

An Investigation of the Electronic Structures of $\text{CpCo}(\text{CO})_2$ and $\text{CpCo}(\text{CO})_2^-$ Using Experimental and Theoretical Techniques

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Received August 7, 1996[⊗]

Abstract: An upper bound for the adiabatic electron affinity of cyclopentadienylcobaltdicarbonyl [$\text{CpCo}(\text{CO})_2$] is 0.86 ± 0.2 eV as determined by fixed-frequency negative-ion photoelectron spectroscopy. During the course of the experimental work, the generation of the binuclear complex [$\text{CpCo}(\text{CO})_2$] $^-$ is detected, and, to our knowledge, this is the first observation of this anionic cluster. Electronic structural calculations using both the density functional theory formalism and ab initio techniques are completed for both $\text{CpCo}(\text{CO})_2$ and the corresponding negative-ion. A DFT/DZVP2 calculation yields the vertical electron affinity of $\text{CpCo}(\text{CO})_2$ as 0.84 ± 1.0 eV. The theoretical results confirm that a weak “allyl-ene” type structure exists in the cyclopentadienyl ligand of both molecules, but the distortion is less pronounced in $\text{CpCo}(\text{CO})_2^-$ than in $\text{CpCo}(\text{CO})_2$. Our results lend further support to the classification of $\text{CpCo}(\text{CO})_2^-$ as a 19-electron complex.

Introduction

The structure of the ground state of the radical anion of cyclopentadienylcobaltdicarbonyl ($\text{CpCo}(\text{CO})_2^-$) has been the subject of considerable, and contrary, conjecture. The root of the dispute rests in the existence of seemingly conflicting experimental data from groups studying the ligand substitution mechanisms of $\text{CpCo}(\text{CO})_2^-$ and $\text{CpCo}(\text{CO})_2$ and those examining the anion by electron spin resonance (ESR) spectroscopy. At the center of the debate is the hapticity of the cyclopentadienyl (Cp) ring. In the neutral molecule the ring is close to planar and bonded to the cobalt atom in an η^5 -type configuration. It has been hypothesized that the presence of the extra electron in the anion promotes the “slipping” of the ring into an η^3 -bonding configuration. Underlying the debate of the geometry of the Cp ring itself is the fundamental question of the electronic structure of the ground state of $\text{CpCo}(\text{CO})_2^-$. If the hapticity of the ligand changes to η^3 -, then the anion is described as a 17-electron complex. If the hapticity of the ring in $\text{CpCo}(\text{CO})_2^-$ is the same as in the neutral analogue, the anion serves as a further example of a 19-electron organometallic complex.^{1,2}

Studies of the reactivity of $\text{CpCo}(\text{CO})_2$ date back to 1961, when Wojcicki and Basolo³ noted that this molecule, along with several other cyclopentadienyl metal carbonyl complexes, underwent CO exchange via a bimolecular, or $\text{S}_{\text{N}}2$, displacement mechanism. This result is in sharp contrast to the $\text{S}_{\text{N}}1$ mechanism observed for CO exchange in the simple binary transition metal carbonyl complexes.⁴ The $\text{S}_{\text{N}}2$ substitution mechanism was further confirmed by investigating the reactions of $\text{CpRh}(\text{CO})_2$, $(\text{Cp}^*)\text{Co}(\text{CO})_2$, and $(\text{Cp}^*)\text{Rh}(\text{CO})_2$, ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$) with phosphines, phosphites, and isocyanides.^{5,6} The suggested mechanism involved the transfer of a pair of electrons from the metal to the cyclopentadienyl ring, leaving behind a low energy vacant orbital on the metal into which the nucleophile could attack.

Fourteen years later, based on studies of nucleophilic displacement reactions of $\eta^5\text{-CpRh}(\text{C}_2\text{H}_4)_2$, Cramer and Seiwel⁷ suggested a modification of the mechanism proposed by Basolo and co-workers. They suggested that, during the reaction, the cyclopentadienyl ligand may undergo a hapticity change from η^5 - to η^3 - and thus form an allylic type bond to the rhodium center in the transition state. This concept of ring-slippage has gained wide acceptance, and the resulting literature has been reviewed by Basolo⁸ and O'Connor and Casey.⁹

One justification of the idea of ring slippage is that it satisfies the acknowledged 18-electron rule. For $\text{CpCo}(\text{CO})_2$, if ring slippage does not occur, and an associative reaction pathway is followed, the resultant transition state will have a high energy 20-electron configuration; with ring slippage, an 18-electron configuration is maintained in both the ground and transition states.

The mechanistic studies initiated investigations into the structure of $\text{CpCo}(\text{CO})_2$ by electron diffraction,¹⁰ matrix-isolation infrared,¹¹ and photoelectron¹² spectroscopies. The photoelectron spectrum was analyzed with the aid of molecular orbital (MO) diagrams, appropriate for $\text{CpCo}(\text{CO})_2$, published by Hofmann¹³ and Albright and Hoffmann.¹⁴ The MO diagrams were obtained from extended Hückel type (Fenske-Hall) calculations. Brown, Clarke, and Fitzpatrick¹⁵ calculated the Co–CO overlap population and the C–O bond order in $\text{CpCo}(\text{CO})_2$ using the SCCMO methodology.

The parent negative-ion $\text{CpCo}(\text{CO})_2^-$ was first observed in mass spectrometric studies by Winters and Kiser.¹⁶ Corderman

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and Beauchamp¹⁷ measured the bimolecular rate constant for the reaction of $\text{CpCo}(\text{CO})_2^-$ with NO to give $\text{CpCo}(\text{NO})^-$ in ICR mass spectrometry experiments. They also observed that $\text{CpCo}(\text{CO})_2^-$ will react with PF_3 to produce $\text{CpCo}(\text{CO})(\text{PF}_3)^-$ with, however, a very low yield. In a flowing afterglow apparatus, McDonald and Schell¹⁸ observed that the main product from the slow reaction of $\text{CpCo}(\text{CO})_2^-$ with PF_3 was the total adduct $\text{CpCo}(\text{PF}_3)(\text{CO})_2^-$, with $\text{CpCo}(\text{CO})(\text{PF}_3)^-$ being the minor product. The observation of the total adduct is consistent with an associative mechanism for ligand substitution in $\text{CpCo}(\text{CO})_2^-$. McDonald and Schell argued that the observed slow rate for this reaction was due to the structural rearrangement of the Cp ligand from η^5 - to η^3 -bonding and hence that $\text{CpCo}(\text{CO})_2^-$ was a 17-electron complex. They also suggested that the electron transfer rate from $\text{CpCo}(\text{CO})_2^-$ to biacetyl was slow due to a proposed hapticity change between the anion, $\eta^3\text{-CpCo}(\text{CO})_2^-$, and the neutral molecule, $\eta^5\text{-CpCo}(\text{CO})_2$.

