPh₂, (C₅H₄PPh₂)₂Fe) are known,⁵³⁻⁵⁵ and most of them present structures very similar to that of **8**. Only

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in the case of $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuPCy}_3)_2]$ and $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuP}(\text{CH}_2\text{Ph})_3)_2]$ the two CuL fragments display a different coordination, that is one μ_3 -bonded to a triangular face of the Ru_4 tetrahedron and the second one μ -coordinated to an edge of the tetrahedron without any cuprophilic contact.⁵⁶

8 possesses 84 CVE [2×1 (2H) + 4×8 (4Ru) + 12×2 (12CO) + 2×11 (2Cu) + 2×1 (Br) + 2 (charge)] as expected for a TBP cluster capped on a triangular face on the basis of the EAN rule.⁵⁷

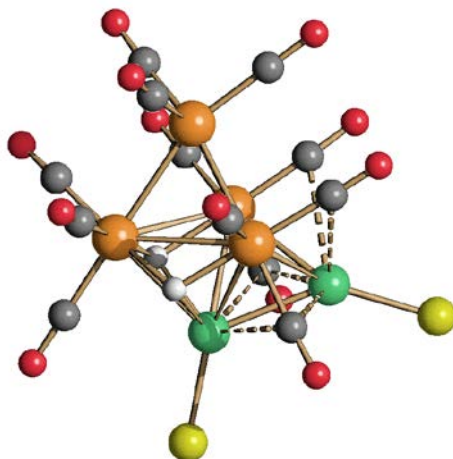


Fig. 8. Molecular structure of $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**) (orange Ru; green Cu; yellow Br; red O; grey C; white H).

The localization of the hydrides in **7** and **8** was confirmed by DFT calculations. In both the clusters the coordination mode is μ_3 -H and involves CuRu_2 faces, but AIM and Mayer analyses indicated that the Ru-H interactions are stronger than the Cu-H ones. This would suggest the unsymmetrical face-bridge model described by Park et al.⁵⁸ for polycopper hydrides, but the fact that the "triangle" in the present case is Ru_2Cu rather than Cu_3 makes any consideration on observed M-H distances more complicated. The properties at M-H bond critical points and the computed M-H bond orders are slightly different between the two clusters. In **7**, the Ru-H interactions are weaker with respect to **8**, while the opposite trend was observed for Cu-H bonds. The differences are perhaps in part related to the global charge of the complexes, the negative charge of **8** favouring the Ru-H interactions. Moreover, it seems that the hydride ligands have stronger interactions with more electron-poor copper fragments. Selected data are summarized in Table 2.

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Table 2. Selected AIM (a.u.) and Mayer data for $[\text{H}_3\text{Ru}_4(\text{CO})_{12}(\text{CuMeCN})]$ (**7**) and $[\text{H}_2\text{Ru}_4(\text{CO})_{12}(\text{CuBr})_2]^{2-}$ (**8**)

	$\rho_{\text{Ru-H}}$ average	$V_{\text{Ru-H}}$ average	$\text{BO}_{\text{Ru-H}}$ average	$\rho_{\text{Cu-H}}$ average	$V_{\text{Cu-H}}$ average	$\text{BO}_{\text{Cu-H}}$ average
7	0.074	-0.085	0.351	0.050	-0.056	0.159
8	0.077	-0.087	0.369	0.042	-0.041	0.108

Conclusions

In summary, it has been shown that **1** can be obtained with a straightforward one-pot synthesis starting from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and operating at CO atmospheric pressure with an overall yield of 82%, rather than using the multistep synthesis previously reported in the literature.³⁶⁻⁴¹ The atmospheric pressure reductive carbonylation procedure herein described results from the optimization of the $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}/\text{KOH}$ ratio as well as reaction time and temperatures. At the end of the reaction, **1** can be precipitated as $[\text{NEt}_4]^+$ salt, but also other organic cations can be employed following a similar procedure. Formation of **1** is accompanied by **2-X** as side product, and the two compounds are separated on the basis of their different solubility in organic solvents. The amount of **2-X** depends on the reaction conditions and, in general, its formation is favoured by adding KOH just in one step rather than two-steps as in the optimized synthesis of **1**.

Since ruthenium hydrides are very important for fundamental and applicative purposes,¹¹⁻²² the readily availability of **1** might promote further studies. Indeed, **1** can be used for the preparation of new homo and heterometallic polyhydride carbonyl clusters, the preparation of heteroleptic complexes for catalytic applications, or as precursor for Ru nanoparticles. As an example, it has been herein reported that the reactions of **1** with copper complexes lead to the synthesis of heterometallic polyhydride clusters such as **7** and **8**.

Experimental

General procedures.

