

# Gas-Phase Synthesis and Structure of Wade-Type Ruthenium Carbonyl and Hydrido Carbonyl Clusters

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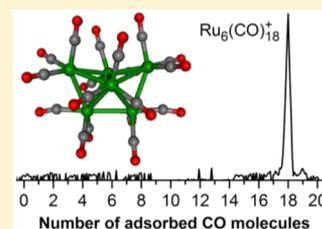
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## S Supporting Information

**ABSTRACT:** The gas-phase reaction of size-selected  $\text{Ru}_n^+$  ( $n = 4-6$ ) clusters with CO in an ion trap yields only one specific ruthenium carbonyl complex for each cluster size,  $\text{Ru}_4(\text{CO})_{14}^+$ ,  $\text{Ru}_5(\text{CO})_{16}^+$ , and  $\text{Ru}_6(\text{CO})_{18}^+$ . First-principles density functional theory calculations reveal structures for these hitherto unknown carbonyl compounds that are in perfect agreement with the geometries predicted by Wade's electron counting rules. Furthermore, reactions with  $\text{D}_2$  show that for  $\text{Ru}_4^+$  and  $\text{Ru}_6^+$ , CO molecules can be partially replaced by  $\text{D}_2$  to form hydrido carbonyl complexes while preserving the total ligand count corresponding to the Wade cluster sizes.



## 1. INTRODUCTION

The chemical interaction of carbon monoxide with transition metals is a fundamental topic in organometallic chemistry and of utmost importance to applications like, for example, catalysis.<sup>1</sup> Already in 1923, Sidgwick introduced the effective atomic number (EAN) rule, which predicts and explains the pronounced stabilities of mono- and multinuclear transition-metal carbonyl clusters with distinct numbers of carbonyl ligands.<sup>2,3</sup> Later, Wade and Mingos postulated rules that related the electronic structure of the carbonyl clusters to particular geometric structures.<sup>4,5</sup> Many of these Wade-type carbonyl clusters have been selectively synthesized in the condensed phase and successfully utilized as homogeneous and heterogeneous catalysts.<sup>6</sup>

In contrast, gas-phase reactions of free mass-selected transition-metal clusters with carbon monoxide yielded distributions of carbonyl complex sizes with the CO saturation limit indicating the Wade-type complexes in some cases (see, e.g., refs 7–11).

In this contribution, we report on the gas-phase reaction of size-selected  $\text{Ru}_n^+$  ( $n = 4-6$ ) clusters with CO in an ion trap under multicollision conditions. Most notably, this approach results in the exclusive synthesis of only one specific ruthenium carbonyl complex for each cluster size. The particular stability of all of these selectively formed gas-phase Ru carbonyl clusters can be inferred from their “closed-shell” electronic structure, which is obtained by applying the EAN rule for each apex atom in the cluster. Complementary first-principles density functional theory (DFT) calculations provide detailed structural characterization in accordance with the geometries predicted by Wade's electron counting rules.

In the case of  $\text{Ru}_4^+$  and  $\text{Ru}_6^+$ , CO molecules can be partially replaced by  $\text{D}_2$  when CO and  $\text{D}_2$  are both present in the ion trap. The resulting hydrido carbonyl complexes always exhibit the same total ligand count, corresponding to the Wade cluster sizes.

## 2. EXPERIMENTAL AND COMPUTATIONAL METHODS

**A. Experimental Method.** Gas-phase ruthenium clusters are prepared by sputtering of Ru metal targets with high-energy Xe ion beams. The produced clusters are mass-selected in a first quadrupole mass filter and are subsequently guided into a home-built radio frequency octopole ion trap, which is prefilled with 2 Pa of helium buffer gas and a small fraction of reactant gases CO and CO/ $\text{D}_2$ . The pressure conditions ensure temperature equilibration of the clusters within a few milliseconds prior to the reaction, which occurs on a considerably longer time scale of 0.1 s to several seconds.<sup>12</sup> During the experiments, the ion trap is held at room temperature, and after a chosen reaction time, that is, storage time inside of the ion trap, all ions, products, and intermediates are extracted and mass-analyzed by a second quadrupole mass filter and finally detected with a channeltron electron amplifier. Throughout the presented experiments, deuterium instead of hydrogen was employed to facilitate the mass assignment.