Observation of an associative pathway for nucleophilic substitution reactions of $\text{CpCo}(\text{CO})_2^-$ is consistent with an η^3 -bound cyclopentadienyl ligand in this anion. The intermediate in this case would be a 19-electron complex, with subsequent expulsion of a CO ligand to yield a 17-electron product. If the Cp-ligand was η^5 -bound in the anion then an associative bimolecular reaction would result in a high energy, unstable, and unfavorable 21-electron intermediate. It is believed that 19-electron complexes will undergo nucleophilic substitution via a dissociative process and thus avoid formation of a 21-electron intermediate.¹⁹

While the above reactivity studies suggest that $\text{CpCo}(\text{CO})_2^-$ is a 17-electron complex, the conclusions have to be viewed with caution. First of all, they are based on observation of the post reaction product data, and there is no direct detection of the intermediate state. Furthermore, reactivity studies may reveal only the kinetically favored pathway. Thus while such studies may be used to infer a proposed geometry for the transition state of a given molecule, they neither definitively prove that the structure exists, nor guarantee that it corresponds to the ground electronic state. In spite of the fact that electronic structure arguments and reactivity pathways which propose the $\eta^3\text{-Cp}$ configuration are widespread, the structure has only been directly observed by spectroscopic methods once.²⁰ In a 1995 review paper, Geiger cautions that direct spectroscopic evidence for a slipped-ring configuration of a Cp ligand in a formally 19-electron transition metal complex has never been observed.²¹ He also asserts that true 19-electron complexes are more common than assumed.

The conclusions obtained from the reactivity studies, documented above, are contradicted by two ESR studies. The first, by Symons and Bratt in 1979,²² determined that there was 55% excess electron population on the cobalt atom in $\text{CpCo}(\text{CO})_2^-$. In 1986, this figure was verified by Connelly and co-workers,²³ who recorded an ESR spectrum and performed a cyclic voltammetry study of the similar compound $(\text{C}_5\text{Ph}_5)\text{Co}(\text{CO})_2^-$ (Ph ... phenyl). Both of these spectral studies on the ground state of $\text{CpCo}(\text{CO})_2^-$ concluded that the extra electron lies

predominantly on the central cobalt atom in the d_{yz} orbital, thus implying a 19-electron configuration for the complex. In these studies, the orientation of the molecule was chosen such that the $\text{Co}(\text{CO})_2$ group was in the yz -plane, and this plane bisected the plane of symmetry of the molecule.

There was also one experiment that suggested that a dissociative mechanism may be operative in $\text{CpCo}(\text{CO})_2$ reactions. In some solution phase photochemical and thermal reaction studies of $\text{CpCo}(\text{CO})_2$ by Lee and Brintzinger^{24,25} the monocarbonyl complex, $\text{CpCo}(\text{CO})$, was detected by IR spectroscopy. They postulated that generation of $\text{CpCo}(\text{CO})$ was the primary step in a number of ligand substitution reactions of $\text{CpCo}(\text{CO})_2$, in contrast to the earlier reactivity studies. However, Crichton et al.¹¹ contradicted these conclusions and reassigned the observed spectrum to the complex $\text{CpCo}(\text{CO})(\text{N}_2)$ rather than the unsaturated monocarbonyl species $\text{CpCo}(\text{CO})$.

Finally, the structure of the cyclopentadienyl ligand has received further attention. The single crystal X-ray diffraction study of the substituted complex, $[\text{C}_5(\text{CH}_3)_5]\text{Co}(\text{CO})_2$, by Byers and Dahl, revealed a small, yet detectable "allyl-ene" distortion in the ring.²⁶ Furthermore, it was suggested by Connelly et al.²³ that in $\text{CpCo}(\text{CO})_2^-$ the distortion in the Cp ring is relieved, rather than enhanced, compared to that in the neutral parent molecule.

In this paper we will present two studies to support further the hypothesis that in its ground state $\text{CpCo}(\text{CO})_2^-$ is a 19-electron complex: the first examination of the electron binding energy of $\text{CpCo}(\text{CO})_2^-$ via fixed-frequency Negative-Ion Photoelectron Spectroscopy (NIPES); and secondly, the most detailed electronic structural calculations performed on the complexes to date, utilizing both Density Functional Theory (DFT)²⁷ and ab initio techniques.

Experimental Section

The focus of the experimental section of the study was the determination of the electron binding energy of the anion through the recording of the kinetic energy spectrum of electrons (e^- KE) photo-detached from $\text{CpCo}(\text{CO})_2^-$ utilizing NIPES. As the spectrometer is similar to that described by Neumark and co-workers²⁸ and the details of our adaptation have been given elsewhere,²⁹ the experiment will only be briefly discussed here. A schematic of the spectrometer is shown in Figure 1. The spectrometer can be separated into three component parts: the ion source region, the time-of-flight mass spectrometer, and the time-of-flight electron spectrometer.

The anions are generated using the pulsed molecular beam/electron gun configuration developed by Johnson et al.³⁰ Anions are formed through a variety of mechanisms, including associative and dissociative attachment, and clustering reactions and are then cooled to low rotational and vibrational temperatures as the expansion continues. For the formation of $\text{CpCo}(\text{CO})_2^-$, carrier gases (helium and argon with typical backing pressures of 25 psig) are passed over liquid $\text{CpCo}(\text{CO})_2$, collecting the vapor pressure, and the mixture is expanded through the pulsed valve. The resultant collection of cool anions is uniformly accelerated to 1 keV before entering the time-of-flight mass spectrometer.

