terpyridine complex, since the ground state of $Co(terpy)_2^{2+}$ is of the $t_{2g}^6e_g^1$ electron configuration.

The oxidation of $Ti(H_2O)_5OH^{2+}$ by $Co(phen)_3^{3+}$, $Co(terpy)_2^{3+}$, and $Co(bpy)_3^{3+}$ proceeds by similar rates (if the latter is corrected for the differences in ionic strength). It appears that the reorganization energy associated with the spin change in these cobalt couples makes a very small contribution to the activation energies and does not influence the rate of the reaction with titanium(III). This observation is not surprising. The standard redox potentials of the cobalt couples considered here have close values[18,19] as have rates of the self-exchange.[20] Similarly, not very different rates were observed for the oxidation of $Co(phen)_3^{2+}$, $Co(terpy)_2^{2+}$, and $Co(bpy)_3^{2+}$ by the common oxidizing agent *trans*-$Co(py)_4Cl_2^+$.[18] The lack of a significant influence of the spin change in these cobalt couples on the reduction rate of the cobalt(III) complexes or on the oxidation rate of the cobalt(II) complexes has been rationalized by the nature of the phenanthroline, terpyridine, and bipyridine ligands. The similar kinetic behavior is most likely caused by delocalization of the cobalt electrons by the unsaturated ligands, which buries an effect of the spin change. Further evidence questioning the "multiplicity barrier" in the reduction of Co(III) has been reported recently.[21] The kinetic effect of the unsaturated ligands vs. saturated ligands is seen by inspection of the rates presented in Table III. The $Co(phen)_3^{3+}$, $Co(terpy)_2^{3+}$, and $Co(bpy)_3^{3+}$ ions oxidize $Ti(H_2O)_5OH^{2+}$ for three orders of magnitude faster than does the $Co(NH_3)_6^{3+}$ ion. This is consistent with a much slower rate of electron exchange between $Co(NH_3)_6^{3+}$ and $Co(NH_3)_6^{2+}$ and with the calculation demonstrating high-energy contribution of the spin change to the activation energy of this electron-exchange reaction.[17]

Registry No. $Co(phen)_3^{3+}$, 18581-79-8; $Co(terpy)_2^{3+}$, 19137-07-6; Ti^{3+}, 22541-75-9; hexaaquatitanium(III), 17524-20-8; $Ti(H_2O)_5OH^{2+}$, 54630-67-0.

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Negative Ion Chemistry of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ in the Gas Phase by Ion Cyclotron Resonance Spectroscopy. The π-Acceptor Ability of PF_3 Compared to CO

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The gas-phase negative ion chemistry of $(\eta^5\text{-}C_5H_5)Co(CO)_2$ is studied using the techniques of ion cyclotron resonance spectroscopy. Attachment of trapped electrons leads to the formation of $CpCo(CO)_2^-$ and $CpCo(CO)^-$. While the molecular anion is unreactive, $CpCo(CO)^-$ reacts with the neutral precursor to yield $[CpCo(CO)]_2^-$, which has been previously characterized in solution. The first observed example of a ligand displacement reaction involving an anionic transition-metal complex, in which PF_3 displaces CO from $CpCo(CO)^-$, is reported and leads directly to the conclusion that PF_3 is a stronger π-acceptor ligand than CO toward $CpCo^-$ in the gas phase. Nitric oxide reacts with both $CpCo(CO)^-$ and $CpCo(CO)_2^-$ to yield the very stable anion $CpCo(NO)^-$, which is isoelectronic with CpNiNO. π acids weaker than CO (C_2F_4, HCN, ethylene oxide, MeCN, NH_3, NMe_3, and PMe_3) were not observed to react with $CpCo(CO)^-$. The relative contribution of σ and π bonding in the metal–ligand bonds of $CpCoB^-$ and $CpNiB^+$ is discussed. Reactions of the anions F^- and CD_3O^- with $CpCo(CO)_2$ are briefly considered.

