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Testing the Limits of the 18-Electron Rule: The Gas-Phase Carbonyls of Sc^+ and Y^+

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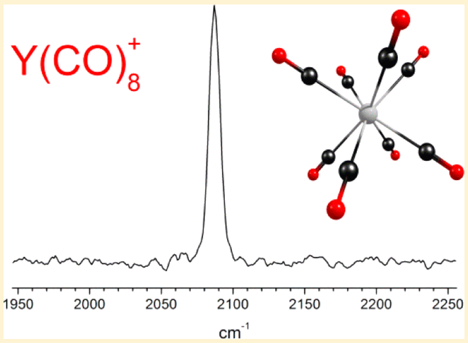
Ⓢ *Supporting Information*

ABSTRACT: Scandium and yttrium carbonyl cations produced in the gas phase via laser vaporization are mass selected and studied with infrared laser spectroscopy in the C−O stretching region. Mass spectra, ion fragmentation behavior, and infrared spectra, complemented by computational chemistry, establish the coordination numbers and structures of these complexes. Sc^+ does not form the eight-coordinate 18-electron complex but instead produces a 16-electron seven-coordinate species. However, Y^+ forms the anticipated eight-coordinate structure. Density functional theory computations provide structures and corresponding vibrational spectra for these complexes. $Sc(CO)_7{}^+$ has a C_{3v} capped octahedral structure, while $Y(CO)_8{}^+$ forms a D_{4d} square antiprism. The C−O stretches at 2086 and 2087 cm^{-1} for $Sc(CO)_7{}^+$ and $Y(CO)_8{}^+$, respectively, are among the most red-shifted frequencies measured for any transition metal carbonyl cation.



INTRODUCTION

Transition metal carbonyls provide prototypical examples of metal−ligand bonding in inorganic and organometallic chemistry, and the familiar 18-electron rule is often employed to predict the relative stabilities and coordination numbers for these complexes.[1,2] $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ are well-known 18-electron neutral carbonyls. Cation and anion analogues of these species have been studied previously in condensed-phase environments, usually stabilized by the presence of appropriate counterions.[1,2] Recent gas-phase work has shown that their isoelectronic cations, $Cu(CO)_4{}^+$, $Co(CO)_5{}^+$, and $Mn(CO)_6{}^+$, are also stable in isolated form and have the same structures as the neutrals.[3−5] Extending the electron counting logic, early transition metals with fewer valence electrons need progressively more carbonyl ligands to achieve stable bonding configurations. Neutral chemistry in the condensed phase has long sought to achieve such higher coordination numbers but has been limited by reaction schemes and synthetic byproducts. However, gas-phase synthesis has fewer constraints, and mass spectrometers provide ideal purification of products, allowing studies of many unusual metal carbonyls.[3−12] Using these methods, the group 5 metals niobium and tantalum, but not vanadium, were found to form seven-coordinate (7C) carbonyls.[6] In the extreme limit, Sc^+ and Y^+ should form eight-coordinate (8C) carbonyls. Stable octacarbonyl ions of these metals have been predicted by theory,[13] but there is no experimental data to confirm this.[14] Here, we produce scandium and yttrium carbonyl ions and determine their structures with infrared spectroscopy and computational chemistry. Under our conditions, scandium forms primarily a seven-coordinate carbonyl, but yttrium forms the expected eight-coordinate species.

EXPERIMENTAL SECTION

$Sc(CO)_n{}^+$ and $Y(CO)_n{}^+$ ions are produced by laser vaporization,[15] cooled in a pulsed-nozzle expansion of pure CO gas, and size-selected in a time-of-flight mass spectrometer.[16] Because the density of mass-selected ions is far too low for absorption spectroscopy, we use laser photodissociation spectroscopy to obtain infrared spectra.[3−12] Density functional theory (DFT) calculations were performed for the complexes of interest using the B3LYP functional[17,18] as implemented in the Gaussian 2003 computational package.[19] The LanL2DZ ECP basis set[20−22] was used for the metal atoms, and the DZP basis set[23] was used for carbon and oxygen. Carbonyl stretching frequencies are scaled by a factor of 0.971.[7,8] This factor was derived by comparing the frequencies computed at this same level of theory for $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ to their known experimental values. Full computational details are provided in the Supporting Information.