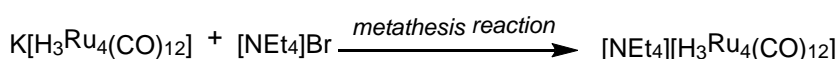
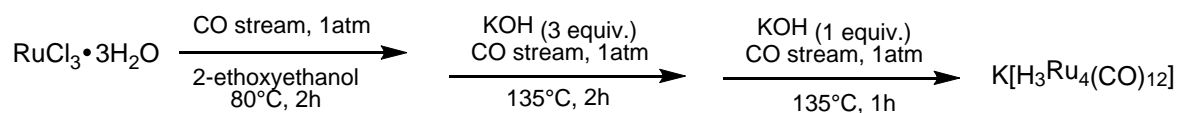
All reactions and sample manipulations were carried out using standard Schlenk techniques under nitrogen and in dried solvents. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. Analyses of C, H and N were obtained with a Thermo Quest Flash EA 1112NC instrument. IR spectra were recorded on a Perkin Elmer Spectrum One interferometer in CaF_2 cells. ^1H , and $^{13}\text{C}\{^1\text{H}\}$ NMR measurements were performed on a Varian

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Mercury Plus 400 MHz instrument. The proton and carbon chemical shifts were referenced to the non-deuterated aliquot of the solvent. Structure drawings have been performed with SCHAKAL99.⁵⁹

One-Pot Synthesis of [NEt₄][H₃Ru₄(CO)₁₂] (1) from RuCl₃·3H₂O



RuCl₃·3H₂O (1.50 g, 5.73 mmol) and 2-ethoxyethanol (70 mL) were introduced in a 500 mL flask. The solution was deaerated by stirring under reduced pressure for a few minutes then, connected to reflux condenser and filled with CO gas. The temperature was first raised to 80°C and the mixture was stirred vigorously under a fast CO stream for 2h, during which the colour of the solution progressively turned red. After that, the temperature was increased up to 135°C and 3 equivalents of KOH (0.966 g, 17.2 mmol) were added to the solution. After 2h at reflux, one more equivalent of KOH (0.322 g, 5.73 mmol) was added and the mixture was stirred under CO atmosphere at 135°C for another hour. The colour of the solution appeared orange red with a brown solid on the bottom of the flask. The solid was eliminated by filtration. Metathesis of K[1] with [NEt₄]Br in H₂O generates [NEt₄][1] that, after washing with H₂O (3×20 mL) and toluene (20 mL), was extracted in CH₂Cl₂ (15 mL)*. Crystals of [NEt₄][1] suitable for SC-XRD were obtained by slow diffusion of *n*-hexane on the CH₂Cl₂ solution (yield 1.16 g, 82% based on Ru).

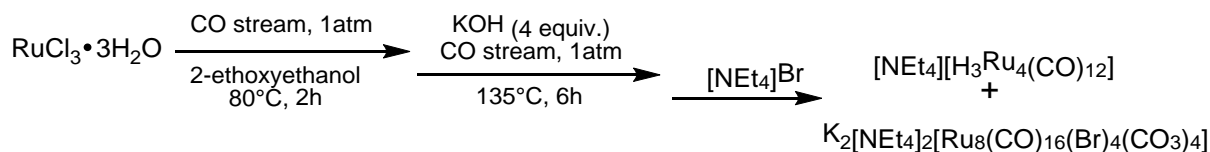
C₂₀H₂₃NO₁₂Ru₄ (873.67): calcd. (%): C 27.49, H 2.65, N 1.60; found: C 27.71, H 2.33, N 1.87. IR (CH₂Cl₂, 298 K) ν_{CO}: 2036(s), 2016(s), 1997(vs), 1975(m) cm⁻¹. ¹H NMR (acetone-d₆, 298 K) δ: -17.06 ppm. ¹³C{¹H} NMR (acetone-d₆, 298 K) δ: 198.4 ppm.

* The residue not soluble in CH₂Cl₂ was extracted in acetone and crystals of K₂[NEt₄]₂[Ru₈(CO)₁₆(Br)₄(CO₃)₄]·5 CH₃COCH₃ were obtained by slow diffusion of *n*-hexane. IR (acetone, 298 K) ν_{CO}: 2020(vs), 1975(w), 1945(s), 1902(w) cm⁻¹.

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Synthesis of $\text{K}_2[\text{NEt}_4]_2[\text{Ru}_8(\text{CO})_{16}(\text{Br})_4(\text{CO}_3)_4]$ (**2-Br**)

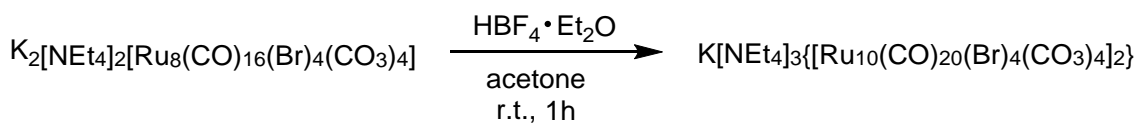


$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1.50 g, 5.73 mmol) and 2-ethoxyethanol (70 mL) were introduced in a 500 mL flask. The solution was deaerated by stirring under reduced pressure for a few minutes then, connected to reflux condenser and filled with CO gas. The temperature was first raised to 80°C and the mixture was stirred vigorously under a fast CO stream for 2h, during which the colour of the solution progressively turned red. After that, the temperature was increased up to 135°C and 4 equivalents of KOH (1.28 g, 22.9 mmol) were added to the solution. After 4h at reflux the colour of the solution appeared deep red with a brown solid on the bottom of the flask. The solid was eliminated by filtration. A saturated solution of $[\text{NEt}_4]\text{Br}$ in H_2O was added to the mixture and the obtained precipitate was isolated by filtration and washed with H_2O (3×20 mL) and toluene (20 mL). $[\text{NEt}_4][\mathbf{1}]$ was extracted in CH_2Cl_2 (15 mL) as described above. Then the residue was extracted in acetone (15 mL) and layered with *n*-hexane affording crystals of $\text{K}_2[\text{NEt}_4]_2[\mathbf{2-Br}] \cdot 5\text{CH}_3\text{COCH}_3$ suitable for SC-XRD* (yield 0.26 g, 15% based on Ru).