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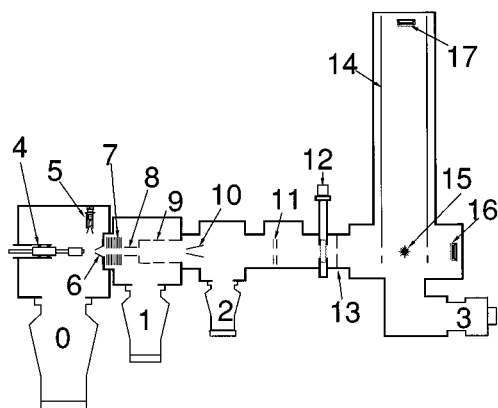


Figure 1. Fixed-frequency negative-ion photoelectron spectrometer. **0:** source diffusion pump; **1:** first differential region diffusion pump; **2:** second differential region diffusion pump; **3:** turbomolecular pump; **4:** pulsed molecular beam valve; **5:** electron gun; **6:** skimmer; **7:** ion acceleration plates; **8:** beam-modulation plates; **9:** ion einzel lens; **10:** ion deflection plates; **11:** temporal focusing lens; **12:** gate valve; **13:** 5 mm defining slit; **14:** double layer of Conetic-AA shielding; **15:** laser interaction region; **16:** ion detector; **17:** electron detector.

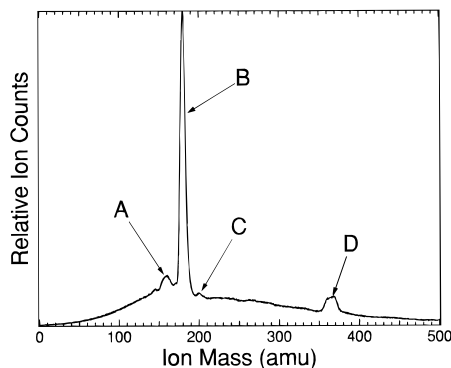
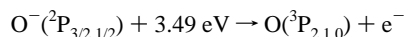


Figure 2. Negative-ion mass spectrum generated from an expansion of $\text{CpCo}(\text{CO})_2$ in helium. A: $\text{CpCo}(\text{CO})^-$; B: $\text{CpCo}(\text{CO})_2^-$; C: $\text{CpCo}(\text{CO})_2 \cdot \text{H}_2\text{O}^-$; D: $[\text{CpCo}(\text{CO})_2]_2^-$.

The Bakker-type mass spectrometer^{31,32} facilitates the temporal separation of the various anions. The mass spectrometer is approximately 1.5 m long, and a series of ion optics, including an einzel lens and a temporal focusing lens, is located on the ion flight path. With the temporal focusing lens, the resolution of the mass spectrometer, $M/\Delta M$, is 100 at 32 amu and is relatively independent of mass.

The mass selected ions intersect at 90° with the output from a fixed-frequency laser. A small portion of the resultant electrons is energy analyzed in a time-of-flight spectrometer, located mutually perpendicular to both the ion flight path and the photon direction. The resolution of the electron spectrometer, determined from the full-width half maximum of the electron peak from atomic oxygen, represented by the equation



is better than 100 meV at 2.02 eV and scales as $E^{3/2}$.

Results

A mass spectrum for the $\text{CpCo}(\text{CO})_2$ expansion in helium is shown in Figure 2.

The electron time-of-flight spectrum for $\text{CpCo}(\text{CO})_2^-$ expanded in helium and photodetached at 355 nm is shown in Figure 3. A strong threshold is observed around 1000 ns in the electron spectrum, followed by a second threshold at 1200

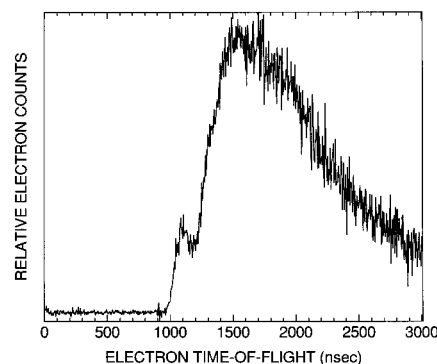


Figure 3. Electron time-of-flight spectrum for electrons photodetached, by 355 nm (3.49 eV) light, from $\text{CpCo}(\text{CO})_2^-$ expanded in helium.

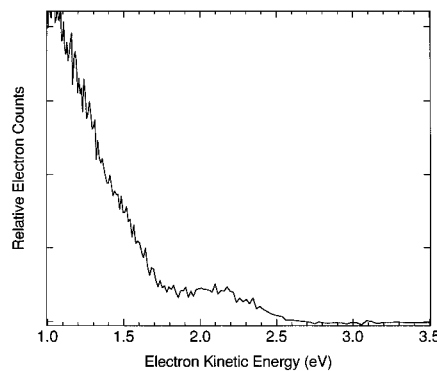


Figure 4. Electron kinetic energy spectrum for electrons photodetached, by 355 nm (3.49 eV) light, from $\text{CpCo}(\text{CO})_2^-$ expanded in helium.

ns. The electron time-of-flight spectra are converted to energy spectra by the relation:

$$t = t_0 + \sqrt{\frac{m_e}{2}} l \frac{1}{\sqrt{E_{\text{lab}}}}$$

where t_0 and l are determined from the NIPES of the calibration molecules: O_2^- and O^- at 355 nm and NO^- , O_2^- , and O^- at 532 nm. The relation between E_{lab} and E_{rel} is given by

$$E_{\text{lab}} = E_{\text{rel}} - \frac{m_e}{M} E_{\text{cm}}$$

where m_e is the mass of an electron, M is the ion mass, and E_{cm} is the center-of-mass energy of the ion. In addition the recorded intensities must be scaled by the Jacobian of the transformation

$$dt \propto \frac{dE}{E^{3/2}}$$

In Figure 4 the 355 nm (3.49 eV) fully corrected negative-ion photoelectron spectrum of $\text{CpCo}(\text{CO})_2^-$ expanded in helium is displayed. The threshold at high electron kinetic energy (e^- KE) for the first broad peak occurs at $2.6 \pm 0.2 \text{ eV e}^-$ KE, with a maximum at $2.1 \pm 0.1 \text{ eV}$. A second threshold is apparent at 1.7 eV e^- KE. When we repeat the experiment utilizing an argon, rather than a helium, expansion. The electron spectrum remains qualitatively the same, and the thresholds for the peaks in the spectrum are unchanged for the two expansion conditions.

