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Site of Attack in the Gas-Phase Reactions of Negative Ions with (η^5-Cyclopentadienyl)dicarbonylcobalt(I)

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The gas-phase reactions of negative ions (NH_2^-, HO^-, RO^-, $O^{\bullet -}$, and HC_2^-) with $CpCo(CO)_2$ have been studied with Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The main reactions are proton transfer and nucleophilic attack leading to elimination of one or two CO molecules from the collision complex. The gas-phase acidity, ΔH°_{acid}, of $CpCo(CO)_2$ is placed at 1559 ± 10 kJ mol^{-1} on the basis of the occurrence/nonoccurrence of proton transfer in the reactions with the RO^- ions. Nucleophilic attack of the NH_2^-, HO^-, RO^-, and HC_2^- ions on $CpCo(CO)_2$ is discussed as proceeding by (i) reaction at a CO ligand with subsequent elimination of the other CO ligand and migration of the HO or RO group to the metal center followed to some extent by the expulsion of a CO molecule and/or by (ii) a η^5 to η^3 change in the bonding of the C_5H_5 ligand prior to bond formation between the nucleophile and the cobalt atom and the subsequent elimination of one or two CO molecules. Competing attack on the Cp ligand and a CO ligand occurs only in the reaction with the $O^{\bullet -}$ radical anion and results in abundant $CoC_5H_5O^-$ ions. Attack of the oxygen radical anion on the Cp ligand is proposed to yield mainly a $(\eta^4\text{-}C_5H_4O)Co(H)^-$ ion, whereas initial attack of $O^{\bullet -}$ on a CO ligand is suggested to result in a metallacyclopentadiene species with a CO ligand and a hydrogen atom bonded to the cobalt atom and/or in a $(\eta^4\text{-cyclobutadiene})Co(H)(CO)^-$ ion.

Introduction

Nucleophilic addition reactions are applied extensively in organotransition-metal chemistry, and coordination to a transition-metal atom is known to activate unsaturated species, such as carbon monoxide, ethene, and benzene toward nucleophilic attack.[1] The attack of a nucleophile on a ligand represents a key step in important industrial processes such as the Wacker reaction, which involves attack of water on an ethene molecule coordinated to palladium(II), and the water gas shift (WGS) reaction, which under alkaline conditions is considered to involve attack of a hydroxide ion on a CO ligand in, for example, $Fe(CO)_5$.[1] Apart from the properties of the ligand itself, the susceptibility toward nucleophilic attack is ascribed usually to (i) the coordinative saturation of the metal center, (ii) the presence of a formal positive charge on the metal center, and (iii) the presence of a ligand, which can accommodate an increase in charge of the substrate. In this respect, the cyclopentadienyl ligand, which is one of the most widely utilized ligands in organometallic chemistry, is reported to be reactive toward nucleophiles only in instances where the organometallic species carries a positive charge, e.g., $(Cp)_2Co^+$ and $CpFe(CO)_3^+$.[1,2]

The present insight into the mechanisms of the reactions between nucleophiles and transition-metal compounds is based almost entirely on results obtained from condensed-phase studies, and one may raise the question of whether the ability of various ligands to undergo nucleophilic attack is a reflection of a molecular property of the metal species. In principle, the relative ease of attack of a charged nucleophile on different ligands in an organometallic compound can be probed by studying the processes in the gas phase,[3-5] thus avoiding the influence of solvent molecules and counterions inevitably present in the condensed phase. A number of studies have documented that typical reactions of transition-metal species such as ligand substitution/addition reactions,[4,5,6-11] oxidations by O_2,[4,9,12,13] and oxidative addition/reductive elimination processes[4,14-27] can occur in gas-phase systems. Notwithstanding the formal resemblance between processes occurring in the two phases, the removal of the solvent causes dramatic changes in the energetics and rates of the reactions.[28,29] In the gas phase, ion/molecule re-

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actions occurring under thermal or near-thermal conditions are bound to be exothermic or thermoneutral and are known to proceed often with overall rate constants approaching the rate constant for collision between the particles.[28,29] The latter rate constant is determined largely by the attractive ion/dipole and ion/induced-dipole interactions, which lead initially to a decrease in potential energy. The total energy of the system will be conserved in the absence of stabilizing collisions with third bodies and/or emission of photons, and as a result, the energy gained upon approach will be present largely as excess internal (rotational and vibrational) energy. The encounter complex, which is often referred to as a loosely bound ion/molecule complex, may either dissociate to reactants or undergo a chemical reaction depending on the internal energy content, the height of the local potential energy barrier toward the chemical reaction, and the geometry of the transition state for the reaction. The products of the chemical reaction can arise by dissociation of the loose ion/molecule complex formed by crossing the barrier, or a series of discrete chemical events may follow the initial step and precede separation of the components. Within the limits of this simplified picture of gas-phase ion/molecule reactions, the competition between nucleophilic attack on different ligands of an organometallic compound may be determined largely by the properties of the transition states of the reactions. This requires, of course, that the steps which may follow the initial attack of the nucleophile are facile and essentially irreversible. In addition, the observation of separated products formed as a consequence of competing nucleophilic attack on different ligands demands that the various overall reactions are thermochemically feasible.

Previous studies of the gas-phase reactions of negative ions with transition-metal compounds have been concerned mainly with carbonyl compounds, e.g., $Fe(CO)_5$.[5,30-33] The mechanistic picture emerging from these studies involves initial attack of the nucleophile on a CO ligand followed by loss of a CO molecule and migration of the nucleophile to the metal center succeeded to some extent by expulsion of a second CO molecule. Nucleophilic attack on an organic ligand is described only for the gas-phase reactions of H^- with $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, which results in a $HCr(CO)_3^-$ ion after migration of a hydrogen atom to the metal center and elimination of C_6H_6.[5,16] With $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ or $CpMn(CO)_3$, alkoxide ions and carbanions are reported to react in a flowing afterglow (FA)[34,35] instrument by proton transfer and formation of stable adducts. The often predominant formation of stable adducts in FA instruments is caused by the occurrence of stabilizing collisions with the carrier gas present in the flow tube at a relatively high pressure (~70 Pa He).[34,35] In the present study, Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry[36,37] is used to investigate the reactions of negative ions with $CpCo(CO)_2$ at very low pressures ($<10^{-4}$ Pa), thus avoiding prevalent adduct formation. The study was undertaken in order to elucidate the mechanism of the gas-phase reactions of negative ions with a typical organometallic compound containing a Cp ligand and in order to examine whether the relative inertness of the Cp ligand toward nucleophiles noted for reactions occurring in the condensed phase is maintained in the gas phase. The $CpCo(CO)_2$ compound was chosen as the substrate in part because of its volatility and in part because a previous report indicated that F^- and methoxide ions react with $CpCo(CO)_2$ under ICR conditions mainly by the loss of one or two CO molecules from the collision complex.[6]