Introduction

While the study of transition-metal complexes using the techniques of ion cyclotron resonance spectroscopy (ICR) is a rapidly expanding field of endeavor,[1-7] the results reported to date deal predominantly with the thermochemical properties and reactions of cationic species.[1-5] Only a very few reports have appeared concerning the negative ion chemistry of transition-metal complexes, and these deal almost exclusively with the photodecomposition spectra[6] and condensation reactions of metal carbonyls.[3-7] Negative ion–molecule reactions have also been observed in the high-pressure ($>5 \times 10^{-6}$ Torr) mass spectra of chromium oxyhalides[8] and perchloroalkylmercury compounds.[9] Neither ligand-displacement nor condensation reactions have been observed for the nickelocene anion, Cp_2Ni^{2-}, or for $Fe(CO)_4^{3-}$, with a variety of simple molecules. Reactions of several anionic species (F^-, $C_2H_5O^-$) with $Fe(CO)_5$, which result in the formation of tetracoordinate 16-electron products, have been investigated.[3]

The present work describes an ICR study of the negative ion chemistry of $(\eta^5\text{-}C_5H_5)Co(CO)_2$, both alone and in mixtures with other molecules. Processes which are of particular interest include the formation of binuclear cobalt complexes which have been observed and characterized in solution.[10-12] The reactions of a series of π acids with cobalt-containing anions and of anions with neutral $CpCo(CO)_2$ are presented. Processes observed in the former instance include the first examples of ligand-displacement reactions involving transition-metal anionic complexes. These studies permit an assessment of the relative π-acceptor abilities of ligands in the gas phase. A previous investigation of the mass spectrometry[13] of $CpCo(CO)_2$ provides information useful in the interpretation of the present results.

Experimental Section

The theory and instrumentation of ICR mass spectrometry have been previously described.[14-16] This work employed an instrument constructed at Caltech equipped with a 15-in. electromagnet capable

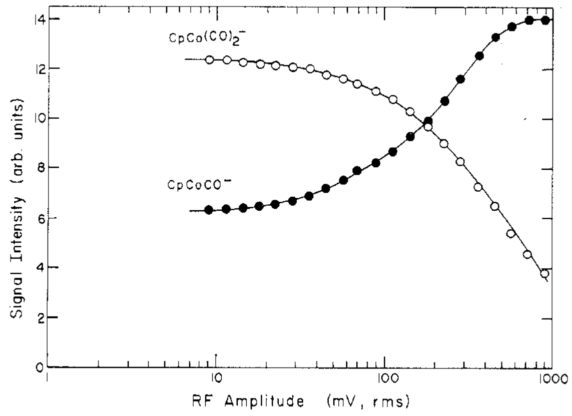


Figure 1. Change in the negative ion mass spectrum of CpCo(CO)$_2$ at 70 eV and 5.0 × 10^{-7} Torr upon radio frequency heating of the electrons scattered and trapped in the ICR cell.

of a maximum field strength of 23.4 kG.

Cyclopentadienylcobalt dicarbonyl was obtained commercially (Alfa Products, Ventron Corp.) and used without further purification; no impurities were observed in the positive ion ICR mass spectrum at 70 eV, which is in excellent agreement with the reported mass spectrum.[13] Because of the high vapor pressure of CpCo(CO)$_2$ at 25 °C (mp −22 °C)[17] the sample was kept in an ice-water bath during use to prevent condensation in the spectrometer inlet. All other chemicals used in this study were readily available from commercial sources. Before use, each sample was degassed by repeated freeze–pump–thaw cycles.

Pressures were measured with a Schulz–Phelps type ion gauge calibrated against an MKS Baratron Model 90H1-E capacitance manometer in a manner previously described.[18] The estimated uncertainty in absolute pressures, and thus in all rate constants reported, is ±20%. All experiments were performed at ambient temperature (20–25 °C). CpCo(CO)$_2$ is well-behaved in the ICR spectrometer and no experimental difficulties were encountered.