**B. Theoretical Method.** The structural properties of the ruthenium cluster cations were studied using DFT with the PBE functional<sup>13</sup> and RI approximation.<sup>14</sup> For the Ru atoms

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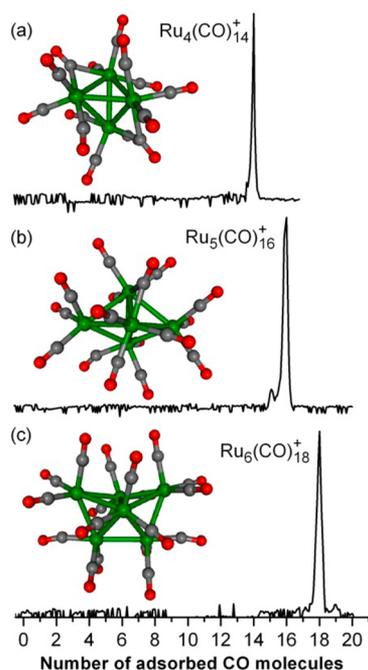
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the triple- $\zeta$ -valence-plus-polarization (TZVP) atomic basis sets combined with the Stuttgart group relativistic effective core potentials (ECPs) were employed.<sup>15</sup> For the C, O, and H atoms, the TZVP basis sets were used.<sup>16</sup> Our previous studies of the reactivity of transition-metal clusters and oxide clusters have shown that such a combination of hybrid density functionals with triple- $\zeta$ -quality basis sets allows the accurate prediction of the reaction energetics and mechanisms.<sup>17–19</sup> All structures presented were fully optimized using gradient minimization techniques, and stationary points were characterized as minima or transition states by calculating the vibrational frequencies.

### 3. RESULTS AND DISCUSSION

Figure 1 displays ion mass distributions obtained after the reaction of  $\text{Ru}_4^+$ ,  $\text{Ru}_5^+$ , and  $\text{Ru}_6^+$  with CO. All three cluster sizes



**Figure 1.** Product mass spectra obtained after the gas-phase reaction of (a)  $\text{Ru}_4^+$ , (b)  $\text{Ru}_5^+$ , and (c)  $\text{Ru}_6^+$  with CO for 0.1 s.  $\text{Ru}_4^+$ :  $p(\text{CO}) = 0.002$  Pa;  $p(\text{He}) = 1.96$  Pa.  $\text{Ru}_5^+$ :  $p(\text{CO}) = 0.007$  Pa;  $p(\text{He}) = 1.98$  Pa.  $\text{Ru}_6^+$ :  $p(\text{CO}) = 0.002$  Pa;  $p(\text{He}) = 1.96$  Pa. The small peak corresponding to  $\text{Ru}_5(\text{CO})_{15}^+$  in (b) disappears at slightly longer reaction times. To enhance the comparability for the different metal cluster sizes, the mass spectra show the linear ion intensity as a function of the number of CO molecules adsorbed on the respective metal cluster. The corresponding calculated structures of the products are shown as insets (Ru, C, and O atoms are indicated by green, gray, and red spheres, respectively).

react very fast with CO in our ion trap (faster than the time resolution of our setup) and form exclusively one single product each ( $\text{Ru}_4(\text{CO})_{14}^+$ ,  $\text{Ru}_5(\text{CO})_{16}^+$ , and  $\text{Ru}_6(\text{CO})_{18}^+$ ). No other products have been detected at longer reaction times or different partial pressure conditions in the ion trap. This observation strongly suggests the particular stability of these carbonyl complexes, which can be explained by the fact that each of these clusters has a “closed-shell” valence electron (VE) count of 18 for each metal atom center, in accordance with the EAN rule.<sup>2,3</sup> For  $\text{Ru}_4(\text{CO})_{14}^+$ , for example, each Ru atom contributes eight VEs, each of the six metal cluster single bonds

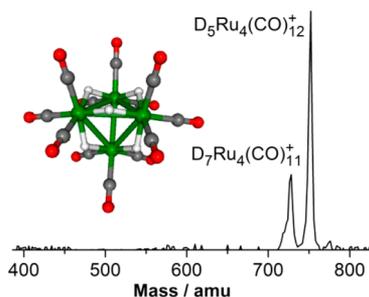
in a tetrahedral structure two VEs, and each CO molecule bond two VEs. This yields 72 VEs in total, 18 VEs for every Ru atom center. Please note that the positive charge of the complexes is neglected in this simple electron counting procedure. Hence, due to the positive charge, the ruthenium cluster carbonyls never exactly obey the EAN rule but are always one electron deficient. This interesting observation will be discussed further below in the context of hydrido carbonyl clusters.

Wade’s rules<sup>4</sup> can now be applied to deduce the geometries of all of these (almost) electronically closed-shell cluster ions. For this purpose, the metal VEs and the respective number of CO ligands are counted followed by a reduction to the corresponding boron hydride fragments via the isolobal analogy (i.e., a  $\text{Ru}(\text{CO})_3$  unit corresponds to  $\text{BH}$ ).<sup>6,20</sup> According to Wade’s original rules,<sup>4</sup>  $\text{Ru}_4(\text{CO})_{14}^+$  thus exhibits a nido-type (tetrahedral) cluster geometry,  $\text{Ru}_5(\text{CO})_{16}^+$  exhibits closo-type (trigonal bipyramidal) structure, and  $\text{Ru}_6(\text{CO})_{18}^+$  represents a hypercloso-Wade-type (bicapped tetrahedral) cluster. These predicted skeletal Wade structures are in perfect agreement with the results of our DFT calculations depicted in Figure 1 (for higher-energy isomers, see Figure S1 of the Supporting Information).