Experimental Section

The experiments were performed with an FT-ICR instrument designed and constructed at the University of Amsterdam.[38,39] In a typical experiment, the primary negative ions were formed by a pulsed electron beam (duration 100 ms) and trapped in a magnetic field of 1.23 T by applying a small negative voltage (~−1 V) to the trapping plates of the cubic inch FT-ICR cell. The $O^{\bullet -}$ ion was formed by dissociative electron capture by N_2O (electron energy ~1.2 eV), while the $^{18}O^{\bullet -}$ ion was generated from a nitrous oxide sample containing 70% $N_2{}^{18}O$ and 30% N_2O. The $O^{\bullet -}$ ions formed by electron impact on the sample and in the subsequent reactions of the $^{18}O^{\bullet -}$ ions with the N_2O molecules[40,41] were ejected from the FT-ICR cell. The NH_2^- and $HO^-/H^{18}O^-/DO^-$ ions were formed by dissociative electron capture by NH_3 (5 eV) and $H_2O/H_2{}^{18}O/D_2O$ (6 eV), respectively. The other anions were formed by proton transfer from the appropriate neutral precursors to the $O^{\bullet -}$ ion. The ions of interest were isolated by removing all other ions from the cell by a series of radio frequency (rf) pulses, which were adjusted in such a way that unwanted translational excitation of the selected ions was minimized. The reactions with a given substrate were studied as a function of time by varying the delay between the selection of the reactant ion and the start of the excitation pulse, which increases the radius of the cyclotron motion of the ions prior to their detection.[36] Impact of low kinetic energy electrons on $CpCo(CO)_2$ results in molecular negative ions and abundant $CpCo(CO)^-$ ions. The formation of primary negative ions from $CpCo(CO)_2$ during the period that the nucleophiles were allowed to react with the organometallic substrate was prevented by ejecting the low kinetic energy electrons from the FT-ICR cell as described elsewhere.[42]

The total pressure was normally around 6×10^{-5} Pa, and the ratio between the partial pressures of $CpCo(CO)_2$, N_2O, and the substrate or the conjugate acid of the nucleophile of interest was typically 1:1:1. The pressures were measured on an uncalibrated ionization gauge placed in a side arm of the main pumping line. The inlet lines and the main vacuum vessel were at room temperature, while the temperature of the trapping plate opposite the filament side varied from 330 to 340 K in a typical experiment.

Materials. Most of the chemicals including the $CpCo(CO)_2$ compound were commercially available and used without further purification. The labeled alcohols and carboxylic acids were either commercially available or prepared by standard methods and purified prior to use.

Results

Reactions of Negative Ions with $CpCo(CO)_2$. The main reactions of negative ions with $CpCo(CO)_2$ are proton transfer and nucleophilic attack, which is followed by elimination of one or two CO molecules from the collision complex (eqs 1–3, where $A^- = NH_2^-$, HO^-, RO^-, and HC_2^-, and Table I). In addition to these processes, CO_2 is ex-

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Table I. Initial Relative Abundances of the Product Ions (in Percent of Total Product Ion Yield) Formed in the Reactions of Negative Ions with CpCo(CO)$_2$ (M) in the Gas Phase[a]

A^-	PA(A^-),[b] kJ mol^{-1}	$[M - H]^-$	$[M + A - CO]^-$	$[M + A - 2CO]^-$	other product ions (%)	% conversn into products[c]
NH_2^-	1689	80	5	15		100
HO^-	1635	80	5	10	$[M + HO - CO_2]^-$ (5)	90
$O^{\bullet -}$[d,e]	1599	15	5	65	$[M + O - H]^-$ trace $[M - 2H]^-$ (5) $CpCo(CO)^-$ (10)	95
CH_3O^-	1592	60	30	10		
$C_2H_5O^-$	1579	45	40	15		85
n-$C_3H_7O^-$	1576	30	45	25		75
$(CH_3)_2CHO^-$	1571	35	35	30		
n-$C_4H_9O^-$	1569	20	50	30		70
$(C_2H_5)_2CHO^-$	1559		70	30		45
$FCH_2CH_2O^-$	1548		85	15		*f*
HC_2^-	1576		95	5		
CH_3S^-	1493		nr[g]			
$CH_3CO_2^-$	1459		nr[g]			

[a] Obtained by following the product ion distribution as a function of time and extrapolated to zero reaction time; see text and Figure 1. [b] The proton affinity values are from ref 44. [c] Reaction time 300 ms, p(CpCo(CO)$_2$) $\approx 2 \times 10^{-5}$ Pa. [d] The $O^{\bullet -}$ ion reacts to some extent with CpCo(CO)$_2$ and trace impurities of 1,3-cyclopentadiene formed by decomposition of the organometallic sample by hydrogen atom abstraction leading to HO^- ions. There ions were ejected during the reaction period from the FT-ICR cell. [e] The $O^{\bullet -}$ ions react with N_2O to form NO^- ions. The NO^- ions were ejected continuously from the FT-ICR cell. [f] Conversion into products was not estimated, since the $FCH_2CH_2O^-$ ion reacts with its neutral procursor to produce HF_2^-, CH_2CHO^-, and $FCH_2CH_2OHF^-$ ions. None of these ions reacts with CpCo(CO)$_2$. [g] No reaction.

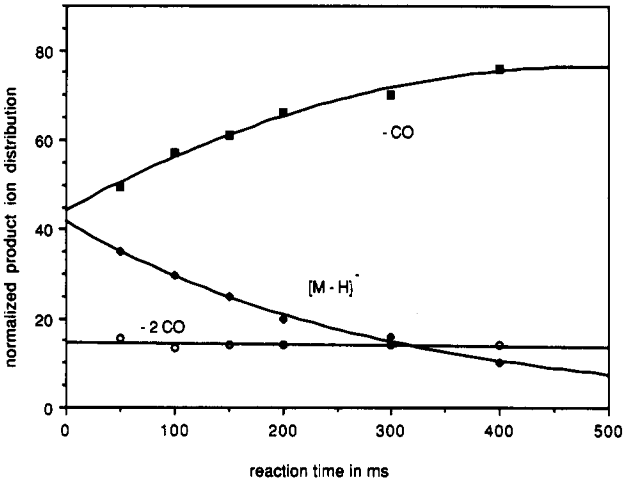

Figure 1. Normalized product ion distribution as a function of reaction time for the $C_2H_5O^-/C_2H_5OH$/CpCo(CO)$_2$ system: p(N_2O) $\approx 2 \times 10^{-5}$ Pa, p(C_2H_5OH) $\approx 2 \times 10^{-5}$ Pa, and p(CpCo(CO)$_2$) $\approx 2 \times 10^{-5}$ Pa. ◆, $[M - H]^-$; ■, $[M + C_2H_5O - CO]^-$; ○, $[M + C_2H_5O - 2\,CO]^-$. The lines represents graphical interpolations based on best fits to the experimental results.