Low-energy dissociative electron attachment processes yield F$^-$ from NF$_3$, CN$^-$ from HCN, and I$^-$ from HI.[19] CD$_3$O$^-$ and Cl$^-$ ions are produced by thermal electron attachment to methyl-d_3 nitrite[20] and carbon tetrachloride,[19] respectively. CD$_3$O$^-$ anions react with neutral CD$_3$ONO to form NO$_2^-$.[21] Methyl-d_3 nitrite was prepared from the corresponding alcohol using standard methods.[22]

Results

Negative Ions. The negative ion ICR mass spectrum of CpCo(CO)$_2$ at 1.7 × 10^{-6} Torr and an electron beam energy of 70 eV agrees qualitatively with that reported by Winters and Kiser.[13] The ions observed and their relative abundances are CpCo(CO)$_2^-$ (84%) and CpCo(CO)$^-$ (16%). The molecular anion, CpCo(CO)$_2^-$, is formed by capture of low-energy electrons scattered and trapped in the ICR cell and appears to have an essentially infinite lifetime against autodetachment; the observed behavior is quite analogous to that exhibited by Cp$_2$Ni[2] and SF$_6$.[23] A low-energy dissociative electron attachment process[19] generates CpCo(CO)$^-$ from CpCo(CO)$_2$. Ions of the formulas (C$_5$H$_4$)Co(CO)$_n^-$ and (C$_5$H$_3$)Co(CO)$_n^-$ (n = 1, 2) are not detected in the present experiments, although they were proposed in an earlier low-resolution study.[13]

The relative abundances of CpCo(CO)$_2^-$ and CpCo(CO)$^-$ are strongly dependent on the electron energy distribution. This is demonstrated in an experiment in which a nonresonant radio frequency electric field is used to excite electrons scattered and trapped in the ICR cell.[24] With CpCo(CO)$_2$ at 5.0 × 10^{-7} Torr and an electron beam energy of 70 eV, the abundance of CpCo(CO)$^-$ increases at the expense of CpCo(CO)$_2^-$ as the rf amplitude is increased (Figure 1). The total production of anions, as given by the sum of the CpCo(CO)$_2^-$ and CpCo(CO)$^-$ signal intensities, remains constant. The coupling between the rf field (~7.1 MHz) and the electron motion is very weak, as strong coupling leads to electron ejection,[14,15,24] in which case the total yield of anions decreases. These results are consistent with the dissociative electron attachment process (eq 1) being slightly endothermic.[25]

$$\mathrm{CpCo(CO)_2 + e^- \rightarrow CpCo(CO)^- + CO} \qquad (1)$$

The possibility that the reverse of eq 1 occurs (associative detachment) was briefly investigated. Addition of excess CO did not lead to an increase in CpCo(CO)$_2^-$ at the expense of CpCoCO$^-$ (i.e., the reverse of eq 1 and subsequent electron capture).

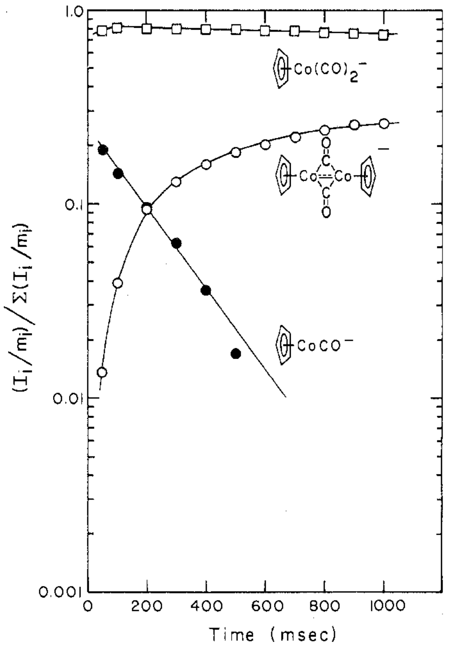


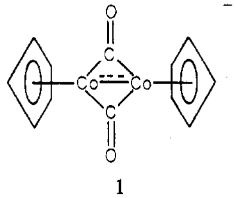
Figure 2. Temporal variation of ion abundance in CpCo(CO)$_2$ at 4.4 × 10^{-7} Torr following ionization by a 70-eV, 10-ms electron beam pulse.

Negative Ion Chemistry of CpCo(CO)$_2$. Figure 2 presents the temporal variation of relative ion abundance for CpCo(CO)$_2$ at 4.4 × 10^{-7} Torr following a 70-eV, 10-ms electron-beam pulse. Double-resonance experiments[14,15] unambiguously identify the condensation reaction 2 as occurring

$$\mathrm{CpCo(CO)^- + CpCo(CO)_2 \rightarrow [CpCo(CO)]_2^- + CO} \qquad (2)$$

in this system. From the slope for the disappearance of CpCo(CO)$^-$ with time, the rate constant of reaction 2 is calculated to be k = 3.2 × 10^{-10} cm^3 molecule^{-1} s^{-1}. The molecular anion, CpCo(CO)$_2^-$, is unreactive.