$\text{C}_{51}\text{H}_{70}\text{Br}_4\text{K}_2\text{N}_2\text{O}_{33}\text{Ru}_8$ (2445.49): calcd. (%): C 25.05, H 2.89, N 1.15; found: C 24.86, H 2.61, N 1.32. IR (acetone, 298 K) ν_{CO} : 2020(vs), 1975(w), 1945(s), 1902(w) cm^{-1} . IR (Nujol, 298 K) ν_{CO} : 2020(s), 1974(m), 1937(s), 1900(m) cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d^6 , 298 K) δ : 211.3, 210.6, 205.9, 205.7 (CO), 170.3 (CO_3^{2-}) ppm

* Depending on the crystallization conditions, sometimes crystals of $\text{K}_2[\text{NEt}_4]_3[\mathbf{2-Br}][\text{Br}] \cdot 4\text{CH}_3\text{COCH}_3$ or $[\text{NEt}_4]_4[\mathbf{2-Br}] \cdot 2\text{CH}_3\text{COCH}_3$ were obtained instead of $\text{K}_2[\text{NEt}_4]_2[\mathbf{2-Br}] \cdot 5\text{CH}_3\text{COCH}_3$. If $[\text{NBu}_4]\text{Br}$ is used for precipitation instead of $[\text{NEt}_4]\text{Br}$, crystals of $\text{K}_2[\text{NBu}_4]_2[\mathbf{2-Br}] \cdot 4\text{CH}_3\text{COCH}_3$ suitable for SC-XRD are obtained. If $[\text{NEt}_4]\text{Cl}$ is used for precipitation instead of $[\text{NEt}_4]\text{Br}$, crystals of $\text{K}_2[\text{NEt}_4]_2[\mathbf{2-Cl}] \cdot 3\text{MeCN}$ suitable for SC-XRD are obtained. If $[\text{NEt}_4]\text{I}$ is used for precipitation instead of $[\text{NEt}_4]\text{Br}$, crystals of $[\text{NEt}_4]_4[\mathbf{2-I}] \cdot 4\text{CH}_3\text{COCH}_3$ suitable for SC-XRD are obtained.

Synthesis of $\text{K}[\text{NEt}_4]_3\{[\text{Ru}_{10}(\text{CO})_{20}(\text{Br})_4(\text{CO}_3)_4]_2\}$ (**3**)



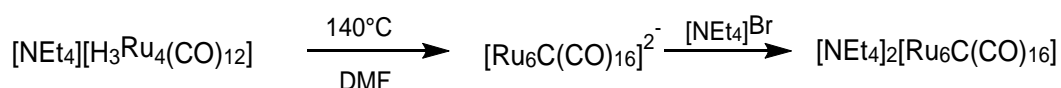
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An excess of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ was added in small portions (80 μL each time) to a solution of $\text{K}_2[\text{NEt}_4]_2[\mathbf{2}\text{-Br}]$ (0.320 g, 0.148 mmol) in acetone and the reaction monitored by IR spectroscopy. The resulting mixture was stirred at room temperature for 1h and then, the solvent removed under reduced pressure. The residue was washed with H_2O (2×10 mL), toluene (10 mL), CH_2Cl_2 (10 mL) and extracted in acetone (15 mL). The acetone solution was layered with n-hexane affording crystals of $\text{K}[\text{NEt}_4]_3\{\mathbf{3}\}_2$ suitable for SC-XRD (yield 0.14 g, 48% based on Ru).

$\text{C}_{39}\text{H}_{36}\text{Br}_4\text{K}_{0.5}\text{N}_{1.5}\text{O}_{33}\text{Ru}_{10}$ (2403.58): calcd. (%): C 19.49, H 1.51, N 0.87; found: C 19.68, H 1.27, N 1.01. IR (acetone, 298 K) ν_{CO} : 2063(w), 2040(vs), 1970(s) cm^{-1} . IR (Nujol, 298 K) ν_{CO} : 2036(s), 1975(ms), 1948(m) cm^{-1} . $^{13}\text{C}\{^1\text{H}\}$ NMR (acetone- d_6 , 298 K) δ : 206.8, 205.9, 203.8, 203.4, 202.9, 202.8, 201.7, 201.4 (CO), 171.3 (CO_3^{2-}) ppm.

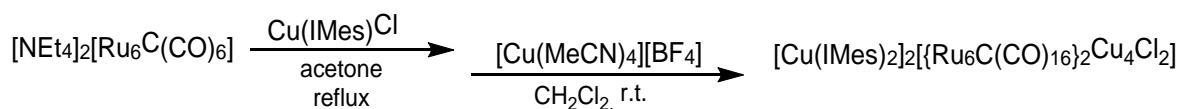
Synthesis of $[\text{NEt}_4]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$ (**5**)



A solution of $[\text{NEt}_4][\mathbf{1}]$ (0.300 g, 0.343 mmol) in 10 mL of DMF was heated at 140°C for 5h, and the reaction monitored by IR spectroscopy. Then, a saturated solution of $[\text{NEt}_4]\text{Br}$ in H_2O (40 mL) was added to complete precipitation. The resulting solid was recovered by filtration, washed with H_2O (3×15 mL) and toluene (15 mL), then extracted in CH_2Cl_2 (10 mL). Crystals of $[\text{NEt}_4]_2[\mathbf{5}] \cdot \text{CH}_2\text{Cl}_2$ suitable for SC-XRD were obtained by layering n-pentane on the CH_2Cl_2 solution (yield 0.26 g, 15% based on Ru).