pelled from the collision complex in the reaction of the hydroxide ion with CpCo(CO)$_2$ (eq 4). In nearly all in-

$$A^- + CpCo(CO)_2 \longrightarrow [M-H]^- + HA \quad (1)$$

$$\longrightarrow CpCo(CO)A^- + CO \quad (2)$$

$$\longrightarrow CpCoA^- + 2CO \quad (3)$$

$$\underset{m/z\ 17}{HO^-} + CpCo(CO)_2 \longrightarrow \underset{m/z\ 153}{CpCo(CO)H^-} + CO_2 \quad (4)$$

stances $C_5H_5^-$ ions were formed, but the yield of these ions varied unsystematically from experiment to experiment. The $C_5H_5^-$ ions are unlikely, therefore, to arise by nucleophilic attack on CpCo(CO)$_2$, and we ascribe their formation to exothermic proton transfer between the negative ions and 1,3-cyclopentadiene generated by thermal decomposition of the organometallic compound.[43]

The uncertainty in the pressure measurements was judged to be too large (see Experimental Section) for a reliable determination of reaction rate constants. A measure of the relative rates of the reactions between the negative ions and the CpCo(CO)$_2$ substrate is obtained, however, from the extent of conversion into products at a certain reaction time. The reaction of the NH_2^-, HO^-, $O^{\bullet -}$, and $CH_3CH_2O^-$ ions is seen from the results in Table I to be almost complete within 300 ms, suggesting that these ions react with CpCo(CO)$_2$ at a rate close to the collision rate. In addition, the results in Table I reveal that the rate of reaction of the NH_2^-, HO^-, and RO^- ions with CpCo(CO)$_2$ tends to decrease with decreasing proton affinity of the reactant ion (PA(A^-) = ΔH°_{acid}(HA)[44]).

The $[M - H]^-$ ions react with the water molecules present in the FT-ICR cell by expulsion of CO and CO_2 from the collision complex (eqs 5 and 6), whereas the re-

$$\underset{m/z\ 179}{[M-H]^-} + H_2O \longrightarrow \underset{m/z\ 169}{CpCo(CO)(OH)^-} + CO \quad (5)$$

$$\longrightarrow \underset{m/z\ 153}{CpCo(CO)(H)^-} + CO_2 \quad (6)$$

$$[M-H]^- + ROH \longrightarrow CpCo(CO)(OR)^- + CO \quad (7)$$

action with the alcohols proceeds by the loss of a CO molecule (eq 7). Loss of two CO molecules occurs only to minor extent in the reactions of the $[M - H]^-$ ions with water or aliphatic alcohols (see Discussion). The secondary reactions of the $[M - H]^-$ ions with the water or alcohol molecules present in the FT-ICR cell cause the product ion distributions to vary as a function of time. In order to determine the relative importance of the different channels in the reactions of the selected nucleophiles with CpCo(CO)$_2$, the product ion distributions were followed as a function of time (exemplified for the $C_2H_5O^-$/C_2H_5OH/CpCo(CO)$_2$ system in Figure 1). Extrapolation of the normalized ion abundances to zero reaction time then yields the initial product ion distributions unaffected by the further reactions of the $[M - H]^-$ ions.

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(43) Proton transfer from 1,3-cyclopentadiene to most of the negative ions listed in Table I is exothermic (PA($C_5H_5^-$) = 1481 kJ mol^{-1}; see ref 44). No reaction was observed between the $C_5H_5^-$ ions and CpCo(CO)$_2$.

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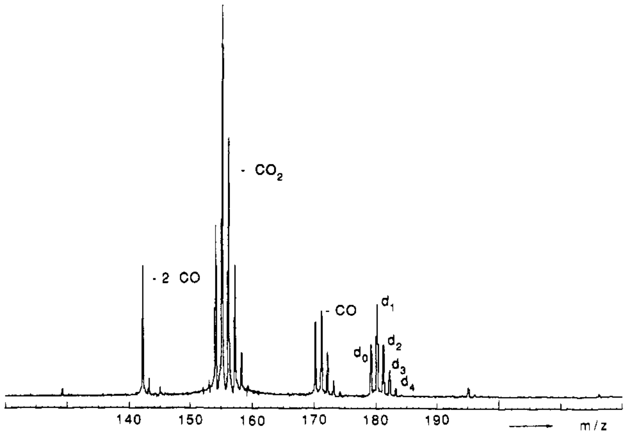

Figure 2. Spectrum obtained of the $DO^-/D_2O/CpCo(CO)_2$ system after a reaction time of 700 ms: $p(D_2O) \approx 3 \times 10^{-5}$ Pa and $p(CpCo(CO)_2) \approx 2 \times 10^{-5}$ Pa. The $[M - H]^-$ ions (*m/z* 179–183) are seen to be capable of exchanging up to four hydrogen atoms for deuterium atoms. The distribution of the d_0–d_4 ions is (percent) 23 (d_0):40 (d_1):23 (d_2):10 (d_3):4 (d_4). The ions with *m/z* 170–174 are formed by loss of CO from the collision complexes. The ions with *m/z* 154–159 are formed by CO_2 loss. The ions with *m/z* 142 and 143 are formed by loss of two CO molecules. See also the text.

The $[M - H]^-$ ions undergo sequential exchange of hydrogen atoms for deuterium atoms in the presence of D_2O (eq 8; see also Figure 2).[45] The ions formed by loss of CO

$$\begin{aligned} &\underset{m/z\ 18}{DO^-} + CpCo(CO)_2 \longrightarrow \underset{m/z\ 179}{{}^-C_5H_4Co(CO)_2} + HDO \\ &\underset{m/z\ 179}{{}^-C_5H_4Co(CO)_2} \longrightarrow \xrightarrow{D_2O} \longrightarrow \underset{m/z\ 183}{{}^-C_5D_4Co(CO)_2} \end{aligned} \qquad (8)$$

and CO_2 during the reaction of the conjugate base of $CpCo(CO)_2$ with water (see eqs 5 and 6) incorporate deuterium atoms as illustrated in Figure 2. However, experiments in which the product ions of reactions 5 and 6 were isolated (see Experimental Section) and subsequently allowed to react with D_2O revealed that these ions themselves do not undergo exchange with D_2O. This suggests that the reactions leading to the loss of CO or CO_2 from the collision complex are preceded by the hydrogen–deuterium exchange between the conjugate base of the organometallic compound and D_2O (see also Discussion).[46]