The dimer ion [CpCo(CO)]$_2^-$ (**1**) has been prepared in



1

solution by the sodium amalgam reduction of CpCo(CO)$_2$.[10] The structure of **1** has been determined by x-ray crystallography of the PPN$^+$ salt, [P(C$_6$H$_5$)$_3$]$_2$N$^+$[CpCo(CO)]$_2^-$, and an unusually short Co–Co bond is found,[26] consistent with molecular orbital predictions of partial double-bond character.[12] The ESR spectrum of PPN$^+$[CpCo(CO)]$_2^-$ indicates that the unpaired electron is shared equally by both cobalt nuclei and suggests that [CpCo(CO)]$_2^-$ may be considered as a mixed-valence complex.[11,12,27]

Reactions of Cobalt Anions with Strong π-Acceptor Ligands. Mixtures of CpCo(CO)$_2$ with the two π-acceptor ligands NO

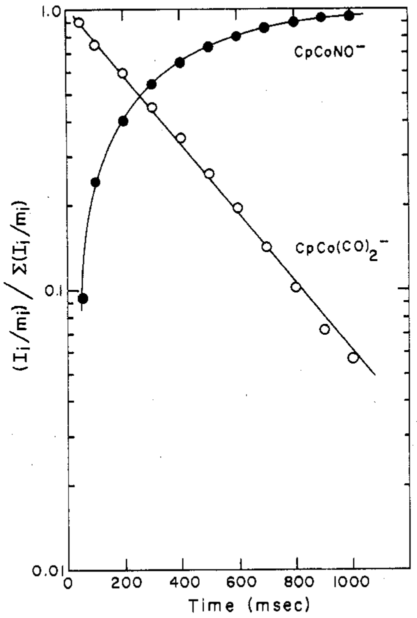


Figure 3. Temporal variation of ion abundance in an 8:1 mixture of NO and $CpCo(CO)_2$ following a 70-eV, 10-ms electron beam pulse at a total pressure of 4.3×10^{-6} Torr.

and PF_3 were studied, principally to elucidate ligand-exchange reactions occurring in these systems.

Figure 3 presents the temporal variation of relative ion abundance in a 8.2:1 mixture of NO and $CpCo(CO)_2$ following a 70-eV, 10-ms electron beam pulse at a total pressure of 4.2×10^{-6} Torr. The only reaction observed in this mixture is the NO displacement of both CO molecules from the molecular anion (eq 3), with a rate constant of $k = 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. At lower NO pressures (ca. (5–10) $\times 10^{-7}$ Torr), both $CpCo(CO)^-$ and consequently $[CpCo(CO)]_2^-$ (eq 2) are observed. Double-resonance experiments verify that $CpCo(CO)^-$ reacts with NO to produce $CpCo(NO)^-$ (eq 4), while $[CpCo(CO)]_2^-$ is unreactive toward ligand substitution by NO. The species $CpCo(NO)^-$ is isoelectronic with CpNiNO[1] and as such is expected to be a very stable 18-electron diamagnetic anion. The neutral dimer of $CpCo(NO)^-$, $[CpCo(NO)]_2$, has been synthesized in solution and characterized by mass spectrometry.[28] $CpCo(NO)^-$ has been prepared by introducing sodium amalgam to a solution of $[CpCo(NO)]_2$.[29]

$$CpCo(CO)_2^- + NO \rightarrow CpCo(NO)^- + 2CO \qquad (3)$$

$$CpCo(CO)^- + NO \rightarrow CpCo(NO)^- + CO \qquad (4)$$

Perhaps the most interesting reactions of $CpCo(CO)^-$ are observed in mixtures of $CpCo(CO)_2$ and PF_3. Figure 4 presents the temporal variation of relative ion abundance in a 4.8:1 mixture of PF_3 with $CpCo(CO)_2$ following a 70-eV, 10-ms electron beam pulse at a total pressure of 5.8×10^{-6} Torr. Double-resonance experiments[14,15] conclusively indicate that the sequence of reactions 2, 5, and 6 occurs in this system.