$\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{N}_2\text{O}_{16}\text{Ru}_6$ (1412.01): calcd. (%): C 28.92, H 3.00, N 1.98; found: C 29.08, H 2.77, N 2.11. IR (acetone, 298 K) ν_{CO} : 1977(vs) cm^{-1} .

Synthesis of $[\text{Cu}(\text{IMes})_2]_2\{[\text{Ru}_6\text{C}(\text{CO})_{16}]_2\text{Cu}_4\text{Cl}_2\}$ (**6**)



Solid $\text{Cu}(\text{IMes})\text{Cl}$ (0.152 g, 0.377 mmol) was added in small portions to a solution of $[\text{NEt}_4]_2[\mathbf{5}]$ (0.250 g, 0.188 mmol) in acetone. The reaction mixture was stirred at reflux temperature under nitrogen atmosphere and monitored by IR spectroscopy. No change in the IR spectrum was observed over 2h, thus the solvent was removed in vacuum and the residue dissolved in CH_2Cl_2 . At this point, 3 equivalents of $[\text{Cu}(\text{MeCN})_4][\text{BF}_4]$ (0.178 g, 0.565 mmol) were added in small portions

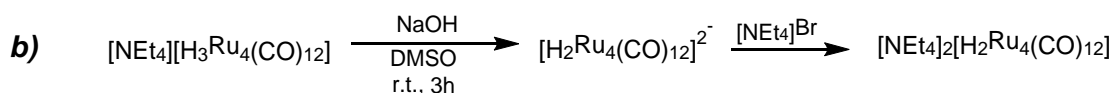
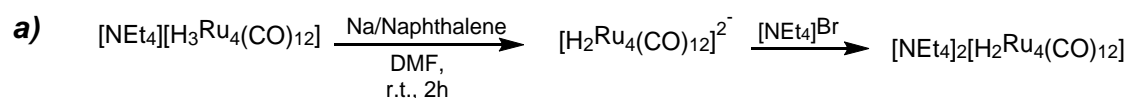
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to the mixture and stirred at room temperature for 2h. Then, the solvent was removed in vacuum and the residue washed with water (20 mL), toluene (10 mL), and extracted with CH₂Cl₂ (10 mL). The dichloromethane solution was layered with pentane affording crystals of [Cu(IMes)₂]₂[**6**]·CH₂Cl₂ suitable for SC-XRD (yield 0.12 g, 34% based on Ru).

C₁₁₉H₉₈Cl₄Cu₆N₈O₃₂Ru₁₂ (3887.93): calcd. (%): C 36.76, H 2.54, N 2.88; found: C 36.52, H 2.34, N 3.05. IR (CH₂Cl₂, 298 K) ν_{CO}: 2021(vs) cm⁻¹.

Synthesis of [NEt₄]₂[H₂Ru₄(CO)₁₂] (**4**)



Method (a)

[NEt₄][**1**] (0.300 g, 0.344 mmol) was dissolved in DMF (10 mL) under nitrogen atmosphere. A solution of Na/Naphthalene in DMF was added dropwise over 2h to the solution of the cluster. The reaction was monitored by IR spectroscopy until the IR spectrum corresponded to that of **4**. The crude product was precipitated by addition of a saturated solution of [NEt₄]Br in H₂O (40 mL) and the solid recovered by filtration, washed with H₂O (30 mL) and toluene (15 mL). The residue was dried under reduced pressure and extracted with acetone (15 mL).

Method (b)

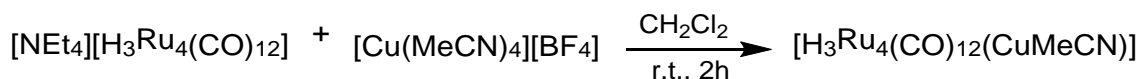
NaOH (0.500 g) was added as a solid to a solution of [NEt₄][**1**] (0.250 g, 0.286 mmol) in DMSO (10 mL), and the resulting mixture was stirred at room temperature for 3h. The crude product was precipitated by addition of a saturated solution of [NEt₄]Br in H₂O (40 mL) and the solid recovered by filtration, washed with H₂O (30 mL), and dried under reduced pressure. The orange solid was further washed with toluene (15 mL) and extracted with acetone (15 mL). The IR spectrum on the solution confirmed the formation of [NEt₄]₂[**4**] cluster (yield 0.21 g, 74% based on Ru).

C₂₈H₄₂N₂O₁₂Ru₄ (1002.91): calcd. (%): C 33.53, H 4.22, N 2.79; found: C 33.74, H 4.01, N 2.28. IR (CH₂Cl₂, 298 K) ν_{CO}: 2035(w), 1992(s), 1956(vs), 1750(m) cm⁻¹. ¹H NMR (acetone d⁶, 298 K) δ: -19.17 ppm.