The exchange of the $[M - H]^-$ ions with D_2O and the reactions of the $[M - H]^-$ ions with water (eqs 5 and 6) or alcohols (eq 7) imply that deprotonation of $CpCo(CO)_2$ does not result in a change in the bonding between the Cp ligand and the cobalt atom. The occurrence/nonoccurrence of proton transfer in the reactions of the alkoxide ions with $CpCo(CO)_2$ (Table I) can be used, therefore, to derive the gas-phase acidity of the Cp ligand in the organometallic compound if it is assumed that the observation of near-thermoneutral proton transfer is not hampered by the competing reaction leading to the loss of one or two CO molecules from the collision complex. Based on this assumption, the gas-phase acidity, $\Delta H°_{acid}$, of the $CpCo(CO)_2$ can be placed between the values for n-C_4H_9OH and FCH_2CH_2OH (see Table I), that is, 1559 ± 10 kJ mol^{-1}. The $CpCo(CO)_2$ compound appears to have a gas-phase acidity similar to $CpMn(CO)_3$ (1556 ± 20 kJ mol^{-1}),[5] and both species are only slightly more acidic than the free $C_5H_5^•$ radical (1577 ± 12 kJ mol^{-1}),[47] indicating that coordination to a metal center does not lead to a dramatic increase in the acidity of $C_5H_5^•$ in contrast to the enhancement in acidity of 100–120 kJ mol^{-1} going from benzene to $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.[5,16]

Reactions of the Oxygen Radical Anion. The reaction of the $O^{•-}$ ion with $CpCo(CO)_2$ proceeds in part as indicated in eqs 1–3 and in part by loss of CO_2 from the collision complex (Table I). Experiments with $^{18}O^{•-}$ reveal that the ions formed by loss of carbon dioxide do not incorporate the oxygen-18 atom (eq 9) whereas the ions formed by the loss of two carbon monoxide molecules retain the label to a large extent (eq 10). Equilibration

$$\underset{m/z\ 18}{^{18}O^{•-}} + CpCo(CO)_2 \longrightarrow \underset{m/z\ 152}{CpCo(CO)^-} + CO^{18}O \qquad (9)$$

$$\underset{m/z\ 18}{^{18}O^{•-}} + CpCo(CO)_2 \xrightarrow{35\%} \underset{m/z\ 140}{CoC_5H_5O^-} + C^{18}O \qquad (10a)$$

$$\xrightarrow{65\%} \underset{m/z\ 142}{CoC_5H_5{}^{18}O^-} + 2CO \qquad (10b)$$

of the three oxygen atoms in the collision complex would result in a ratio of 2:1 for the abundances of the $CoC_5H_5O^-$ and $CoC_5H_5{}^{18}O^-$ ions and would also lead to a ratio between CO_2 and $CO^{18}O$ loss of 1:2. The obtained ratio for the $CoC_5H_5O^-$ and $CoC_5H_5{}^{18}O^{•-}$ ion abundances and the absence of incorporation of the ^{18}O atom in the ions formed by carbon dioxide loss thus reveal that the oxygen atoms do not become equivalent prior to product ion formation (vide infra).

Reactions and Structures of the $CoC_5H_5A^-$ Ions. The present approach to determine the site of nucleophilic attack on $CpCo(CO)_2$ in the gas phase is based largely on a characterization of the structure of the product ions. With the FT-ICR method it is possible, in principle, to establish ion structures by examination of the chemical reactivity of the ions and by performing collision-induced dissociation or photodissociation experiments. In this study, the $CoC_5H_5A^-$ ions formed by the loss of two CO molecules from the collision complex (eq 3) have been allowed to react with selected substrates in order to obtain structural information.

The $CoC_5H_5A^-$ ions formed by attack of the hydroxide ion on $CpCo(CO)_2$ react with 2-butanethiol and acetic acid exclusively and completely by elimination of a water molecule from the collision complex (eq 11). Similarly,

$$CpCoA^- + BH \rightarrow CpCoB^- + AH \qquad (11)$$

$$AH = H_2O,\ n\text{-}C_4H_9OH$$

$$BH = CH_3CH_2(CH_3)CHSH,\ CH_3CO_2H$$

the $CoC_5H_5A^-$ ions formed as a result of attack by the n-$C_4H_9O^-$ ion on $CpCo(CO)_2$ react with 2-butanethiol and acetic acid to expel a n-butanol molecule from the collision complex. On the basis of the occurrence of these reactions, the $CoC_5H_5A^-$ ions formed by nucleophilic attack of the HO^- and RO^- ions on $CpCo(CO)_2$ are assigned a $CpCoA^-$ structure as implied in eqs 3 and 11.

The bimolecular chemistry of the $CoC_5H_5O^-$ ions formed by attack of $O^{•-}$ on $CpCo(CO)_2$ is completely different and much more complex than the chemistry of the $CpCo(OH)^-$ or $CpCo(OR)^-$ ions. With acetic acid as the substrate, the $CoC_5H_5O^-$ ions react by proton transfer and elimination of H_2, (C_4H_6), and (H_2CO_2) from the collision complex.

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[45] Hydrogen–deuterium exchange reactions of negative ions in the gas phase are discussed in ref 28 and: Grabowski, J. J.; DePuy, C. H.; van Doren, J. M.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1985**, *107*, 7384.

[46] Similar observations have been reported for the reactions of the $[M - H]^-$ ions from 2-, 3-, and 4-fluoroanisole with water or aliphatic alcohols; see: Ingemann, S., Nibbering, N. M. M. *J. Org. Chem.* **1983**, *48*, 183.

[47] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6461.

Similar reactions occur with formic acid as the substrate, and experiments with deuterium-labeled acetic acid reveal that the neutral products incorporate one deuterium atom as indicated in eqs 12–14, where the percentages refer to a reaction time of 300 ms.

$$\underset{m/z\ 140}{CoC_5H_5O^-} + CD_3CO_2D \xrightarrow{\sim 50\%} \underset{m/z\ 201}{CoC_7H_4D_3O_3^-} + HD \qquad (12)$$

$$\xrightarrow{\sim 20\%} \underset{m/z\ 157}{CoC_6H_4D_3O^-} + (CHDO_2) \qquad (13)$$

$$\xrightarrow{\sim 30\%} \underset{m/z\ 149}{CoC_3D_3O_3^-} + (C_4H_5D) \qquad (14)$$

Although the detection and characterization of the neutral products of gas-phase ion/molecule reactions has been accomplished, such experiments require unique instruments.[48,49] With the instrument applied in the present study, analysis of the neutral products is not achievable, thus precluding any conclusion as to whether (C_4H_6) represents the loss of one neutral species or, for example, the loss of $C_4H_4 + H_2$. Nevertheless, the occurrence of reaction 14 indicates that an extensive rearrangement involving the carbon and hydrogen atoms of the original Cp ligand may accompany the attack $O^{\bullet -}$ on $CpCo(CO)_2$.