In Figure 5 the 532 nm (2.33 eV) negative-ion photoelectron spectrum of $\text{CpCo}(\text{CO})_2^-$ expanded in helium is displayed. The threshold for the first broad peak occurs at 1.5 eV e^- KE. The second threshold is apparent at 0.55 eV e^- KE.

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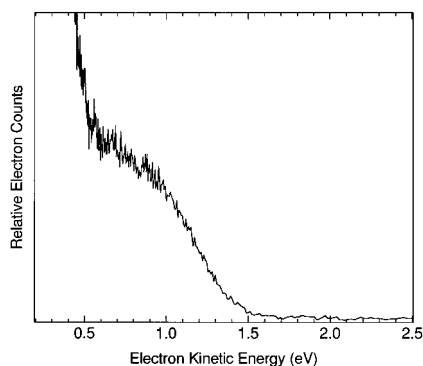


Figure 5. Electron kinetic energy spectrum for electrons photodetached, by 532 nm (2.33 eV) light, from $\text{CpCo}(\text{CO})_2^-$ expanded in helium.

Table 1. Electron Binding Energy of $\text{CpCo}(\text{CO})_2^-$.

$h\nu$ (nm)	carrier gas	first threshold e ⁻ KE (eV)	first threshold e ⁻ binding energy (eV)	second threshold e ⁻ KE (eV)	second threshold e ⁻ binding energy (eV)
532	helium	1.5 ± 0.2	0.83 ± 0.2	0.55 ± 0.2	1.78 ± 0.2
355	helium	2.6 ± 0.2	0.89 ± 0.2	1.7 ± 0.2	1.79 ± 0.2
355	argon	2.6 ± 0.2	0.89 ± 0.2	1.7 ± 0.2	1.79 ± 0.2

A laser power study indicates that the observed spectra are due to one-photon processes. The spectra are independent of laser polarization indicating that the electron distribution is isotropic.

The values for the electron binding energies are determined by subtracting the energy of the observed spectral threshold from that of the fixed-frequency laser, and the results are summarized in Table 1. By averaging the results from the two different photodetachment wavelengths, the first threshold corresponds to an electron binding energy of 0.86 ± 0.2 eV for $\text{CpCo}(\text{CO})_2^-$, while that for the second threshold is 1.79 ± 0.2 eV.

Discussion

Mass Spectra. In the mass spectra, we detect formation of $\text{CpCo}(\text{CO})^-$, $\text{CpCo}(\text{CO})_2^-$, $[\text{CpCo}(\text{CO})_2]^- \cdot \text{H}_2\text{O}$, $[\text{CpCo}(\text{CO})_2]^- \cdot 2\text{H}_2\text{O}$, $[\text{CpCo}(\text{CO})_2]_2^-$, and $[\text{CpCo}(\text{CO})_2]_3^-$, under varying experimental conditions. The clustering of $\text{CpCo}(\text{CO})_2^-$ with water is the result of the presence of residual water vapor in the gas lines leading to the pulsed valve and is an indication of the cooling in the molecular beam expansion. The observation of the binuclear complex, $[\text{CpCo}(\text{CO})_2]_2^-$, is interesting and deserves further comment since, to our knowledge, it has not been isolated before. Several related Co-binuclear complexes have been reported in the literature. These will be summarized here in order to gain insight into the structure of $[\text{CpCo}(\text{CO})_2]_2^-$.

Photolysis of $\text{CpCo}(\text{CO})_2$ in inert gas matrices led to the production of the $\text{Cp}_2\text{Co}_2(\text{CO})_2$ and $\text{Cp}_2\text{Co}_2(\text{CO})_3$ binuclear complexes. The first complex has two bridging μ -CO groups, while the second complex was proposed to have a single bridging μ -CO group.¹¹

Irradiation of $\text{CpCo}(\text{CO})_2$ in solution resulted in the formation of $\text{Cp}_2\text{Co}_2(\text{CO})_3$ which was characterized by IR and mass spectroscopies as well as elemental analysis.³³ This material contained two terminal CO ligands and one bridging μ -CO group. It was also speculated that $[\text{CpCo}(\text{CO})]_2$ was formed during these solution experiments but not isolated.

In a toluene solution at -78 °C, the ultraviolet irradiation of $\text{CpCo}(\text{CO})_2$ generated $\text{CpCo}(\text{CO})$ which dimerized to $[\text{CpCo}$

$(\mu\text{-CO})]_2$ or reacted with more of the starting material to give $\text{Cp}_2\text{Co}_2(\text{CO})_3$. In $[\text{CpCo}(\mu\text{-CO})]_2$ a Co-Co double bond was postulated.³⁴

Reduction of $\text{CpCo}(\text{CO})_2$ in tetrahydrofuran resulted in the formation of the binuclear anion $[\text{CpCo}(\text{CO})]_2^-$.³⁵ Crystals of the bis(triphenylphosphine)iminium salt of this anion were prepared, and the structure was obtained by X-ray diffraction.^{36,37} The anionic complex contained two bridging μ -CO groups, and the cobalt-to-cobalt bond length of 2.36 Å was consistent with a bond order of 1.5. Chemical and electrochemical oxidation of this anion yielded the neutral complex $[\text{CpCo}(\text{CO})]_2$. In this material the Co-Co bond order would presumably be 2.0. The anion $[\text{CpCo}(\text{CO})]_2^-$ was observed to react with CH_3I to give the neutral complex $[\text{CpCo}(\text{CO})(\text{CH}_3)]_2$ which contained two bridging μ -CO groups, and which, to satisfy the 18 electron rule, would have a Co-Co bond order of 1.0.³⁸