$$CpCo(CO)^- + PF_3 \rightarrow CpCo(PF_3)^- + CO \qquad (5)$$

$$CpCo(PF_3)^- + PF_3 \rightarrow CpCo(PF_3)_2^- \qquad (6)$$

The addition of PF_3 to $CpCo(CO)_2$ causes two new ions, $CpCo(PF_3)^-$ and $CpCo(PF_3)_2^-$, to appear in addition to $[CpCO(CO)]_2^-$ which is present in $CpCo(CO)_2$ alone (reaction 2). Although many examples of cationic ligand-displacement reactions are known,[1,3,4,30] reaction 5, in which PF_3 displaces CO from $CpCoCO^-$ ($k = 5.3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}), is the first-observed example of an anionic ligand-displacement reaction. The species $CpCo(PF_3)^-$ further reacts with PF_3 (eq 6, $k = 4.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) to produce $CpCo(PF_3)_2^-$ which is analogous to the molecular anion $CpCo(CO)_2^-$ where both carbonyls have been replaced by PF_3. The neutral species $CpCo(PF_3)_2$ has been synthesized in solution by the reaction of cobaltocene with PF_3,[31] and considerable π-bonding contribution to the Co–P bond was found from interpretation of the IR spectrum, consistent with the similar conclusion reached from these results. The molecular anion $CpCo(CO)_2^-$ accounts for ~85% of the total ionization in the $CpCo(CO)_2$–PF_3 mixture. A small fraction of the parent anion, possibly with excess internal energy, reacts to produce $CpCo(CO)PF_3^-$ (eq 7) in <1% yield. Neither $CpCo(CO)_2^-$ nor $CpCo(CO)PF_3^-$ is included in the normalization of data presented in Figure 4.

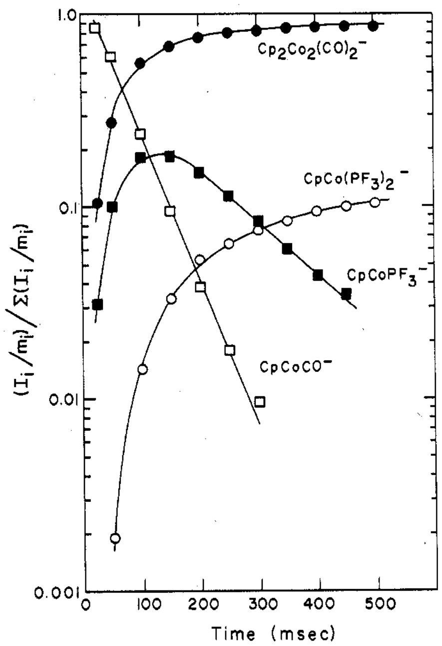


Figure 4. Temporal variation of ion abundance in a 4.8:1 mixture of PF_3 and $CpCo(CO)_2$ following a 70-eV, 10-ms electron beam pulse at a total pressure of 5.8×10^{-6} Torr.

$$CpCo(CO)_2^- + PF_3 \rightarrow CpCo(CO)PF_3^- + CO \qquad (7)$$

A mixture of $CpCo(CO)_2$, PF_3, and NO was examined with the purpose of determining the preferred direction of ligand displacement (reaction 8). While both the $CpCo(PF_3)^-$ and $CpCo(NO)^-$ anions are observed in this mixture, double-resonance experiments[14,15] indicate that neither the forward nor reverse reactions (eq 8) occur. The failure to observe either of these reactions is not particularly well understood, especially for the forward reaction since NO is a stronger π acid than PF_3,[32] but is possibly because the reactions are too slow to observe ($k < 10^{-11}$ cm^3 molecule^{-1} s^{-1}) using ICR techniques.[14]

$$CpCo(PF_3)^- + NO \rightleftharpoons CpCo(NO)^- + PF_3 \qquad (8)$$

Reactions of Cobalt Anions with Weak π-Acceptor Ligands. Mixtures of $CpCo(CO)_2$ with a wide variety of weak π-acceptor ligands were investigated. The ligands included C_2F_4, HCN, ethylene oxide, MeCN, NH_3, NMe_3, and PMe_3, all of which are much weaker π acids than NO, PF_3, and CO.[32,33] In no instance are ligand-displacement reactions analogous to eq 5 observed. In fact, the yield of *any* product ions from the reactions of $CpCo(CO)_2^-$ and $CpCo(CO)^-$ with the weak π-acceptor ligands was so small as to be undetectable in these experiments.