Some insight into the structure(s) of the $CoC_5H_5O^-$ ions is obtained from the reactions of these ions with SO_2, NO, and aliphatic alcohols. With SO_2, the $CoC_5H_5O^-$ ions react predominantly by the loss of a CO molecule from the collision complex (eq 15). In addition to CO loss, the reaction with SO_2 results in an ion with m/z 124. The elemental composition of this product ion is assigned as $CoHSO_2$ instead of CoC_5H_5 on the basis of an accurate mass measurement[50] indicating that (C_5H_4O) is expelled (eq 16) either as one neutral species or, for example, as CO + C_4H_4.

$$\underset{m/z\ 140}{CoC_5H_5O^-} + SO_2 \xrightarrow{85\%} \underset{m/z\ 176}{CoC_4H_5SO_2^-} + CO \qquad (15)$$

$$\xrightarrow{15\%} \underset{m/z\ 124}{CoHSO_2^-} + (C_5H_4O) \qquad (16)$$

The $CoC_5H_5O^-$ ions react also with NO to expel a CO molecule from the collision complex, but the loss of (C_5H_4O) is not observed with this substrate.

$$\underset{m/z\ 140}{CoC_5H_5O^-} + NO \longrightarrow \underset{m/z\ 142}{CoC_4H_5NO^-} + CO \qquad (17)$$

The $CoC_5H_5O^-$ ions react with aliphatic alcohols (ROH, R = CH_3, C_2H_5, $CH_3CH_2CH_2$, $(CH_3)_2CH$) in part by oxidation of the substrate to an aldehyde or a ketone and in part by loss of a hydrogen molecule from the collision complex. Deuterium labeling reveals that the hydrogen atoms added to the reactant ion in the former process originate from the OH function and the α position of the alcohol (Table II and eq 18). The results for the deuterium-labeled alcohols in Table II show that the eliminated hydrogen molecule consists of one hydrogen atom from the hydroxylic position of the alcohol and one hydrogen atom from the $CoC_5H_5O^-$ ions (eq 19).

$$\underset{m/z\ 140}{CoC_5H_5O^-} + RCD_2OD \longrightarrow \underset{m/z\ 144}{CoC_5H_5D_2O^-} + RCDO \qquad (18)$$

$$\underset{m/z\ 140}{CoC_5H_5O^-} + CD_3OD \longrightarrow \underset{m/z\ 173}{CoC_6H_4D_3O_2^-} + HD \qquad (19)$$

Table II. Results of the Reactions of the $CoC_5H_5O^-$ Ions with Deuterium-Labeled Alcohols[a]

substrate	added to the reactant ion	lost from the collision complex
CD_3OH	H + D	H_2
CD_3OD	2D	HD
CH_3CH_2OD	H + D	HD
CD_3CD_2OH	H + D	H_2
$CH_3CH_2CD_2OH$	H + D	H_2
$(CD_3)_2CDOD$	2D	HD

[a] The two reactions occur to an equal extent in all instances.

The determination of the structure(s) of the $CoC_5H_5O^-$ ions by examination of their bimolecular chemistry is complicated to some extent by the occurrence of a reaction between these ions and the $CpCo(CO)_2$ molecules present in the FT-ICR cell. This reaction yields stable adducts in addition to ions formed by loss of one or two CO molecules from the collision complex and is relatively slow, with conversion into products being complete at a reaction time of ~5 s. The reaction with the parent organometallic compound was unable to compete with the reaction of the $CoC_5H_5O^-$ ions with SO_2 or formic acid, and only traces of the ions from the former reaction were observed in the experiments with these substrates. By contrast, significant amounts of the product ions of the reaction between $CoC_5H_5O^-$ and $CpCo(CO)_2$ were formed when NO or an aliphatic alcohol was present in the cell.

In the experiments with the aliphatic alcohols, only a minor part of the $CoC_5H_5O^-$ ions (~20%) were reactive toward these substrates. The occurrence of the reaction with the parent organometallic compounds precludes an accurate determination of the amount of $CoC_5H_5O^-$ ions capable of reacting with the alcohols. The formation of $CoC_5H_5O^-$ ions with a different reactivity is supported by experiments in which the reactions with ethanol and $CpCo(CO)_2$ were allowed to proceed for 1–1.5 s before the remaining $CoC_5H_5O^-$ ions were isolated (see Experimental Section). No products ions were formed in the subsequent reactions of the remaining $CoC_5H_5O^-$ ions with ethanol, and merely the product ions from the reactions with the parent compound were detected. Such results may mean that some of the $CoC_5H_5O^-$ ions formed by attack of $O^{\bullet -}$ on $CpCo(CO)_2$ contain excess internal/translational energy, which enables them to react with the aliphatic alcohols. However, only the $CoC_5H_5{}^{18}O^-$ ions generated in the reactions of the $^{18}O^{\bullet -}$ ion with $CpCo(CO)_2$ (eq 10b) react with ethanol as shown in eqs 20 and 21, whereas the $CoC_5H_5O^-$ ions formed through the route in eq 10a show no reactivity toward this substrate. Furthermore, both ions formed as indicated in eqs 10a and 10b react with acetic acid by elimination of (C_4H_6) (eq 14) and by proton transfer, whereas H_2 loss (eq 12) is observed solely for the $CoC_5H_5{}^{18}O^-$ ions. In conclusion, the results indicate that attack of $O^{\bullet -}$ on the cobalt compound leads to isomeric $CoC_5H_5O^-$

$$\underset{m/z\ 142}{CoC_5H_5{}^{18}O^-}\ (\text{eq 10b}) + C_2H_5OH$$

$$\xrightarrow{\sim 50\%} \underset{m/z\ 144}{CoC_5H_7{}^{18}O^-} + C_2H_4O \qquad (20)$$

$$\xrightarrow{\sim 50\%} \underset{m/z\ 186}{CoC_7H_9O^{18}O^-} + H_2 \qquad (21)$$

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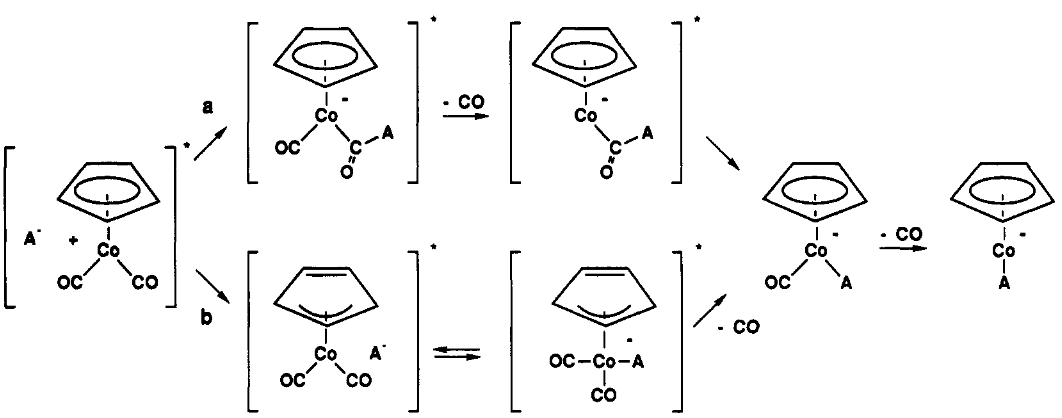
(48) Morton, T. H. In *Techniques for the Study of Ion–Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley-Interscience, New York, 1988; Chapter III, p 119.