$[\text{CpCo}(\text{CO})]_2^-$ has also been prepared in the gas-phase by the reaction of $\text{CpCo}(\text{CO})^-$ with $\text{CpCo}(\text{CO})_2$. The parent anion, $\text{CpCo}(\text{CO})_2^-$, did not react with $\text{CpCo}(\text{CO})_2$ under the conditions used in these ICR experiments.¹⁷

The dimer $[\text{CpCo}(\text{CO})]_2^-$ was prepared by irradiating a sample of $\text{CpCo}(\text{CO})_2$ at 77 K, and the solid state ESR spectra was obtained.²² The analysis showed that the two cobalt atoms were in identical environments and that the extra electron was in an orbital of predominantly metal character (77% cobalt).

With the above information available from the literature, we can propose that one possible structure for the binuclear anion that we isolate involves two bridging carbonyl ligands and no cobalt-cobalt bond. This would be an example of a mixed valence complex where there are formally 18 electrons around one of the cobalt centers and 19 electrons around the other. We expect that the extra electron is fully delocalized over the two cobalt atoms. A possible mechanism for formation of $[\text{CpCo}(\text{CO})_2]_2^-$ is consistent with the mechanism proposed by Schore et al.³⁷ for the formation of $[\text{CpCo}(\text{CO})]_2^-$. The first step in the mechanism involves attack of $\text{CpCo}(\text{CO})_2^-$ onto a carbonyl ligand of $\text{CpCo}(\text{CO})_2$. One of the other carbonyl ligands may migrate into a μ -bridging structure forming $[\text{CpCo}(\text{CO})_2]_2^-$. This complex is stabilized in our source due to the low temperatures afforded by the supersonic molecular beam expansion. In the room temperature solution work of Schore et al., two carbonyl groups are expelled to form $[\text{CpCo}(\text{CO})]_2^-$, the product they isolated. The observation of $[\text{CpCo}(\text{CO})_2]_2^-$ completes the picture of a series of binuclear cobalt complexes that span the range of Co-Co bond orders from zero to two.

Electron Spectra. Since $\text{CpCo}(\text{CO})_2^-$ is such a large molecule we do not expect vibrational structure to be resolved using the technique of fixed-frequency negative-ion photoelectron spectroscopy. However, information about the electron affinity of $\text{CpCo}(\text{CO})_2$ can be inferred from the observed high e⁻ KE thresholds in the photodetachment spectra.

The adiabatic electron affinity, EA_{ad} , is the minimum energy required to remove an electron from the ground electronic, vibrational, and rotational state of the anion and form the corresponding neutral molecule in its ground electronic, vibra-

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tional, and rotational state, and an electron with zero kinetic energy. Since the intensities of vibrational features in NIPES spectra are determined by the Franck–Condon principle, from the maximum electron kinetic energy threshold observed in the photoelectron spectrum an upper bound to the true EA_{ad} may be inferred, as long as interferences from hot band transitions are not present. In our experiments the presence of hot bands should be minimized since the anions are formed and cooled in a molecular beam expansion. As a further verification of this assumption the experiment is carried out using two different carrier gases. Argon has been shown to cool molecular anions more efficiently than helium. The observed threshold is identical for the two expansion conditions, indicating minimal interference from hot band transitions. This test, of course, is not definitive.

The observed kinetic energy spectra are very broad indicating that the equilibrium geometries of $CpCo(CO)_2^-$ and $CpCo(CO)_2$ are significantly different. Considering both the spectral line shape and the above discussion on cooling, we assign 0.86 ± 0.2 eV as an upper bound to the EA_{ad} of $CpCo(CO)_2$.

Previously, McDonald and Schell¹⁸ assigned the electron affinity of $CpCo(CO)_2$ as 0.60 ± 0.1 eV by bracketing the electron affinity between those of biacetyl (2,3-butanedione) and carbon disulfide. In their flowing afterglow apparatus, they observed that $CpCo(CO)_2^-$ will undergo electron transfer to biacetyl but not to C_2 . The electron transfer rate to biacetyl was slow (only 14% of the collision-limited rate constant) suggesting that there may be an appreciable geometry change between $CpCo(CO)_2^-$ and $CpCo(CO)_2$ and that the electron affinity of $CpCo(CO)_2$ may be close to that of biacetyl. The electron affinity of $(H_3CC=O)_2$ is 0.69 ± 0.1 eV as determined in gas-phase electron transfer equilibria, while that for C_2 was found to be 0.51 ± 0.1 eV.^{39,40}

Some comments on the value of the electron affinity can be made through comparing it to that measured for similar molecules. We propose that $EA[CpCo(CO)_2] = 0.86 \pm 0.2$ eV. From bracketing experiments, McDonald and Schell¹⁸ have established that $EA[(\eta^3-C_3H_5)Co(CO)_3] - EA[CpCo(CO)_2]$ and that $EA[(\eta^3-C_3H_5)Co(CO)_2] = 0.9 \pm 0.2$ eV, although for the latter complex, the upper bound is not definite. Other work in our group²⁹ has established that $EA[Co(CO)_2(NO)] = 1.73 \pm 0.03$ eV. The 16-electron complex $Co(CO)_2(NO)$ has a much higher electron affinity than the 18-electron complex $CpCo(CO)_2$. Intuitively, if both molecules formed 17-electron anions, it would be expected that the electron affinities might be similar. In fact, one might argue that $CpCo(CO)_2$ would have a higher electron affinity due to the greater ability of the cyclopentadienyl group to delocalize an extra electron as compared to the nitrosyl ligand. This behavior is in contrast to what we observe experimentally. However, as there are many factors which combine to affect the EA value, this comparison does not definitively prove that $CpCo(CO)_2^-$ is a 19-electron complex.