Reactions of Anions with $CpCo(CO)_2$. The ion chemistry of a variety of anions of differing proton affinity[21] (kcal/mol), including CD_3O^- (376.8), F^- (371.3), CN^- (348.9), NO_2^-

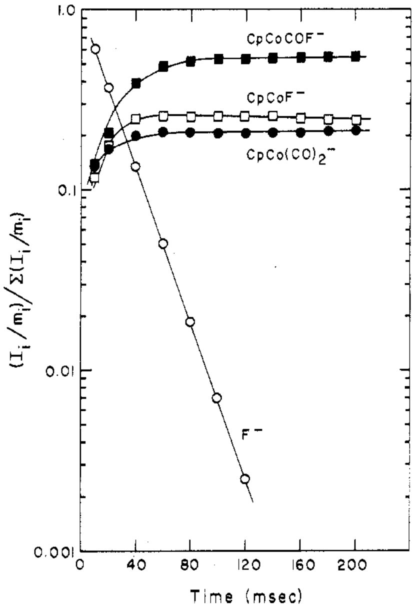


Figure 5. Temporal variation of ion abundance in a 9:1 mixture of NF_3 and $CpCo(CO)_2$ following a 70-eV, 10-ms electron beam pulse at a total pressure of 5.0×10^{-6} Torr.

(340.0), Cl^- (333.3), and I^- (314.4) with $CpCo(CO)_2$, was studied. Only F^- and CD_3O^- were reactive with $CpCo(CO)_2$; the remaining anions were unreactive and no product ions were detected. Figure 5 shows the temporal variation of ion abundance in a 9:1 mixture of NF_3 and $CpCo(CO)_2$ following a 70-eV, 10-ms electron beam pulse at a total pressure of 5.0×10^{-6} Torr. F^- produced by the dissociative attachment of electrons to NF_3[19,34] is the reactive anion in this mixture, producing the $CpCo(CO)F^-$ (eq 9; $k = 2.1 \times 10^{-9}$ cm^3

$$F^- + CpCo(CO)_2 \xrightarrow{68\%} CpCo(CO)F^- + CO \qquad (9)$$

$$F^- + CpCo(CO)_2 \xrightarrow{32\%} CpCo(F)^- + 2CO \qquad (10)$$

molecule^{-1} s^{-1}) and $CpCo(F)^-$ (eq 10; $k = 9.9 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}) ions. Neither $CpCo(CO)^-$ nor $[CpCo(CO)]_2^-$ is observed in this system. This indicates that excess NF_3 efficiently scavenges epithermal electrons necessary for the formation of $CpCo(CO)^-$.[34]

Processes analogous to reactions 9 and 10 produce $CpCo(CO)OCD_3^-$ and $CpCo(OCD_3)^-$ in a mixture of $CpCo(CO)_2$ and CD_3ONO (eq 11, 12). The CpCo-

$$CD_3O^- + CpCo(CO)_2 \xrightarrow{84\%} CpCo(CO)OCD_3^- + CO \qquad (11)$$

$$CD_3O^- + CpCo(CO)_2 \xrightarrow{8\%} CpCo(OCD_3)^- + 2CO \qquad (12)$$

$$CD_3O^- + CpCo(CO)_2 \xrightarrow{8\%} CpCo(CO)_2OCD_3^- \qquad (13)$$

$(CO)_2OCD_3^-$ ion formed in the bimolecular condensation of CD_3O^- with $CpCo(CO)_2$ is also observed (eq 13).