(49) Jones, M. E.; Ellison, G. B. *J. Am. Chem. Soc.* 1989, *111*, 1645.

(50) The exact mass of the $CoHSO_2^-$ ions is 123.903 83 Da; the exact mass of the $CoC_5H_5^-$ ion is 123.976 83 Da. The mass of the product ion is measured to be 123.901 ± 0.002 Da (four measurements). See ref 38.

Scheme I. Proposed Reaction Mechanisms for Nucleophilic Addition of Negative Ions on a CO Ligand (Path a) or on the Metal Center (Path b) of CpCo(CO)$_2$ in the Gas Phase



ions, which display a different chemical reactivity.

Discussion

Site of Attack. In principle, the negative ions can attack the CpCo(CO)$_2$ compound on the Cp ligand, a CO ligand, or the cobalt atom. Ions with a CpCoA$^-$ structure are suggested to be formed in the reactions with the HO$^-$ and RO$^-$ ions (see eqs 3 and 11), implying that the Cp ligand is not involved directly in these instances. In other words, nucleophilic attack of HO$^-$ and RO$^-$ ions is inclined to occur initially on a CO ligand and/or the cobalt atom.

The reaction of the HO$^-$ and RO$^-$ ions with CpCo(CO)$_2$ can proceed as shown in Scheme I, where path a represents initial attack on a CO ligand and path b a mechanistic proposal for direct attack on the cobalt atom. Both reaction sequences start with formation of a loosely bound complex composed of the A$^-$ ion and the CpCo(CO)$_2$ molecule. In this complex, the A$^-$ ion may react at a CO ligand, leading to a 16-electron CpCo(CO–A)$^-$ ion, which can rearrange to an 18-electron CpCo(CO)A$^-$ species by migration of the A group to the metal center as shown in path a, Scheme I. Subsequent elimination of a CO molecule then yields the CpCoA$^-$ ions.

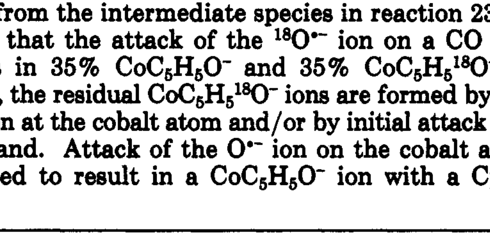
Support for the occurrence of attack on a CO ligand can be found also in the elimination of CO$_2$ from the collision complex formed in the reaction of the hydroxide ion with CpCo(CO)$_2$ (eq 4) or in the reaction of the [M − H]$^-$ ions with water (eq 6). Initial attack on a CO ligand can be followed by migration of the hydrogen atom of the OH group to the metal center concomitant with CO$_2$ loss and formation of the 18-electron CpCo(CO)H$^-$ ion shown in eq 22 for H^{18}O$^-$ as the reactant ion. Exclusive loss of CO^{18}O occurs in the reaction with the H^{18}O$^-$ ion, indicating that oxygen atom interchange is not occurring in the intermediate species.

$$\underset{m/z\ 19}{H^{18}O^-} + CpCo(CO)_2 \longrightarrow [CpCo(CO)(CO^{18}OH)^-]^* \longrightarrow \longrightarrow \underset{m/z\ 153}{CpCo(H)(CO)^-} + CO^{18}O \quad (22)$$

Loss of a C^{18}O molecule from the collision complex formed in the reactions with H^{18}O$^-$ occurs only to a very minor extent compared to the loss of CO. This may mean that 1,3-H shifts between the oxygen atoms in the initially formed species (eq 22 and Scheme I) do not compete effectively with the ensuing reactions and/or that the loss of one or two carbon monoxide molecules proceeds in part by direct attack of the hydroxide ion on the cobalt atom. The latter possibility (path b in Scheme I) can involve an η^5 to η^3 change in the bonding between the C$_5$H$_5$ ligand and the cobalt atom, thus creating a 16-electron species with a vacant position for bond formation between the nucleophile and metal center. Ligand substitutions driven by an η^5 to η^3 change in the bonding of a Cp[51–53] or an indenyl ligand[52,54] have been discussed for condensed-phase reactions, e.g., the displacement of a CO ligand in (η^5-C$_5$H$_4$NO$_2$)Rh(CO)$_2$ by (Ph)$_3$P.[51] The energy requirement for the implied η^5 to η^3 change in bonding between the C$_5$H$_5$ ligand and the cobalt atom is unknown, and we are unable to conclude whether the energy gained upon approach of the reactant ion to the CpCo(CO)$_2$ molecule is sufficient for the occurrence of mechanism b in Scheme I.

Although the details of the reaction between the HO$^-$ and RO$^-$ ions and the cobalt compound are uncertain, the obtained results strongly indicate that nucleophilic attack by these ions does not occur at the Cp ligand. A different conclusion is reached for the O$^{\bullet-}$ radical anion on the basis of the bimolecular chemistry of the CoC$_5$H$_5$O$^-$ ions formed by the loss of two CO molecules from the collision complex in combination with the relative abundances of the CoC$_5$H$_5$^{18}O$^-$ (~65%) and CoC$_5$H$_5$O$^-$ (~35%) ions generated by attack of ^{18}O$^{\bullet-}$ on CpCo(CO)$_2$ (eq 10).

The ~35% CoC$_5$H$_5$O$^-$ ions (eq 10a) can arise only by attack of the ^{18}O$^{\bullet-}$ ion on a CO ligand. Attack on this site can be succeeded by the loss of the other CO ligand and elimination of CO or C^{18}O as illustrated in eq 23. Loss of C^{18}O and CO is anticipated to occur with equal probability from the intermediate species in reaction 23, indicating that the attack of the ^{18}O$^{\bullet-}$ ion on a CO ligand results in 35% CoC$_5$H$_5$O$^-$ and 35% CoC$_5$H$_5$^{18}O$^-$ ions. Hence, the residual CoC$_5$H$_5$^{18}O$^-$ ions are formed by direct reaction at the cobalt atom and/or by initial attack on the Cp ligand. Attack of the O$^{\bullet-}$ ion on the cobalt atom is expected to result in a CoC$_5$H$_5$O$^-$ ion with a CpCoO$^-$



$$\underset{m/z\ 18}{^{18}O^{\bullet-}} + CpCo(CO)_2 \xrightarrow[-CO]{} [CpCoC(^{18}O^-)(O^\bullet)]^* \quad (23)$$
$$\longrightarrow \underset{m/z\ 140}{CoC_5H_5O^-} + C^{18}O$$
$$\longrightarrow \underset{m/z\ 142}{CoC_5H_5{}^{18}O^-} + CO$$