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Synthesis of [H₃Ru₄(CO)₁₂(CuMeCN)] (7)

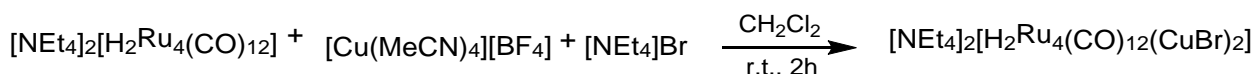


Solid [Cu(MeCN)₄][BF₄] was added in small portions (108 mg each time, 0.343 mmol) to a CH₂Cl₂ (20 mL) solution of [NEt₄][1] (0.300 g, 0.343 mmol). The mixture was stirred at room temperature under nitrogen for 30 min after each addition, and the reaction was monitored by FT-IR spectroscopy. After an overall addition of 3 equivalents of [Cu(MeCN)₄][BF₄], the solvent was removed in vacuum. The residue was washed with water (20 mL) and extracted with toluene (10 mL), and CH₂Cl₂ (10 mL). Crystals of 7 suitable for SC-XRD were obtained by layering pentane on the toluene solution (yield 0.15 g, 53% based on Ru).*

C₁₄H₆CuNO₁₂Ru₄ (848.02): calcd. (%): C 19.83, H 0.71, N 1.65; found: C 20.04, H 0.98, N 1.33. IR (CH₂Cl₂, 298 K) ν_{CO}: 2086(w), 2056(s), 2047(vs), 1997(m) cm⁻¹. ¹H NMR (acetone-d₆, 298 K) δ: -17.58 (hydride), 2.32 (MeCN) ppm. ¹³C{¹H} NMR (acetone-d₆, 298 K) δ: 194.9 (CO), 189.7 (CO), 118.2 (CN), 2.2 (CH₃) ppm.

* The residue not soluble in toluene was extracted in acetone and some crystals of [NEt₄]₂[H₂Ru₁₂(CO)₃₄Cu₆Br₂]·solv ([NEt₄]₂[9]·solv) were obtained after slow diffusion of n-hexane.

Synthesis of [NEt₄]₂[H₂Ru₄(CO)₁₂(CuBr)₂]·CH₂Cl₂ (8)



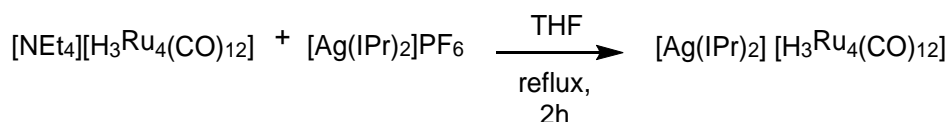
Solid [Cu(MeCN)₄][BF₄] was added in small portions (2 equivalents, 39 mg each time, 0.125 mmol) to a CH₂Cl₂ (20 mL) solution of [NEt₄]₂[4] (0.250 g, 0.249 mmol) and [NEt₄]Br (0.100 g, 0.477 mmol). The mixture was stirred at room temperature for 2h, and then the solvent was removed in vacuum. The residue was washed with water (20 mL) and toluene (10 mL), dried under reduced pressure, and then extracted with CH₂Cl₂ (15 mL). Crystals of [NEt₄]₂[8]·CH₂Cl₂ suitable for SC-XRD were obtained by layering n-pentane on the CH₂Cl₂ solution (yield 0.14 g, 41% based on Ru).

C₂₉H₄₄Br₂Cl₂Cu₂N₂O₁₂Ru₄ (1374.74): calcd. (%): C 25.34, H 3.23, N 2.04; found: C 25.11, H 3.58, N 1.85. IR (CH₂Cl₂, 298 K) ν_{CO}: 2053(w), 2017(s), 1998(s) cm⁻¹. ¹H NMR (acetone-d₆, 298 K) δ: -16.73 ppm.

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Synthesis of [Ag(IPr)₂][H₃Ru₄(CO)₁₂]



A solution of [Ag(IPr)₂][PF₆] (0.643 g, 0.585 mmol) in THF (5 mL) was added to a solution of [NEt₄][1] (0.170 g, 0.195 mmol) in THF (10 mL) over a period of 30 minutes. The resulting mixture was stirred at reflux temperature for 2h and then the solvent removed in vacuo. The residue was washed with water (20 mL), toluene (10 mL), and extracted with CH₂Cl₂ (10 mL). Crystals of [Ag(IPr)₂][1] suitable for SC-XRD were obtained by layering n-pentane on the CH₂Cl₂ solution (yield 0.26 g, 81% based on Ru).

C₆₆H₇₂AgN₄O₁₂Ru₄ (1625.42): calcd. (%): C 48.77, H 4.46, N 3.45; found: C 48.53, H 4.19, N 3.88. IR (CH₂Cl₂, 298 K) ν_{CO}: 2035(s), 2016(s), 1997(vs), 1977(m) cm⁻¹. ¹H NMR (acetone-d₆, 298 K) δ: -17.06 ppm.

X-ray Crystallographic Study.

Crystal data and collection details for [NEt₄][1], K₂[NEt₄]₂[2-Br]·5CH₃COCH₃, K₂[NEt₄]₃[2-Br][Br]·4CH₃COCH₃, [NEt₄]₄[2-Br]·2CH₃COCH₃, K₂[NBu₄]₂[2-Br]·4CH₃COCH₃, K₂[NEt₄]₂[2-Cl]·3MeCN, [NEt₄]₄[2-I]·4CH₃COCH₃, K[NEt₄]₃{[3]₂}, [NEt₄]₂[4], [Ag(IPr)₂][1]·solv, [NEt₄]₂[5]·CH₂Cl₂, [Cu(IMes)₂]₂[6]·CH₂Cl₂·solv, 7, [NEt₄]₂[8], and [NEt₄]₂[9]·solv are reported in Table S1 in the ESI. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON2 detector using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).⁶⁰ Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F².⁶¹ 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 2082095-2082104 and 2082111-2082115 contain the supplementary crystallographic data for this paper.