RESULTS AND DISCUSSION

The mass spectra of $Sc(CO)_n{}^+$ and $Y(CO)_n{}^+$ complexes are shown in Figure 1. Complexes containing up to 20 or more carbonyls are produced, which is clearly more ligands than can be coordinated directly to the metal atom. Instead, these complexes are understood to consist of a strongly bound core ion, with the remaining "external" CO ligands attached in the second sphere via weak electrostatic interactions.[8] Extensive clustering is possible because of the cold supersonic expansion employed in ion production. As demonstrated in previous work, the external carbonyls are eliminated efficiently upon infrared absorption.[3−8] The enhanced abundances of the $n = 7$ and $n = 8$ species for scandium and yttrium, respectively, suggest stability for these complexes. However, mass spectral

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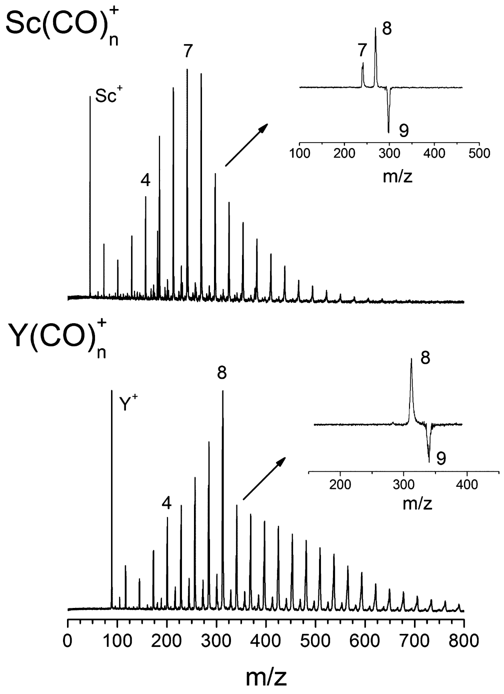

Figure 1. Mass spectra of $M(CO)_n^+$ ions (M = Sc, Y) produced from our laser vaporization source. Weaker mass peaks in between the carbonyls are oxides formed from sample impurities. The insets show representative photodissociation patterns for scandium and yttrium carbonyl cations.

abundances are not reliable indicators of ion stability, as peak intensities may vary with source conditions and spectrometer focusing.[8] The insets show the fragmentation patterns of $Sc(CO)_9^+$ and $Y(CO)_9^+$ obtained by subtracting a mass spectrum obtained with the photodissociation laser off from one with it on. The negative peaks indicate the depletion of the parent ion, and the positive peaks indicate the fragments produced. The energy of IR photons is enough to eliminate one or more weakly bound ligands but not the strong bonds of the ligands in the core ion. Additional examples of fragmentation patterns for other cluster sizes are presented in the Supporting Information. In these and larger complexes, ligand elimination terminates at $n = 7$ for scandium and $n = 8$ for yttrium. This fragmentation behavior suggests that $Sc(CO)_7^+$ is the fully coordinated scandium complex, whereas that of yttrium is the 8C 18-electron $Y(CO)_8^+$ ion. However, this fragmentation data is also not completely definitive because not all of the cluster ions at each size dissociate.

The wavelength dependence of these fragmentation processes provides their infrared spectra. Larger complexes are measured in the mass channel corresponding to CO loss. However, the $Sc(CO)_7^+$, $Y(CO)_7^+$, and $Y(CO)_8^+$ complexes do not fragment appreciably when excited with infrared light, consistent with the strong binding expected for core ligands. To measure spectra for these complexes, we employ the method of “tagging” with argon.[3−8] $M(CO)_n^+Ar$ complexes are produced using expansion gas mixtures containing both argon and CO. Following infrared excitation, these ions fragment via the elimination of argon. Previous experiments have confirmed that tagging has a negligible effect on the spectra of metal carbonyls and that this method provides the best approximation to the true absorption spectra.[3−8]

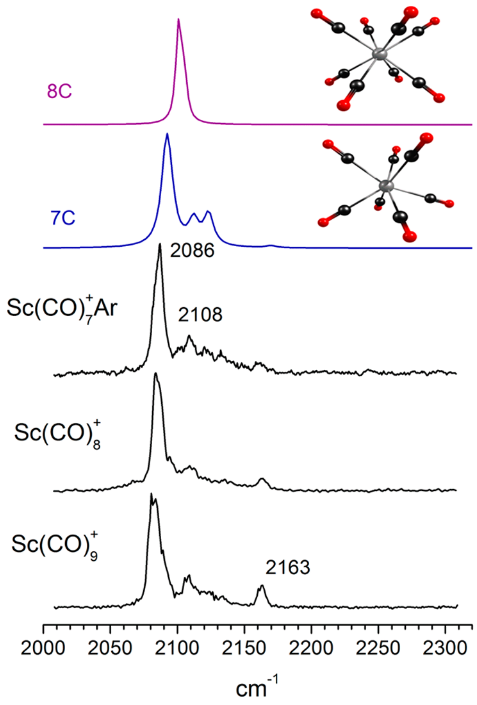

Figure 2. Predicted infrared spectra for 7C $Sc(CO)_7^+$ and 8C $Sc(CO)_8^+$ and experimental photodissociation spectra for $Sc(CO)_7^+Ar$, $Sc(CO)_8^+$, and $Sc(CO)_9^+$.