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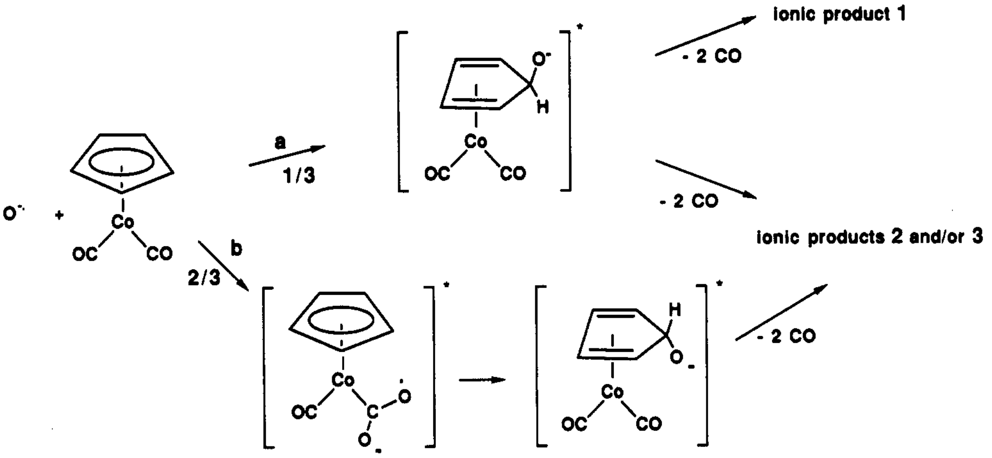
(51) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.

(52) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(53) Vest, P.; Anhaus, J.; Bajaj, H. C.; Eldik, R. van *Organometallics* **1991**, *10*, 818.

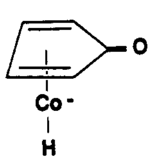
(54) Merola, J. S.; Kacmarcik, R. T.; Engen, D. van *J. Am. Chem. Soc.* **1986**, *108*, 329.

Scheme II. Proposed Reaction Mechanisms for Attack of the O$^{\bullet-}$ on the Cp Ligand (Path a) or on a CO Ligand (Path b) of CpCo(CO)$_2$ in the Gas Phase

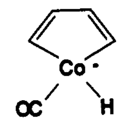


structure.[24] The formation of such an ion is hard to reconcile with the observed ion/molecule chemistry of the CoC$_5$H$_5$O$^-$ ions, which indicates that the Cp ligand is not retained as a structural entity upon attack of the O$^{\bullet-}$ ion. In conclusion, the experiments with the ^{18}O$^{\bullet-}$ ion indicate that 70% of the product ions from loss of two carbon monoxide molecules from the collision complex arise by attack on a CO ligand, whereas the remaining 30% are generated by initial attack on the Cp ligand.

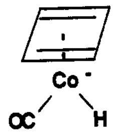
The present results do not allow for detailed considerations of the precise structure(s) of the CoC$_5$H$_5$O$^-$ ions. Agreement between the described observations can be obtained, however, by postulating the formation of species such as 1–3. The generation of these ions by competing attack of O$^{\bullet-}$ on the Cp and CO ligands is rationalized in Scheme II. Initial attack on the Cp ligand is likely to occur on the exo side of the ring as indicated in path a. Loss of two CO molecules and migration of the hydrogen atom now at the endo side with respect to the cobalt atom leads to the 15-electron (η^4-C$_5$H$_4$O)Co(H)$^-$ ion (1). Attack of the O$^{\bullet-}$ ion on a CO ligand could be expected to be followed by a shift of an oxygen atom to the metal center with formation of a CpCoO$^-$ ion[24] after the expulsion of two CO molecules in analogy with the reactions of the HO$^-$ and RO$^-$ (see Scheme I). The lack of evidence for the generation of a CpCoO$^-$ ion, however, suggests that migration of an oxygen atom to the Cp ligand occurs after the initial attack on a CO ligand (path b in Scheme II). Cleavage of the ring concomitant with the expulsion of two CO molecules then leads to the proposed metallacyclopentadiene[55] species (2) and/or the (η^4-cyclobutadiene)-Co(H)(CO)$^-$ ion (3).



1



2



3

The generation of a unique ion structure by attack on the Cp ligand is in agreement with the observation that only the ions retaining the label in the reaction with the ^{18}O$^{\bullet-}$ ion react with ethanol (eqs 20 and 21), and the generation of ion 1 is supported by the loss of (C$_5$H$_4$O) in the reaction with SO$_2$ (eq 16). The formation of ion 1 in which one of the hydrogen atoms of the original Cp ligand has become structurally different from the others may be held responsible also for the exclusive occurrence of HD loss in the reactions with fully deuterated alcohols (eq 19 and Table II). The observation that only ~15% of the CoC$_5$H$_5$O$^-$ ions react with SO$_2$ to expel (C$_5$H$_4$O) (eq 16) whereas the oxygen-18 experiments indicate that ~30% of all the CoC$_5$H$_5$O$^-$ ions are formed by attack on the Cp ligand implies that species other than 1 can be formed by path a in Scheme II. These other species could well be 2 and 3, which are thought to be formed mainly by initial attack on a CO ligand (path b). The generation of ions like 2 or 3 is supported by the loss of CO from the collision complex in the reaction with SO$_2$ (eq 15) and NO (eq 17) and also by the elimination of (C$_4$H$_6$) in the reactions with acetic acid (eq 14) or formic acid.

Competing Reactions and Energetic Considerations. Exothermic to near-thermoneutral proton transfer in gas-phase ion/molecule systems occurs often with a rate essentially equal to the rate of collision between the particles.[28] Nucleophilic substitutions such as S$_N$2 reactions in organic gas-phase systems are known to be associated with local energy barriers, which can cause the rate of these reactions to be much lower than the collision rates even if the overall processes are strongly exothermic.[28,29] In organic systems where proton transfer is exothermic, it is often observed, therefore, that this process kinetically suppresses the occurrence of thermochemically favorable substitutions reactions. Relatively little is known about the potential energy surfaces describing nucleophilic attack on organometallic compounds. In the present system, proton transfer from CpCo(CO)$_2$ to the most basic anions (NH$_2^-$, HO$^-$) is by far the dominant channel and only ~20% of the total amount of product ions arises from nucleophilic attack in these instances (see Table I and eqs 1–4). The relative importance of proton transfer in comparison with nucleophilic attack leading to the expulsion of one or two CO molecules decreases as expected with decreasing PA of the reactant ion. A decrease in the PA of the reactant ions results also in a reduction in the rate of the overall process (Table I; see also Results). These observations suggest that nucleophilic attack on a CO ligand and/or the metal center is associated with a local potential energy barrier decreasing the rate of the overall process if proton transfer is not the dominant pathway.

Some insight into the energy surface describing the attack of negative ions on CpCo(CO)$_2$ can be obtained from the reactions of the [M − H]$^-$ ions with water or alcohols. In the reaction of the HO$^-$ ion with CpCo(CO)$_2$, a

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[55] Schore, N. E. *Chem. Rev.* 1988, *88*, 1081.