Computational details

Geometry optimizations of the clusters were performed in the gas phase using the range-separated hybrid DFT functional ωB97X.⁶² The basis set used was the Ahlrichs' def2 split-valence, with

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relativistic ECP for Ru.⁶³ The “restricted” approach was used in all the cases. The software used was Gaussian 09.⁶⁴ The output was used for AIM and Mayer analyses,⁶⁵ performed with the software Multiwfn, version 3.5.⁶⁶ Cartesian coordinates of the DFT-optimized structures are collected in a separated.xyz file.

ACKNOWLEDGMENTS

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References

- (1) J. R. Norton and J. R. Sowa, *Chem. Rev.*, 2016, **116**, 8315-8317.
- (2) (a) R. Bau and M. H. Drabnis, *Inorg. Chim. Acta*, 1997, **259**, 27-50; (b) G. G. Hlatky and R. H. Crabtree, *Coord. Chem. Rev.*, 1985, **65**, 1-48.
- (3) K. R. Brereton, N. E. Smith, N. Hazari and A. J. M. Miller, *Chem. Soc. Rev.*, 2020, **49**, 7929-7948.
- (4) R. E. Adams, T. A. Grusenmeyer, A. L. Griffith and R. H. Schmehl, *Coord. Chem. Rev.*, 2018, **362**, 44-53.
- (5) C. Sun, B. K. Teo, C. Deng, J. Lin, G.-G. Luo, C.-H. Tung and D. Sun, *Coord. Chem. Rev.*, 2021, **427**, 213576.
- (6) G. S. McGrady and G. Guilera, *Chem. Soc. Rev.*, 2003, **32**, 383-392.
- (7) M. Bortoluzzi, I. Ciabatti, C. Femoni, M. Hayatifar, M. C. Iapalucci, G. Longoni and S. Zacchini, *Angew. Chem. Int. Ed.*, 2014, **53**, 7233-7237.
- (8) A. Schneemann, J. L. White, S. Kang, S. Jeong, L. F. Wan, E. S. Cho, T. W. Heo, D. Prendergast, J. J. Urban, B. C. Wood, M. D. Allendorf and V. Stavila, *Chem. Rev.*, 2018, **118**, 10775-10839.
- (9) L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353-358.
- (10) S. L. Shevick, C. V. Wilson, S. Kotesova, D. Kim, P. L. Holland and R. A. Shenvi, *Chem. Sci.*, 2020, **11**, 12401-12422.
- (11) N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, 1997.
- (12) T. D. Humpries, D. A. Sheppard and C. E. Buckley, *Coord. Chem. Rev.*, 2017, **342**, 19-33.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

- (13) (a) L. M. Martínéz-Prieto, S. Carencó, C. H. Wu, E. Bonnefille, S. Axnanda, Z. Liu, P. F. Fazzini, K. Philippot, M. Salmeron and B. Chaudret, *ACS Catal.*, 2014, **4**, 3160-3168; (b) H.-H. Limbach, T. Pery, N. Rothermel, B. Chaudret, T. Gutmann and G. Buntkowsky, *Phys. Chem. Chem. Phys.*, 2018, **20**, 10697-10712.
- (14) L. M. Martínéz-Prieto and B. Chaudret, *Acc. Chem. Res.*, 2018, **51**, 376-384.
- (15) S. E. Clapham, A. Hadzovic and R. H. Morris, *Coord. Chem. Rev.*, 2004, **248**, 2201-2237.
- (16) (a) V. S. Marakatti and E. M. Gaigneaux, *ChemCatChem*, 2020, **12**, 5838-3857; (b) A. F. Abdel-Magied, Y. Theibich, A. K. Singh, A. Rahaman, I. Doverbratt, A. K. Raha, M. Haukka, M. G. Richmond and E. Nordlander, *Dalton Trans.*, 2020, **49**, 4244-4256.
- (17) M. Zaun, A. Goepfert, R. May, R. Haiges, G. K. S. Prakash and G. A. Olah, *ChemSusChem*, 2011, **4**, 1241-1248.
- (18) R. Noyori and T. Ohkuma, *Angew. Chem. Int. Ed.*, 2001, **40**, 40-73.
- (19) B. L. Conley, M. K. Pennington-Boggio, Emine Boz and T. J. Williams, *Chem. Rev.*, 2010, **110**, 2294-2312.
- (20) R. A. Farrar-Tobar, A. Dell'Acqua, S. Tin and J. G. de Vries, *Green. Chem.*, 2020, **22**, 3323-3357.
- (21) (a) I. del Rosal, T. Gutmann, B. Walaszek, I. C. Gerber, B. Chaudret, H.-H. Limbach, G. Buntkowsky and R. Poteau, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20199-20207; (b) T. Gutmann, I. del Rosal, B. Chaudret, R. Poteau, H.-H. Limbach and G. Buntkowsky, *ChemPhysChem*, 2013, **14**, 3026-3033.
- (22) T. Gutmann, B. Walaszek, X. Yeping, M. Wächtler, I. del Rosal, A. Grünberg, R. Poteau, R. Axet, G. Lavigne, B. Chaudret, H.-H. Limbach and G. Buntkowsky, *J. Am. Chem. Soc.*, 2010, **132**, 11759-11767.
- (23) (a) Y.-C. Liu, W.-Y. Yeh, G.-H. Lee and S.-M. Penn, *Organometallics*, 2003, **20**, 4163-4166, (b) F. Furno, T. Fox, M. Alfonso and H. Berke, *Eur. J. Inorg. Chem.*, 2001, 1559-1565; (c) J. A. Cabeza, M. Damonte, P. Garcíá-Álvarez and E. Pérez-Carreño, *Chem. Commun.*, 2013, **49**, 2813-2815.
- (24) (a) J. A. Jensen, D. E. Fjare and W. L. Gladfelter, *Inorg. Chem.*, 1983, **22**, 1250-1253; (b) S. V. Osintseva, N. A. Shtel'tser, A. S. Peregudov, A. Z. Kreindlin and F. M. Dolgushin, *Polyhedron*, 2018, **148**, 147-160.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