Figure 2 shows the infrared photodissociation spectra of the $Sc(CO)_n^+$ complexes for $n = 7–9$, along with spectra and structures predicted by theory for the 8C and 7C species. The $n = 7$ species does not fragment efficiently unless it is tagged. The $n = 8$ species fragments by losing CO, but it is conceivable that there is a population of more strongly bound 8C ions present that does not fragment. The $n = 9$ complex would then have an excess CO to probe for this population, if it existed. However, each of these spectra are quite similar, with the same most intense band at 2086 cm^{-1}, along with weaker structures toward higher energy. The 2086 cm^{-1} bands are shifted to lower frequencies than the free molecular CO stretch at 2143 cm^{-1}.[24] All three complexes have similar structures in the region above 2100 cm^{-1}, where weaker bands are predicted for the 7C complex. An additional band at 2163 cm^{-1} is evident for the $Sc(CO)_8^+$ and $Sc(CO)_9^+$ complexes; a weak structure is also present near here for the $n = 7$ complex (assigned to a predicted core ion vibration with weak intensity), but it is more clear for the $n = 8$ and 9 species. As described in previous work,[3−8] a band at this position is characteristic of external CO ligands. None of these spectra has the clear single-peak pattern expected for the 8C complex. Therefore, we conclude that scandium does not form the eight-coordinate complex and that the $n = 8$ and 9 complexes represent 7C core ions with external ligands. We cannot exclude the presence of a small amount of 8C complexes, which might have a resonance near 2100 cm^{-1} obscured by the weak signal in this area, but it is clear that the main signal for the scandium carbonyls is that of the 7C complexes.

Experimental spectra for the corresponding $n = 7–9$ complexes of $Y(CO)_n^+$ are shown in Figure 3, along with spectra predicted for the 7C and 8C complexes. Unlike the scandium system, the spectra for the $n = 7$ and $n = 8$ yttrium species are quite different. The $n = 7$ spectrum has three bands at 2071, 2104, and 2114 cm^{-1}, consistent with the pattern

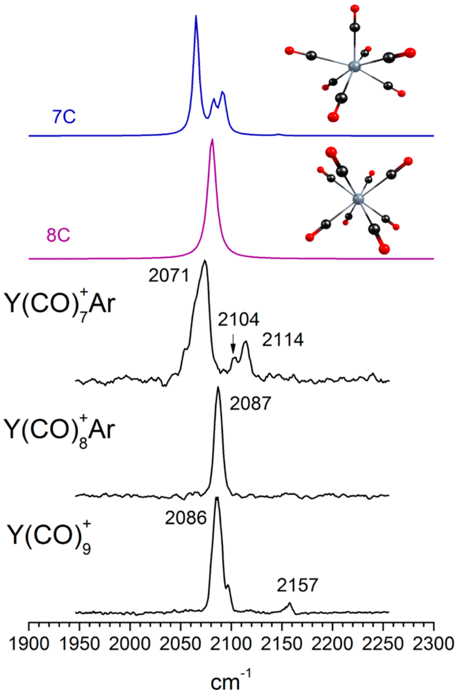

Figure 3. Predicted infrared spectra for 7C $Y(CO)_7^+$ and 8C $Y(CO)_8^+$ complexes and experimental photodissociation spectra for $Y(CO)_7^+Ar$, $Y(CO)_8^+Ar$, and $Y(CO)_9^+$.

predicted for the lowest energy 7C complex. This ion has a capped octahedral geometry and C_{3v} symmetry. In striking contrast to this, the $n = 8$ spectrum consists of a single band at 2087 cm^{-1}. Unlike the similar pattern for the different scandium complexes, this main band shifts significantly from the $n = 7$ to the $n = 8$ species. This single band is exactly the pattern for an 8C structure, which is predicted to have a square antiprism geometry with D_{4d} symmetry. The spectrum for $Y(CO)_9^+$ in the bottom trace is similar to that of $Y(CO)_8^+$ but with the addition of a weak feature at 2157 cm^{-1}. This is consistent with an 8C core ion and a weakly bound external CO ligand. We therefore conclude that yttrium forms the eight-coordinate $Y(CO)_8^+$ complex, which has 18 electrons. This is the first confirmed example of a homoleptic 8C transition metal carbonyl complex. The only previous example of an eight-carbonyl complex is $U(CO)_8^+$, which has the same kind of square antiprism structure.[9]