The optimized structures show furthermore that in  $\text{Ru}_4(\text{CO})_{14}^+$ , each Ru atom of the tetrahedral  $\text{Ru}_4^+$  metal core has three CO ligands bound via the carbon atom in a  $\mu_1$ -atop geometry. In addition, two CO molecules are arranged each in a  $\mu_2$ -bridging position on opposite edges of the  $\text{Ru}_4^+$  tetrahedron. Similarly, three CO molecules are bound in a  $\mu_1$ -atop geometry to each of the five Ru atoms of the  $\text{Ru}_5^+$  core, while one additional CO molecule bridges two of the four-fold-coordinated Ru atoms. In  $\text{Ru}_6(\text{CO})_{18}^+$ , each Ru atom interacts with three atop-bound CO molecules, and no bridging by CO molecules occur. The calculated average CO binding energies in these three Ru carbonyl cluster amount to 1.89, 1.83, and 1.79 eV, respectively. The CO bonds are extended in average when bound to the Ru clusters (1.151 Å in  $\text{Ru}_4\text{CO}_{14}^+$ ; 1.151 Å in  $\text{Ru}_5\text{CO}_{16}^+$ ; 1.149 Å in  $\text{Ru}_6\text{CO}_{18}^+$ ) compared to free CO (1.136 Å). Structural data and vibrational frequencies are provided in the Supporting Information.

Interestingly, the condensed-phase synthesis of the corresponding neutral tetra- and pentanuclear ruthenium carbonyl clusters  $\text{Ru}_4(\text{CO})_{14}$  and  $\text{Ru}_5(\text{CO})_{16}$  with an electronically closed-shell structure has not been reported yet, but the isoelectronic  $\text{Os}_4(\text{CO})_{14}$ <sup>21</sup> and  $\text{Os}_5(\text{CO})_{16}$ <sup>22</sup> have been prepared. Similarly, neutral  $\text{Ru}_6(\text{CO})_{18}$  has not been synthesized; however, the dianion<sup>23</sup>  $\text{Ru}_6(\text{CO})_{18}^{2-}$  represents a well-characterized ruthenium carbonyl complex that has even been functionalized as catalytic material via anchoring in zeolites<sup>24</sup> and on oxide supports.<sup>25,26</sup> It should be noted that  $\text{Ru}_6(\text{CO})_{18}^{2-}$  has an octahedral structure due to the additional two electrons.<sup>23</sup>

Exposing the ruthenium tetramer  $\text{Ru}_4^+$  to a 1:11 CO/ $\text{D}_2$  mixture changes the product distribution completely, as is apparent from the mass spectrum shown in Figure 2. At these partial pressure conditions, up to three CO ligands of the carbonyl complex  $\text{Ru}_4(\text{CO})_{14}^+$  can be replaced by deuterium, yielding the hydrido carbonyl clusters  $\text{D}_7\text{Ru}_4(\text{CO})_{11}^+$  and  $\text{D}_5\text{Ru}_4(\text{CO})_{12}^+$ . The relative stability of  $\text{D}_7\text{Ru}_4(\text{CO})_{11}^+ + \text{CO}$  and  $\text{D}_5\text{Ru}_4(\text{CO})_{12}^+ + \text{H}_2$  amounts to 0.5 eV in favor of the latter. This gives a direct explanation for the relative intensity of these two products. At lower  $\text{D}_2$  partial pressures, the ligand exchange is less pronounced. Most notably, the observed product stoichiometries reveal an odd number of D atoms in



**Figure 2.** Product mass spectrum (intensity in arbitrary units) obtained after the gas-phase reaction of  $\text{Ru}_4^+$  with CO and  $\text{D}_2$  for 0.1 s ( $p(\text{CO}) = 0.008$  Pa;  $p(\text{D}_2) = 0.090$  Pa;  $p(\text{He}) = 1.88$  Pa). The corresponding calculated DFT structure of  $\text{H}_5\text{Ru}_4(\text{CO})_{12}^+$  is shown as an inset (Ru, C, O, and H atoms are indicated by green, gray, red, and white spheres, respectively).

these product complexes, which indicates that not only CO molecules have been exchanged by  $\text{D}_2$  but that also one additional D atom is adsorbed on the cluster. As discussed above, the  $\text{Ru}_4(\text{CO})_{14}^+$  has a one-electron deficiency in order to fully obey the EAN rule. On the basis of the assumption that each D atom donates one electron to the complex,<sup>6</sup> this additional D atom now balances the positive charge, which leads to a perfect closed electronic shell configuration.