A second point of note from the spectra is the position of the maximum in the electron counts, which is observed at 2.0 ± 0.1 eV e-KE in the 355 nm photodetachment experiment. This maximum corresponds to the first vertical ionization potential of the anion, which is defined by:

$$FIP_{vert} = -[E^-(R_e^-) - E(R_e^-)]$$

where E^- and E are the energies of the anion and neutral molecule, respectively, determined at R_e^- , the equilibrium geometry of the anion in its ground electronic, vibrational, and

rotational state. By subtracting the electron kinetic energy of the peak maximum from the laser photon energy, we obtain $FIP_{vert}[CpCo(CO)_2^-] = 1.5 \pm 0.1$ eV.

A third interesting point in the e-KE spectra is the existence of a second rise in the spectral profile, approximately 0.9 eV above the first threshold. This second feature most likely corresponds to a transition to a low lying electronic state of $CpCo(CO)_2$. Information about low lying electronic states of $CpCo(CO)_2$ is not available in the literature, and no attempt was made to identify it.

Calculations

Two computational methodologies for electronic structural calculations were at our disposal: the first was Hartree–Fock (HF) based calculations from the GAUSSIAN 94⁴¹ package; the second, the DFT based program, deMon.^{42,43}

Given the capabilities of the available computer resources, the size of the calculation, limited disk space, and convergence problems resulted in the inability to complete both post-HF calculations and any geometry optimizations. Unfortunately, this limited the scope of information available for our analyses. However, as these are, to our knowledge, the first full ab initio calculations on either $CpCo(CO)_2$ or $CpCo(CO)_2^-$ we present and comment upon our results in the spirit of an initial study.

The theoretical adiabatic electron affinity (EA_{ad}) is represented by the equation

$$EA_{ad} = [E(R_e) - E^-(R_e^-)]$$

where R_e is the geometry of the neutral molecule in its ground electronic, vibrational, and rotational state. The anion ground state geometry, however, is undetermined experimentally and proved to be impossible to optimize computationally. The geometry of $CpCo(CO)_2$, R_e , by comparison, has been experimentally established through both gas-phase electron diffraction¹⁰ and microwave spectroscopy⁴⁴ studies. Given the lack of a reasonable quantity for R_e^- we could not calculate EA_{ad} , FIP_{vert} , or an upper bound for EA_{ad} .

As the experimental geometry of $CpCo(CO)_2$ was available, the most prudent quantity to calculate was the vertical electron affinity EA_{vert} .

$$EA_{tert} = [E(R_e) - E^-(R_e)]$$

the energy difference between the neutral molecule at its equilibrium geometry, and the anion at this same geometry. This value is a lower bound on the EA_{ad} and thus a lower bound on our experimentally determined quantity.

For our calculations, we use the structure found for $CpCo(CO)_2$ by the gas-phase electron diffraction studies of Beagley et al.¹⁰ We constrain the anion to have the identical geometry. Our numbering system for the carbons in the ring is shown in Figure 6. The ring carbon that we label as number seven is in

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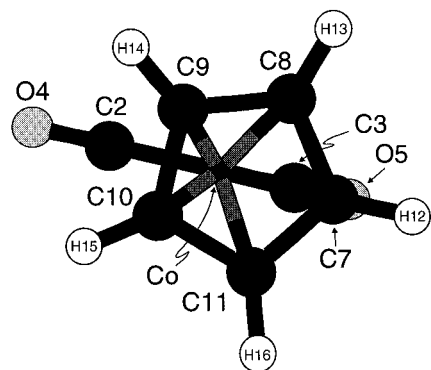


Figure 6. Geometry and labeling system for $\text{CpCo}(\text{CO})_2$ used in the electronic structure calculations. Graphic generated using: XMol, version 1.3.1, Minnesota Supercomputer Center, Inc., Minneapolis, MN, 1993.

the same plane as the $\text{Co}(\text{CO})_2$ moiety and eclipses the carbonyl group composed of carbon number 3 and oxygen number 5. Note that to analyze their ESR results both Symons and Bratt²² and Connelly et al.²³ used a geometry in which the plane of symmetry in the Cp ring bisected the $\text{OC}-\text{Co}-\text{CO}$ angle. In comparing results between the ESR work and our group, the different geometries effectively reverse the x - and y -axis labels. All DFT calculations are completed on deMon utilizing the Local Spin Density functional of Vosko, Wilk, and Musair, and a medium density grid.

The problems associated with calculating EA's of molecules have been summarized in numerous review papers.^{45–48} Of most concern is basis set choice, the determination of the extent of orbital relaxation, and the change in the magnitude of the electron correlation between the anion and the neutral molecule.

GAUSSIAN provides only effective core potential and minimum basis sets for cobalt. The best available effective core potential basis set, that is LANLDZ2, defined as Dunning/Hunzinger valence double- ζ on first row atoms, and Los Alamos effective core potential and double- ζ on second and third row atoms, was used. deMon provides numerous basis sets for cobalt, however, the largest which could support the 15 atom calculation with available disk space was the DZVP2 set. Using a program developed by Barone,⁴⁹ this basis set was converted to GAUSSIAN compatible format, thereby providing us with a decent quality full basis set for G94 calculations. While this is a reasonable basis set for producing qualitatively accurate results, a high level of quantitative accuracy could not be expected.

Relaxation can be taken into account by completing separate electronic structural calculations for the anion and the neutral molecule. HF calculations can be extended to take into account electron–electron correlation effects by using a variety of post-HF methods.⁵⁰ DFT methods, on the other hand, incorporate correlation energy within the computational methodology.⁵¹

The achieved absolute energies and subsequent vertical electron affinities from our calculations are shown in Table 2. Note that the HF/DZVP2 calculation results in a negative EA_{vert} , implying that the anion would not be stable at the geometry of $\text{CpCo}(\text{CO})_2$. The DFT/DZVP2 calculation using our best basis

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Table 2. Calculated Absolute Energies and $\text{EA}_{\text{vert}}[\text{CpCo}(\text{CO})_2]$

method	basis set	$\text{CpCo}(\text{CO})_2^-$ energy (hartree)	$\text{CpCo}(\text{CO})_2$ energy (hartree)	EA_{vert} of $\text{CpCo}(\text{CO})_2$ (eV) ^a
HF	LANLDZ2	−561.4953	−561.5255	0.82
HF	DZVP2	−1798.6668	−1798.5990	−1.85
HF	STO-3G ^a	−1779.5556	−1779.3065	−6.78
DFT	DZVP2	−1796.9707	−1797.0017	0.84

^a 1 hartree = 27.212 eV.