It is interesting to consider why yttrium forms the eight-coordinate carbonyl, but scandium does not. It is of course tempting to conclude that ion size is responsible for this. However, DFT computations by Tang and co-workers[13] and also those by our group (Supporting Information) predict a stable 8C complex for scandium that is significantly lower in energy than the 7C+1 species seen experimentally. The CO ligand binding energy computed for the $Sc(CO)_8^+$ complex is actually greater than that for $Y(CO)_8^+$ (30.4 vs 14.0 kcal/mol; Supporting Information). Apparently, ion size is not the only consideration. Similar anomalies in experimental versus predicted coordination numbers were also seen in our recent studies of the group 4 and 5 metal carbonyl ions.[6,7] In the vanadium group, V^+, Nb^+, and Ta^+ were all predicted to form 7C 18-electron complexes, but only Nb and Ta actually did this in the experiment.[6] In the titanium group, Ti^+, Hf^+, and Zr^+ were also predicted to form 7C (17-electron) complexes, but *none* of these metals did.[7] Instead, six-coordinate complexes formed for all three metals.[7] Experiments under other conditions by Armentrout and co-workers found evidence for 7C complexes of V^+ and Ti^+, in direct contrast to our results.[25,26]

As we discussed in our earlier work, the kinetics of cluster synthesis in our laser ablation source may be responsible for these puzzling results. As shown in the Supporting Information, the lowest energy states predicted by theory for the $n = 7$ complexes of Sc^+ and Y^+ are triplets, while those of the $n = 8$ complexes are singlets. In cluster growth by sequential ligand addition, a spin change is therefore required to add the last ligand that produces the $n = 8$ complex. As shown in previous work, this situation can cause a kinetic “bottleneck” in the cluster growth. Weitz and co-workers investigated the spin-forbidden and spin-allowed recombination of CO to unsaturated $M(CO)_n$ complexes,[27,28] finding that CO additions involving spin changes occurred at rates as much as 400 times slower than spin-conserving reactions. These observations were corroborated in computational work by Harvey et al.[29−31] Using the Landau−Zener theory and nonadiabatic transition state theory, the probabilities of curve crossing reactions were calculated from first principles. The rates were shown to be proportional to the strength of spin−orbit coupling of the system, thus explaining the differences in spin-changing reaction rates for different complexes. This same behavior was invoked to explain our results for the vanadium group metals, where only the heavier metals, Nb and Ta, expected to have stronger spin−orbit coupling formed the high coordination complexes.[6] It also explained the inconsistencies between our work and that of Armentrout. Apparently, the kinetic bottleneck that limited cluster growth in our low-temperature experiment is not as important under their higher temperature conditions. Similar ideas about cluster growth seem to apply here. If there is a spin-changing bottleneck in cluster growth, it would likely be less of a limitation for the heavier metal yttrium, which should have stronger spin−orbit coupling than scandium. This may explain why yttrium is able to form the 8C complex under our conditions, while scandium is not.

One final point of interest is the band positions of the carbonyl stretches measured for these complexes. The main bands for the fully coordinated complexes were measured at 2086 and 2087 cm^{-1} for $Sc(CO)_7^+$ and $Y(CO)_8^+$, respectively. These C−O stretches are among the most red-shifted for any metal carbonyl ions yet studied, compared, for example, to the values of 2110 and 2097 cm^{-1} for $Ti(CO)_6^+$ and $V(CO)_6^+$, respectively.[6,7] As discussed in our recent review, the red shifts for metal carbonyl cations are all much less than those for corresponding neutrals due to the reduced π-backbonding caused by the charge.[8] Scandium and yttrium have lower d orbital occupations than later transition metals, but the effective nuclear charge is also smaller in these atoms. This apparently results in less d contraction and greater availability of electron density, enhancing the backbonding compared to heavier metals.

■ CONCLUSION

This study provides the first spectroscopic evidence for an 8C transition metal carbonyl in the gas phase. Both scandium and yttrium are predicted by theory to form stable 18-electron eight-coordinate complexes, but only yttrium does this efficiently under our conditions. $Y(CO)_8^+$ has a square antiprism (D_{4d}) structure, analogous to that found previously for $U(CO)_8^+$ complexes.[9] Although these complexes could be difficult to synthesize by traditional methods and may not survive under real-world conditions, the 18-electron configuration is a strong enough driving force to allow this exotic structure to form in the gas phase.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The full citation for ref 19. Additional details are provided on the DFT computations, including the structures, energetics, and vibrational frequencies for the structures considered. 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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