Discussion

The present result that both PF_3 and NO displace CO from $CpCo(CO)^-$ (eq 4, 5) demonstrates the feasibility of employing ICR techniques to investigate ligand-displacement reactions involving anionic transition-metal complexes. While photoelectron spectroscopy of $Ni(PF_3)_4$[32,35] and a series of chromium, maganese, and iron trifluorophosphine metal complexes[36] indicates that PF_3 is as strong a π acid as CO, or stronger,[36] these results unambiguously show that PF_3 is a better π acceptor than CO toward $CpCo^-$, or $D(PF_3–CpCo^-) > D(CO–CpCo^-)$. The result that π acids such as C_2F_4, MeCN, and PMe_3 do not displace CO from $CpCo(CO)^-$ indicates that $D(CO–CpCo^-) > D(B–CpCo^-)$ or that these ligands, B, are weaker π acids than CO. This conclusion has been previously verified by measurement of carbonyl stretching frequencies in π-acceptor substituted metal complexes.[32] Conversely, these results indicate that $D(B–CpCo^-)$ is predominantly dependent upon the π-acceptor ability of B and that the σ-donor ability of B plays a much less important role in $D(B–CpCo^-)$.

Figure 6. Qualitative description of metal–ligand bonding in $CpCo^-$ and $CpNi^+$.

Precisely the opposite effects are present in the bonding of n-donor ligands to $CpNi^+$.[1,4] In this system the dissociative bond energy $D(B–CpNi^+)$ is largely determined by the σ-donor ability of B, while π-bonding effects, where they occur, are much less important, and account for only ~10% of $D(B–CpNi^+)$.[14] PF_3 and CO are very poor σ donors,[37] so that both $D(PF_3–CpNi^+) \approx 42 \pm 5$ kcal/mol[38] and $D(CO–CpNi^+) \approx 40 \pm 5$ kcal/mol[5] are much less than $D(NH_3–CpNi^+) = 52.3 \pm 2.0$ kcal/mol[1,4] and $D(Me_3P–CpNi^+) = 57.6 \pm 2.0$ kcal/mol.[1,4] A qualitative picture of these two different metal–ligand bonding schemes for $CpCo^-$ and $CpNi^+$ is presented in Figure 6. These results suggest that by starting with a cyclopentadienylcobalt complex with weakly bound π-acceptor ligands [e.g., $CpCo(PMe_3)_2$ or $CpCo(P(C_6H_5)_3)_2$],[32] a quantitative scale of π-acceptor ability can be measured using ICR techniques, as such scales for H^+,[39] Li^+,[30] and $CpNi^+$ [1,4] have been constructed.

The results concerning formation of the cobalt dimer anion $[CpCo(CO)]_2^-$ are of particular interest because the scheme of reaction 2, verified by double-resonance methods,[14,15] is exactly the same as the mechanism proposed to occur in solution.[10] This demonstrates the utility of ICR techniques in elucidating anionic reaction mechanisms which have solution analogues.

Reactions of the strong bases F^- and CD_3O^-[21] lead to formation of substituted anionic even-electron cyclopentadienylcobalt species, $CpCo(CO)_nX^-$ ($n = 0–2$). The anions CN^-, NO_2^-, Cl^-, and I^- are not observed to react with $CpCo(CO)_2$. This result may reflect the much weaker gas-phase basicity of these species as compared to F^- and CD_3O^-.[21]

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Registry No. $CpCo(CO)_2$, 12078-23-8; $CpCo(CO)_2^-$, 64236-04-0; $CpCo(CO)^-$, 64236-03-9; $[CpCo(CO)]_2^-$, 58543-12-7; $CpCo(NO)^-$, 64236-02-8; $CpCo(PF_3)_2^-$, 64236-01-7; $CpCo(PF_3)^-$, 64236-00-6; $CpCo(CO)F^-$, 64235-99-0; $CpCoF^-$, 64235-98-9; $CpCo(CO)OCD_3^-$, 64235-97-8; $CpCo(OCD_3)^-$, 64235-96-7; $CpCo(CO)_2OCD_3^-$, 64235-95-6; PF_3, 7783-55-3; NO, 10102-43-9; CD_3O^-, 51679-31-3; NF_3, 7783-54-2.