$[CpCo(CO)_2 + HO^-]^*$ complex is formed directly, whereas the reactions of the $[M - H]^-$ ion with water lead initially to a $[[M - H]^- + H_2O]^*$ complex. The formation of the $[[M - H]^- + H_2O]^*$ complex is associated with a gain in energy, which is sufficiently large to allow for conversion into a $[CpCo(CO)_2 + HO^-]^*$ complex (eq 24). Proton transfer between the $[M - H]^-$ ion and water to give free HO^- ions is not observed, since this process is endothermic by the difference in gas-phase acidities of the organometallic compound and water (~76 kJ mol^{-1}; see Results). The difference in acidities of $CpCo(CO)_2$ and H_2O causes the intermediate $[CpCo(CO)_2 + HO^-]^*$ complex to be formed with lower internal energy in the reactions of the $[M - H]^-$ ions with water than in the direct reaction of HO^- with the substrate. The $[CpCo(CO)_2 + HO^-]^*$ complex in eq 24 may react to regenerate free $[M - H]^-$ ions, or nucleophilic attack on a CO ligand and/or the metal atom can take place as illustrated in eqs 25 and 26 for the reaction with D_2O. The observation of hydrogen-deuterium exchange between the $[M - H]^-$ ions and D_2O (see Results and Figure 2) indicates that formation of the conjugate base of the organometallic compound is competing with nucleophilic attack. The exchange between the $[M - H]^-$ ions and D_2O results in a distribution of *m/z* 179–183 ions (indicated with d_0–d_4 in Figure 2). The d_0–d_4 ions all react with D_2O to expel CO or CO_2 from the collision complex, thus leading to the observed extensive incorporation of deuterium atoms in the product ions of nucleophilic attack.[46]

$$\underset{m/z\ 179}{[M-H]^-} + H_2O \rightleftharpoons [[M-H]^- + H_2O]^* \rightleftharpoons$$

$$[CpCo(CO)_2 + HO^-]^* \not\longrightarrow CpCo(CO)_2 + \underset{m/z\ 17}{HO^-} \qquad (24)$$

$$\underset{m/z\ 179}{[M-H]^-} + D_2O \rightleftharpoons [[M-H]^- + D_2O]^* \rightleftharpoons$$

$$[(\eta^5\text{-}C_5H_4D)Co(CO)_2 + DO^-]^* \rightarrow \underset{m/z\ 155}{(\eta^5\text{-}C_5H_4D)Co(D)(CO)^-} + CO_2 \qquad (25)$$

$$[(\eta^5\text{-}C_5H_4D)Co(CO)_2 + DO^-]^* \rightarrow \underset{m/z\ 171}{(\eta^5\text{-}C_5H_4D)Co(CO)(OD)^-} + CO \qquad (26)$$

In the reactions of the $[M - H]^-$ ions with the water or alcohol molecules hardly any loss of two CO molecules is occurring, whereas significant amounts of $CpCo(OH)^-$ or $CpCo(OR)^-$ ions are formed by direct attack of HO^- and RO^-, respectively, on $CpCo(CO)_2$ (Table I). This is evident from the near-constant relative abundance of the $CpCo(OC_2H_5)^-$ ion with time in the $C_2H_5O^-/C_2H_5OH/CpCo(CO)_2$ system (Figure 1) and is revealed also in the generation of only minor amounts of $(\eta^5\text{-}C_5H_4D)Co(OD)^-$ (*m/z* 143) ions compared to the $CpCo(OD)^-$ (*m/z* 142) ions in the $DO^-/D_2O/CpCo(CO)_2$ system (Figure 2). The lower internal energy of the intermediate complexes in the reactions of the $[M - H]^-$ ions with H_2O or ROH than in the direct reactions of the HO^- or RO^- with $CpCo(CO)_2$ results clearly in $CpCo(CO)OH^-$ or $CpCo(CO)OR^-$ ions with an internal energy below the threshold for elimination of a CO molecule. This, in turn, substantiates the implicitly assumed consecutive loss of two CO molecules in the reactions of the negative ions with the cobalt compound (Scheme I).

Conclusions

Nucleophilic attack on $CpCo(CO)_2$ by NH_2^-, HO^-, RO^-, and HC_2^- occurs initially on a CO ligand and/or the cobalt atom and is likely to proceed by mechanisms comparable to those advanced for condensed-phase reactions. The elimination of CO_2 from the collision complexes in the gas-phase $HO^-/H_2O/CpCo(CO)_2$ system resembles formally one of the central steps in the $Fe(CO)_5$-catalyzed water gas shift reaction.[1] Expulsion of CO_2 appears a favorable pathway in the $HO^-/H_2O/CpCo(CO)_2$ system in contrast to the gas-phase reaction of HO^- with $Fe(CO)_5$, which is reported to yield only $Fe(CO)_3(OH)^-$ ions after the elimination of two CO molecules from the collision complex.[5]

Competing attack on the Cp ligand and one of the CO ligands occurs only in the reactions of the $O^{\bullet-}$ radical anion with the $CpCo(CO)_2$ compound and results in isomeric $CoC_5H_5O^-$ ions. The bimolecular chemistry of these product ions suggests that attack of the oxygen radical anion on the Cp ligand yields mainly a $(\eta^4\text{-}C_5H_4O)Co(H)^-$ ion, whereas initial attack on a CO ligand is accompanied by a rearrangement involving cleavage of the carbon skeleton of the Cp ligand, possibly with the formation of a metallacyclopentadiene[55] species and/or a $(\eta^4$-cyclobutadiene)Co(CO)(H)$^-$ ion.

Acknowledgment. We thank Prof. Dr. A. Oskam and Dr. D. J. Stufkens from the Laboratory of Inorganic Chemistry at the University of Amsterdam for stimulating discussions. The Netherlands Organization for Scientific Research (SON/NWO) is acknowledged for financial support.

Registry No. $CpCo(CO)_2$, 12078-25-0; NH_2^-, 17655-31-1; HO^-, 14280-30-9; $O^{\bullet-}$, 14337-01-0; CH_3O^-, 3315-60-4; $C_2H_5O^-$, 16331-64-9; *n*-$C_3H_7O^-$, 26232-83-7; $(CH_3)_2CHO^-$, 15520-32-8; *n*-$C_4H_9O^-$, 26232-84-8; $(C_2H_5)_2CHO^-$, 117951-42-5; $FCH_2CH_2O^-$, 74279-90-6; HC_2^-, 29075-95-4; CH_3S^-, 17302-63-5; $CH_3CO_2^-$, 71-50-1; $CoC_5H_5O^-$, 111189-21-0; CD_3OH, 1849-29-2; CD_3OD, 811-98-3; CH_3CH_2OD, 925-93-9; CD_3CD_2OH, 1859-08-1; $CH_3CH_2CD_2OH$, 40422-04-6; $(CD_3)_2CDOD$, 22739-76-0.

OM910491J