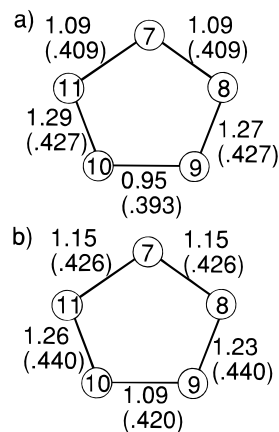


Figure 7. DFT C—C bond orders around the cyclopentadienyl ring and, in parentheses, HF Mulliken overlap populations for (a) $\text{CpCo}(\text{CO})_2$ and (b) $\text{CpCo}(\text{CO})_2^-$. The numbers enclosed in circles represent the labeling system for the ring carbons. For the calculations, the geometry of both species is constrained to be the gas-phase geometry found for $\text{CpCo}(\text{CO})_2$ (ref 10).

set generated an EA_{vert} of 0.84 eV, and we ascribe an error of ± 1.0 eV to the calculation. Recall that the calculated value should be viewed as a lower bound to the experimentally measured binding energy of 0.86 ± 0.2 eV.

Next, we investigated the structure of the Cp ring through use of the Mulliken population analysis,^{52,53} and the examination of the results had three foci: bond order, charge distribution, and the total electron population on each atom. In interpreting these results, one must remember that, in our calculation, we use identical geometries for both the anion and the neutral molecule. Thus our results for the anion reflect a qualitative picture of how the extra electron delocalizes over the experimental geometry of $\text{CpCo}(\text{CO})_2$.

The program deMon provides the Mayer bond matrix from the DFT calculations and the methodology proved to be a convenient platform in which to examine the question of ring behavior.^{54–58} The DFT bond order results are shown in Figure 7. Both the anion and the neutral molecule display a level of variance in the bond order around the ring, which is indicative of the presence of ring strain in both. However, the bond order varies from 1.09 to 1.25 in the anion with an average and standard deviation of 1.18 ± 0.07 . By comparison, the bond orders in the neutral molecule range from 0.95 to 1.29 with an average of 1.14 ± 0.14 , indicating that the ring C—C bond orders have less variance in the anion than in the neutral species. The total bond order around the ring is 5.84 in the anion and 5.69 in the neutral molecule. These results suggest that the

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Table 3. DFT Bond Orders and HF Mulliken Overlap Populations

bond ^a	DFT bond orders		HF Mulliken overlap populations	
	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻
Co– ⁷ C	0.47	0.33	0.128	0.100
Co– ⁸ C	0.36	0.34	0.026	–0.003
Co– ⁹ C	0.43	0.34	0.055	0.037
Co– ¹⁰ C	0.42	0.33	0.055	0.037
Co– ¹¹ C	0.35	0.34	0.026	–0.003
Co– ² CO	1.32	1.47	0.148	0.207
Co– ³ CO	1.28	1.43	0.135	0.172
² C– ⁴ O	2.17	2.06	0.550	0.407
³ C– ⁵ O	2.24	2.13	0.576	0.487

^a Superscripts refer to the labeling system of Figure 6.

bonding around the ring in the anion is more symmetrical, approaching that of the ideal fully conjugated moiety, than in the neutral molecule. Similar trends are evident in examining the differences in the Co–C(ring) bond order matrix elements shown in Table 3. The overall bond order of the ring to the cobalt decreases significantly from 2.03 in the neutral molecule, to 1.69 in the anion. For the neutral molecule, the average bond order between a ring carbon and the cobalt atom is 0.41 ± 0.05 , while in the anion the average bond order becomes 0.34 ± 0.005 , a 10-fold decrease in the standard deviation.

The trends in the behavior of the cyclopentadienyl ligand that we have seen from our DFT/DZVP2 calculations are also reflected in the results for the lower level HF/DZVP2 calculations from the G94 program; however, the differences are not quite so pronounced. The charge distribution around the cyclopentadienyl ligand is more uniform in the anion than in the neutral molecule. This point is demonstrated by the Mulliken overlap populations between the carbons of the ring as shown in Figure 7. In the neutral molecule the average electron overlap population for each C–C neighbor is 0.413 ± 0.014 , while that in the anion is 0.430 ± 0.009 . From examination of the Co–C overlap populations tabulated in Table 3, it is apparent that the Cp ligand is less firmly bound to the cobalt atom in CpCo(CO)₂⁻ than in CpCo(CO)₂.

Presented in Table 4 are the total Mulliken electron populations as calculated using DFT/DZVP2. The atomic charges are determined by subtracting the Mulliken population from the total number of electrons in the ground state of the free neutral atom.⁵² These are also tabulated in Table 4, along with the atomic charges calculated using HF/DZVP2. Both methodologies give the same result: a substantial portion of the excess electron density in the anion resides on the cyclopentadienyl ligand. From the DFT (HF) calculations, the carbons of the ring in the anion hold 0.38e (0.26e) excess electron population compared to the neutral molecule.

In summary, the results from the DFT based bond orders and the HF based overlap populations independently confirm that the Cp ligands of both the anion and the neutral molecule have an allyl-ene structure. Furthermore our calculations concur with the work of Connelly et al.²³ that the extent of this distortion is less pronounced in CpCo(CO)₂⁻ than in CpCo(CO)₂. In the anion the carbons of the Cp ligand are symmetrically bound to the cobalt atom, approaching that observed in a true η^5 -bound ligand.