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Determination of the Mechanism for the Aquation of Cobalt(III) and Chromium(III) Pentaammine Complexes by the Use of a Volume Profile Diagram

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The rate of aquation of $Co(NH_3)_5Me_2SO^{3+}$ was measured as a function of pressure up to 1.5 kbar at 25 °C and at an ionic strength of 0.1 M. The volume of activation was found to be -1.7 ± 0.7 cm^3 mol^{-1}. The partial molar volumes of a series of $Co(NH_3)_5X^{(3-n)+}$ complexes were determined at 25 °C, where $X^{n-} = F^-, Cl^-, I^-, SO_4^{2-}, NO_3^-, NCS^-, N_3^-$, Me_2SO, OH_2, and NH_3. These values were combined to formulate a volume equation from which the volume of a hypothetical transition state, formed according to a dissociative mechanism, could be calculated. The partial molar volume of the appropriate hexaammine complex was then used to test the validity of the proposed mechanism. This treatment confirmed the assignment of an I_d or D mechanism to the cobalt system and an I_a mechanism to the chromium system.

Introduction

The spontaneous reactions of pentaamminecobalt(III) complexes have been extensively investigated[1] using a wide variety of approaches[2–6] to establish the underlying mechanism. The mechanism is now commonly accepted to be dissociative in character with the bulk of recent evidence[2–5] pointing to the I_d type. Consequently these reactions represent a model system for testing the reliability of a different approach. Despite the almost equally abundant kinetic data[1] on the hydrolysis of the analogous chromium(III) complexes, and to a lesser extent the rhodium(III) analogues, the nature of the mechanisms involved remains controversial.[7,8] Indeed, detailed high-pressure studies[9] have not been able to unambiguously solve this dilemma.

Therefore we undertook to look in detail at the total volume changes incurred in such reactions in the form of a volume profile diagram. This method has been used in only a limited number of cases in organic chemistry,[10] either to simply rationalize the volumes of activation found in more complicated reactions or to attempt to quantitatively establish the reaction mechanism. This requires both precision measurements of the partial molar volumes of the reactants and, if possible, the products and accurate measurements of the pressure dependence of the rate constants themselves. Such a diagram has the advantage over the more commonly used energy profile diagram in that it involves absolute measurements, thereby allowing direct, quantitative comparisons to be made between reactions of different substrates. In addition, one can assign an absolute volume to the transition state itself.

Experimental Section

Materials. The complexes were prepared, recrystallized, and converted, in the majority of cases, to perchlorate salts by established methods: $[Co(NH_3)_6](ClO_4)_3$,[11] $[Co(NH_3)_5OH_2](ClO_4)_3$,[12] $[Co(NH_3)_5Cl](ClO_4)_2$,[13] $[Co(NH_3)_5Br](ClO_4)_2$,[14] $[Co(NH_3)_5F](ClO_4)_2$,[15] $[Co(NH_3)_5NCS](ClO_4)_2$,[2] $[Co(NH_3)_5SO_4]ClO_4$,[2] $[Co(NH_3)_5N_3]Cl_2$,[16] $[Co(NH_3)_5NO_3](NO_3)_2$,[17] $[Co(NH_3)_5Me_2SO](ClO_4)_3\cdot 2H_2O$,[18] $[Cr(NH_3)_6]I_3$,[19] $[Cr(NH_3)_5OH_2](NO_3)_3$,[20] $[Cr(NH_3)_5Cl](ClO_4)_2\cdot H_2O$,[21] $[Cr(NH_3)_5Br]Br_2$,[20] $[Cr(NH_3)_5NCS](ClO_4)_2$,[22] $[Cr(NH_3)_5I](ClO_4)_2$.[23] The latter complex was converted to the perchlorate salt by stirring small amounts of the corresponding iodide salt in 70% $HClO_4$ for 1 h, during which time the iodide ions were oxidized to iodine. The mixture was filtered and washed with small amounts of ice-cold water, followed by acetone. This procedure was repeated three times.

The purity of the complexes was checked by microanalysis (Hoechst AG, Analytical Laboratory, Frankfurt, West Germany) and by comparison of their visible and/or UV spectra with literature values. The solvent water was first passed through a commercial ion-exchange column and then doubly distilled. It showed an average density at 25 °C of 0.997 065 g cm^{-3} (cf. 0.997 075 g cm^{-3} [24]).

Density Measurements. These measurements were carried out using a digital density apparatus, DMA 02 (Anton Paar KG, Austria) thermostated at 25.000 ± 0.002 °C. In general, densities were measured at a minimum of six different complex concentrations over