- (25) (a) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, 1972, **11**, 838-844; (b) J. D. Yang, X. Wang, C. X. Song, W. Q. Zhang, G. F. Zhang, Z. Gao, J. Fan and H. M. Sun, *Chem. Sel.*, 2016, **1**, 5397-5403.
- (26) (a) R. Suter, A. A. Bhattacharyya, L.-Y. Hsu, J. A. Krause Bauer and S. G. Shore, *Polyedron*, 1998, **17**, 2889-2897; (b) C. E. Ellul, J. P. Lowe, M. F. Mahon, P. R. Raithby and M. K. Whittlesey, *Dalton Trans.*, 2018, **47**, 4518-4523.
- (27) (a) M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1986, 1557-1563; (b) P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1978, 920-921; (c) C. E. Ellul, M. G. Mahon, O. Saker and M. K. Whittlesey, *Angew. Chem. Int. Ed.*, 2007, **46**, 6343-6345.
- (28) R. D. Wilson, S. M. Wu, R. A. Love and R. Bau, *Inorg. Chem.*, 1978, **17**, 1271-1280.
- (29) (a) C. R. Eady, B. F. G. Johnson, J. Lewis, M. C. Malatesta, P. Machin and M. McPartlin, *J. Chem. Soc., Chem. Commun.*, 1976, 945-946; (b) P. F. Jackson, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. McPartlin, W. J. H. Nelson, K. D. Rouse, J. Allibon and S. A. Mason, *J. Chem. Soc., Chem. Commun.*, 1980, 295-297.
- (30) M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, 1971, **93**, 5670-5677.
- (31) D. A. McCarthy, J. A. Krause and S. G. Shore, *J. Am. Chem. Soc.*, 1990, **112**, 8587-8589.
- (32) C. E. Housecroft, A. L. Rheingold and X. Song, *Inorg. Chem.*, 1992, **31**, 4023-4025.
- (33) T. Chihara, Y. Matsuura and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 1988, 886-887.
- (34) P. J. Bailey, M. A. Beswick, B. F. G. Johnson, J. Lewis, M. McPartlin, P. R. Raithby and M. C. Ramirez de Arellano, *J. Chem. Soc., Dalton Trans.*, 1996, 3515-3520.
- (35) A. Béguin, J. M. Soulié and J. Suss-Fink, *Inorg. Synth.*, 1998, **32**, 268-270.
- (36) M. I. Bruce, C. M. Jensen and N. L. Jones, *Inorg. Synth.*, 1989, **26**, 259-261.
- (37) A. Mantovani and S. Cenini, *Inorg. Synth.*, 1975, **16**, 47-48.
- (38) M. Fauré, C. Saccavini and G. Lavigne, *Chem. Commun.*, 2003, 1578-1579.
- (39) S. A. R. Knox, J. W. Koepke, M. A. Andrews and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3942-3947.
- (40) (a) M. I. Bruce and M. L. Williams, *Inorg. Synth.*, 1989, **26**, 262-263; (b) F. Piacenti, M. Bianchi, P. Frediani and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759-2763.
- (41) K. E. Inkrott and S. G. Shore, *Inorg. Chem.*, 1979, **18**, 2817-2821.
- (42) A. F. Hill, *Angew. Chem. Int. Ed.*, 2000, **39**, 130-133.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