We return to the Mayer bond order matrix results in Table 3 to examine the changes that occur in the carbonyl ligands. The C–O bonds in the carbonyl groups are weakened in the anion as compared to the neutral molecule with the DFT bond orders changing from 2.17 and 2.34 in the neutral molecule to 2.06 and 2.13 in the anion. However, the Co–CO bond orders increase from 1.32 and 1.28 in CpCo(CO)₂ to 1.47 and 1.42 in

the anion indicating a strengthening of the metal–carbonyl bond due to increased back-bonding from the cobalt atom into the π^* -orbitals of the carbonyl groups in the anion. The HF Mulliken overlap populations display the same behavior. The Co–CO overlap population increases in the anion relative to the neutral molecule, whereas the C–O overlap populations decrease. These results are also tabulated in Table 3.

The change in the extent of back-bonding is also reflected in the orbital decomposition of the total Mulliken populations for the two species involved. The DFT based program deMon describes atomic orbitals through the use of Cartesian Gaussian functions.⁵⁹ The delocalization of the extra electron on the anion is examined by subtracting the orbital populations of the anion from that of the neutral molecule. The Mulliken population of the cobalt atom in the anion is 0.11e higher than that on the neutral molecule, while net gains of 0.34e and 0.55e are found on the carbonyl and Cp (including both C and H changes) ligands, respectively. The gains in electron population exhibit strong directional preferences. On the ligands the gross increases are almost exclusively in the p_x (0.48e) and p_z (0.40e) orbitals. By comparison the populations in the p_y orbitals increase by 0.09e on the carbonyl ligands and decreased by 0.01e on the Cp ring. On the cobalt atom, the increases are almost exclusively in the d_{xx} (0.14e) and d_{zz} (0.14e) orbitals, with losses in population (average loss is 0.05e) occurring on the other d-orbitals.

Qualitatively these results present a picture where the extra electron in CpCo(CO)₂⁻ is predominantly delocalized in the xz -plane. This is in agreement with the work of Symons and Bratt²² and that of Connelly et al.²³ as long as the differing geometries are taken into account. The xz -plane is the plane of symmetry of the constrained geometry that we have chosen, containing within it the Co(CO)₂ group and the carbon atom labeled number 7 in the Cp ring. The Mulliken analysis shows that the “19th electron” significantly delocalizes into the carbonyl ligands as well as onto the cyclopentadienyl group. The results suggest that a significant geometry change should occur in both these groups. We were not able to explore this further due to our inability to obtain optimized geometries.

One further point of note in the Mulliken population analyses tabulated in Table 4 is that the DFT calculation assigns a total of 27.53 electrons to the cobalt atom in CpCo(CO)₂⁻ as compared to 27.42e on the cobalt center in the neutral complex. This 0.53e excess electron density on the cobalt atom in the anion is consistent with the ESR results by Symons and Bratt²² and Connelly et al.,²³ who determined that there was 55% excess electron population on the cobalt atom.

The final DFT result that we shall mention is that the calculated free valence on the cobalt atom is 0.22e out of a total free valence of 0.28e on the whole anion. With this result for the free valence, and the above observation that the cobalt atom holds 53% of the excess electron population, and the bond order and overlap population analyses indicating that the cyclopentadienyl ring is symmetrically bound, we propose that CpCo(CO)₂⁻ should be categorized as a true 19-electron complex.

Conclusions

The impact of 1 keV electrons on the expansion region of a pulsed molecular beam of CpCo(CO)₂, seeded in helium or argon, results in the formation of gas-phase CpCo(CO)₂⁻. Furthermore, we observe the binuclear anion [CpCo(CO)₂]₂⁻ and to our knowledge this is the first observation of this cluster.

Table 4. Total Mulliken Populations and Atomic Charges

<i>a</i>	DFT total mulliken populations		DFT atomic charges		HF atomic charges	
	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻	CpCo(CO) ₂ ⁻
Co	27.415	27.526	-0.415	-0.526	-0.354	-0.368
² C	5.709	5.779	0.291	0.221	0.374	0.162
³ C	5.806	5.871	0.194	0.129	0.321	0.210
⁴ O	8.254	8.359	-0.254	-0.359	-0.309	-0.448
⁵ O	8.229	8.331	-0.229	-0.331	-0.298	-0.419
⁷ C	6.057	6.121	-0.057	-0.121	-0.049	-0.077
⁸ C	6.104	6.189	-0.104	-0.189	0.020	-0.052
⁹ C	6.027	6.095	-0.027	-0.095	0.001	-0.044
¹⁰ C	6.020	6.095	-0.020	-0.095	0.001	-0.044
¹¹ C	6.100	6.187	-0.100	-0.187	0.020	-0.052
¹² H	0.862	0.896	0.1379	0.104	0.055	0.029
¹³ H	0.851	0.885	0.149	0.115	0.053	0.025
¹⁴ H	0.854	0.886	0.146	0.114	0.055	0.027
¹⁵ H	0.857	0.890	0.143	0.110	0.055	0.027
¹⁶ H	0.855	0.891	0.145	0.109	0.053	0.025

^a Superscripts refer to the labeling system of Figure 6.

The electron binding energy of CpCo(CO)₂⁻ is 0.86 ± 0.2 eV. This corresponds to an upper bound to the EA_{ad}[CpCo(CO)₂].

A DFT/DZVP2 level calculation is completed, and a value of 0.84 ± 1.0 eV for the EA_{vert}[CpCo(CO)₂] is determined. EA_{vert} corresponds to a lower bound for EA_{ad}[CpCo(CO)₂].

The examination of the Mulliken population analyses through both the Mayer bond order matrices and the overlap populations demonstrates that the electrons are more evenly distributed within the carbons of the ring in CpCo(CO)₂⁻ than in the neutral molecule. Our theoretical results show that the distortion in the cyclopentadienyl ring is relieved in the anion compared to that in the neutral molecule. The alleviation of the ring

distortion in the anion relative to the neutral molecule occurs simultaneously with an increase in back-bonding from the cobalt atom into the carbonyl π^* -orbitals.

Our results are consistent with classification of CpCo(CO)₂⁻ as a true 19-electron complex.

Acknowledgment. his work is supported by funding from NSERC (Canada) and UBC start-up funds. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. I.M.W. thanks Professor D. P. Chong for discussions about relaxation and correlation energies.

JA9627508