Figure 2 also shows the calculated structure corresponding to the experimentally observed hydrido carbonyl cluster  $\text{H}_5\text{Ru}_4(\text{CO})_{12}^+$ , which reveals that the hydrogen ( $\text{D}_2$  in the experiment) molecules are adsorbed dissociatively with each of the altogether five hydrogen atoms  $\mu_2$ -bridging two neighboring Ru atoms resulting in a  $C_{2v}$  symmetry for  $\text{H}_5\text{Ru}_4(\text{CO})_{12}^+$ . Due to the fact that two hydrogen atoms provide as many electrons as one CO molecule, the tetrahedral geometry of the  $\text{Ru}_4$  cluster core is maintained upon CO substitution by  $\text{H}_2$ . Isomers containing also terminal or interstitial hydrogen atoms are found to be considerably higher in energy (cf. Figure S2 of the Supporting Information).

In the condensed phase, the tetranuclear hydrido carbonyl clusters  $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ ,<sup>27,28</sup>  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$ ,<sup>29,30</sup> and  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ <sup>28,31,32</sup> have been synthesized and structurally characterized. Also, the gas-phase reactivity of  $\text{H}_3\text{Ru}_4(\text{CO})_{12}^-$  has been investigated recently.<sup>33</sup> All of these complexes are isoelectronic to  $\text{H}_5\text{Ru}_4(\text{CO})_{12}^+$ . The difference in the number of hydrogen atoms of these condensed-phase complexes and our gas-phase analogue is caused by the positive charge of the  $\text{Ru}_4^+$  metal core, which is balanced by an additional fifth deuterium atom. However, in agreement with our optimized DFT structures, the metal cores of all of these complexes exhibit a tetrahedral structure, and hydrogen has also been found to be adsorbed dissociatively on the edges of the  $\text{Ru}_4$  tetrahedrons of these complexes in  $\mu_2$ -bridging positions.<sup>28,31,32</sup>

Interestingly, in our experiments, no pentanuclear ruthenium hydrido carbonyl clusters were detected. However, the reaction of  $\text{Ru}_6^+$  with a CO/ $\text{D}_2$  mixture also results in an exchange of carbon monoxide ligands by an equal number of  $\text{D}_2$  units to yield hexanuclear hydrido carbonyl clusters  $\text{D}_{2m}\text{Ru}_6(\text{CO})_{18-m}^+$  ( $m = 1, 2$ ). Yet, no additional single D atom adsorption onto the  $\text{Ru}_6^+$  complexes could be identified so far.

In the condensed phase, the hydrido carbonyl cluster  $\text{HRu}_6(\text{CO})_{18}^-$  has been synthesized, and X-ray diffraction as well as infrared spectroscopic experiments revealed an octahedral metal core structure with an interstitial H

atom.<sup>34–37</sup> As discussed above, the positive charge of  $\text{Ru}_6(\text{CO})_{18}^+$  leads to a VE count that corresponds to a bicapped tetrahedral Wade motif of the cluster core geometry instead of an octahedral. The bicapped tetrahedral Wade structure is preserved upon CO to  $\text{D}_2$  exchange because the number of electrons does not change. Thus, the reason why no  $\text{D}_{2m+1}\text{Ru}_6(\text{CO})_{18-m}^+$  complexes have been observed may be attributed to the bicapped tetrahedral geometry of  $\text{Ru}_6^+$ , which hampers interstitial H ligation and stabilization of the closed electronic shell configuration.

## 4. CONCLUSION

In summary, Wade-type ruthenium carbonyl and ruthenium hydrido carbonyl clusters were for the first time selectively synthesized in the gas phase. The exclusive formation of distinct cluster carbonyl sizes is in agreement with the stabilities predicted by simple electron counting rules, and the geometric structure of the metal cores can be determined on the basis of Wade's rules. However, full insight into the structure of the ruthenium carbonyl complexes as well as the hydrido carbonyl clusters is provided by detailed ab initio calculations.

Condensed-phase analogues  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  and  $\text{Ru}_6(\text{CO})_{18}^{2-}$  have been previously shown to be catalytically active in several basic chemical transformations like, for example, the hydrogenation of carbon monoxide<sup>25</sup> or of olefins<sup>38</sup> and the homologation of methane.<sup>24</sup> Work is in progress in our laboratories to elucidate whether such reactions might also be mediated by the analogous gas-phase complexes.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

DFT structures of higher-energy isomers as well as vibrational frequencies of the shown complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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