- (43) L. Maurette, B. Donnadiou, G. Lavigne, *Angew. Chem. Int. Ed.* **1999**, *38*, 3707-3710.
- (44) (a) B. F. G. Johnson, J. Lewis, S. W. Sankey, K. Wong, M. McPartlin and W. J. H. Nelson, *J. Organomet. Chem.*, **1980**, *191*, C3-C7; (b) C.-M. T. Hayward and J. R. Shapley, *Inorg. Chem.*, **1982**, *21*, 3816-3820.
- (45) M. A. Beswick, J. Lewis, P. R. Raithby and M. C. R. de Arellano, *J. Chem. Soc., Dalton Trans.*, **1996**, 4033-4034.
- (46) M. A. Beswick, J. Lewis, P. R. Raithby and M. C. R. de Arellano, *Angew. Chem. Int. Ed.*, **1997**, *36*, 291-293.
- (47) R. A. Brice, S. C. Pearse, I. D. Salter and K. Henrick, *J. Chem. Soc., Dalton Trans.*, **1986**, 2181-2192.
- (48) T. Adatia and, I. D. Salter, *Polyhedron*, **1996**, *15*, 597-603.
- (49) S. M. Owen, *Polyhedron* 1988, *7*, 253-283.
- (50) D. M. P. Mingos, and R. L. Johnson, *Struct. Bonding (Berlin)*, 1987, *68*, 29-87.
- (51) B. Berti, M. Bortoluzzi, C. Cesari, C. Femoni, M. Hayatifar, M. C. Iapalucci and S. Zacchini, *J. Clust. Sci.*, <https://doi.org/10.1007/s10876-020-01839-y>.
- (52) N. V. S. Harisomayajula, S. Makovetskyi and Y.-C. Tsai, *Chem. Eur. J.*, **2019**, *25*, 8936-8954.
- (53) (a) M. J. Freeman, A. G. Orpen and I. D. Salter, *J. Chem. Soc., Dalton Trans.*, **1987**, 379-390; (b) S. S. D. Brown, I. D. Salter, V. Sik, I. J. Colquhoun, W. McFarlane, P. A. Bates, M. B. Hursthouse and M. Murray, *J. Chem. Soc., Dalton Trans.*, **1988**, 2177-2185; (c) S. S. D. Brown, I. D. Salter and L. Toupet, *J. Chem. Soc., Dalton Trans.*, **1988**, 757-767.
- (54) (a) S. S. D. Brown, P. J. McCarthy, I. D. Salter, P. A. Bates, M. B. Hursthouse, I. J. Colquhoun, W. McFarlane and M. Murray, *J. Chem. Soc., Dalton Trans.*, **1988**, 2787-2796; (b) S. S. D. Brown, I. D. Salter and T. Adatia, *J. Chem. Soc., Dalton Trans.*, **1993**, 559-566; (b) P. J. McCarthy, I. D. Salter and T. Adatia, *J. Organomet. Chem.*, **1995**, *485*, 191-199.
- (55) (a) I. D. Salter, S. A. Williams and T. Adatia, *Polyhedron*, **1995**, *14*, 2803-2817; (b) I. D. Salter, V. Sik, S. A. Williams and T. Adatia, *J. Chem. Soc., Dalton Trans.*, **1996**, 643-652.
- (56) (a) T. Adatia, P. J. McCarthy, M. McPartlin, M. Rizza and I. D. Salter, *J. Chem. Soc., Chem. Commun.*, **1988**, 1106-1108; (b) P. J. McCarthy, I. D. Salter, K. P. Armstrong, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, **1989**, *377*, C73-C76; (c) C. J. Brown, P. J.

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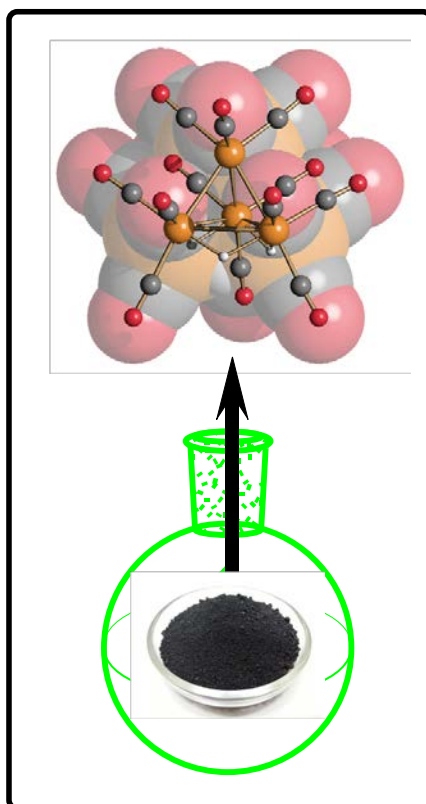
When citing, please refer to the published version.

- McCarthy, I. D. Salter, K. P. Armstrong, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, **1990**, *394*, 711-732.
- (57) D. M. P. Mingos and A. S. May, *Chemistry of Metal Cluster Complexes* (Eds.: D. S. Shriver, H. D. Kaesz and R. D. Adams), VCH, **1990**.
- (58) E. L. Bennett, P. J. Murphy, S. Imberti and S. F. Parker, *Inorg. Chem.*, **2014**, *53*, 2963-2967.
- (59) E. Keller, SCHAKAL99, University of Freiburg, Germany, **1999**.
- (60) G. M. Sheldrick, SADABS, Program for empirical absorption correction; University of Göttingen: Germany, **1996**.
- (61) G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.
- (62) (a) Y. Minenkov, Å. Singstad, G. Occhipinti and V. R. Jensen, *Dalton Trans.*, **2012**, *41*, 5526-5541. (b) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.*, **2008**, *10*, 6615-6620. (c) I. C. Gerber and J. G. Ángyán, *Chem. Phys. Lett.*, **2005**, *415*, 100-105.
- (63) (a) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, **2005**, *7*, 3297-3305. (b) D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*, **1990**, *77*, 123-141.
- (64) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision C.01*, Gaussian Inc., Wallingford, CT, 2010.
- (65) (a) F. Jensen, *Introduction to Computational Chemistry*, 2nd ed., Wiley, Chichester, 2007. (b) C. J. Cramer, *Essentials of Computational Chemistry*, 2nd ed., Wiley, Chichester, 2004.
- (66) T. Lu and F. Chen, *J. Comput. Chem.*, 2012, *33*, 580-592.

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The $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ polyhydride carbonyl cluster has been obtained in an one-pot synthesis by reductive carbonylation of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ at CO-atmospheric pressure.

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