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Electron impact ionization of cobalt-tricarbonyl-nitrosyl, cyclopentadienyl-cobalt-dicarbonyl and biscyclopentadienyl-cobalt: appearance energies, bond energies and enthalpies of formation

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Abstract

Mass spectra of the title compounds on electron impact (EI) ionization, appearance energies and metastable ion decays are reported. Bond energies (D), as dissociation energies, and gas-phase enthalpies of formation (ΔH_f°) are derived from these data. Obtained ΔH_f° values are (-4.20 ± 0.3) eV for $Co(CO)_3NO$, (-0.92 ± 0.3) eV for $CpCo(CO)_2$ ($Cp = C_5H_5$ = cyclopentadienyl) and (3.18 ± 0.3) eV for Cp_2Co. In neutral $Co(CO)_3NO$, the (Co–NO) bond energy is 1.89 eV. In the cation, the mean bond energy (D_m) for $(Co–NO)^+$ is (1.74 ± 0.35) eV. For carbonyl ligands the mean (Co–CO) bond energy amounts to 1.42 eV. In cations, the mean $(Co–CO)^+$ bond energy ranges from (1.34 ± 0.61) eV in $Co(CO)_3NO$ to (1.35 ± 0.05) eV in $CpCo(CO)_2$. For $CpCo(CO)_2$, $D(Co–Cp) = 2.77$ eV and $D(Co–Cp)^+ = 3.70$ eV are found. For neutral Cp_2Co, dissociation energies of $D(CpCo–Cp) = 3.54$ eV and $D(Co–Cp) = 2.77$ eV are obtained for the sequential elimination of the first and the second Cp ligand, respectively. In Cp_2Co^+, $D(CpCo–Cp)^+ = 4.86$ eV and $D(Co–Cp)^+ = 3.98$ eV are obtained, respectively.

Keywords: Gas-phase enthalpies of formation; Bond energies; Dissociation energies; Metastable ion decay; Mass spectra

1. Introduction

Our recent studies on the nanosecond multiphoton ionization (MPI) of a variety of organometallic compounds have established an ionization preceding dissociation mechanism comprising the initial formation of molecular ions [1]. This mechanism was found to be in a wavelength-dependent competition with the well established dissociation preceding ionization pathway with a complete disintegration of the parent neutral compound to yield bare metal atoms following their ionization [2]. Molecular ions containing carbonyl (CO) ligands, however, tend to a rapid elimination of these ligands. Reasons for this are the low metal to carbonyl dissociation energy and the usually high amount of excess energy in the molecular ions formed under these experimental conditions. In contrast, cyclopentadienyl and nitrosyl (NO) ligands are bound more strongly to the central metal entity [3]. Nitrosyl acts as a 3-electron-ligand with interesting

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back-bonding abilities. However, very little information is available for the strength of the metal to nitrosyl bond [4,5]. A useful gateway to a variety of related thermodynamic parameters, such as individual bond energies and formation enthalpies of ions, and in some cases for the corresponding neutral compounds as well, are mass spectrometric appearance energy determinations. Sometimes, however, this method has limitations which are commonly discussed with a potential formation of ions with excess energy in a vertical excitation or with unreliabilities in detecting the minimum ion abundance threshold due to a slow fragment ion formation (the kinetic shift). However, during our MPI studies we found that carefully measured electron impact ionization and appearance energies can be correlated very well to the corresponding absorbed photon energies for the formation of a specific ion. Therefore, this and the recent study of manganese compounds [6] gave encouragement to an extension to related cobalt compounds, for which very few data are available.

2. Experimental

Cyclopentadienyl-cobalt-dicarbonyl and cobalt-tricarbonyl-nitrosyl were purchased from Strem Chemicals (Kehl, Germany) and biscyclopentadienyl-cobalt from Aldrich. The samples were stored under argon and used as received. The measurements were performed with a Finnigan MAT-95 mass spectrometer (Finnigan MAT, Bremen) with reversed Nier-Johnson geometry. Cyclopentadienyl-cobalt-dicarbonyl and cobalt-tricarbonyl-nitrosyl, as liquids, and all the reference compounds were introduced into the ion source using the reference inlet at room temperature. Biscyclopentadienyl-cobalt was introduced on the sample rod at room temperature as well. For the ion at *m*/*z* 87 of $CpCo(CO)_2$ the sum formula $CoCO^+$ was confirmed by accurate mass determination. Metastable ions were recorded in the two field-free regions between the ion acceleration sector and the magnet sector (region I) or between the magnetic and the electrostatic sector (region II). The appropriate scan laws for the daughter ion, the parent ion, and the neutral loss scan were automatically set by the instrument. For the determination of the ionization and appearance energies (IE, AE), the electron capture dynode was deactivated and the voltage of the draw-out aperture was set to zero. Minimum energy thresholds were calculated by extrapolation of the line of log (ion intensity) vs. electron energy to a vanishing ion intensity [7]. A variety of references with masses and IEs (AEs) close to the ion under investigation were used for calibration of the energy scale: 1,3-dibromopropane (IE = 10.26 eV), 1,2-dibromoethane (IE = 10.37 eV, $AE(C_2H_4Br^+) = 10.53$ eV), dibromomethane (IE = 10.49 eV), dibutylether (IE = 9.51 eV), dibutylamine (IE = 7.69 eV), cyclohexane (IE = 9.88 eV, $AE(C_4H_7^+) = 11.21$ eV), dichloromethane (IE = 11.32 eV, $AE(CH_2Cl^+) = 12.14$ eV), chloroform (IE = 12.37 eV).

All values were taken from [8a] and [8b]. In this way, a mass-dependent nonlinearity in the ion transmission at threshold conditions was corrected. Sample and reference ions were measured at the same particle density in the ion source.

3. Results and discussion

3.1. Cobalt-tricarbonyl-nitrosyl

A mass spectrum of $Co(CO)_3NO$ on EI ionization is shown in Fig. 1. The metastable ion decay (Fig. 2, Table 1) provides detailed insight into the fragmentation mechanism. Molecular ions are abundant at *m*/*z* 173. Detachment of the first CO ligand leads to $Co(CO)_2NO^+$ ions at *m*/*z* 145. From these $Co(CO)_2NO^+$ ions, two different fragmentation pathways are observed. On the first, the elimination of the NO ligand leads to ${Co(CO)_2}^+$ ions. Further degradation occurs by successive detachment of two CO ligands to $CoCO^+$ at *m*/*z* 87 and finally to Co^+ at *m*/*z* 59. On the second pathway $Co(CO)_2NO^+$ ions eliminate CO forming $CoCONO^+$ ions at *m*/*z* 117. Further degradation is performed by loss of CO and the resulting $CoNO^+$ ions at *m*/*z* 89 eliminate NO, thus finally ending in Co^+ as well. CoC^+ ions are seen at *m*/*z* 71.

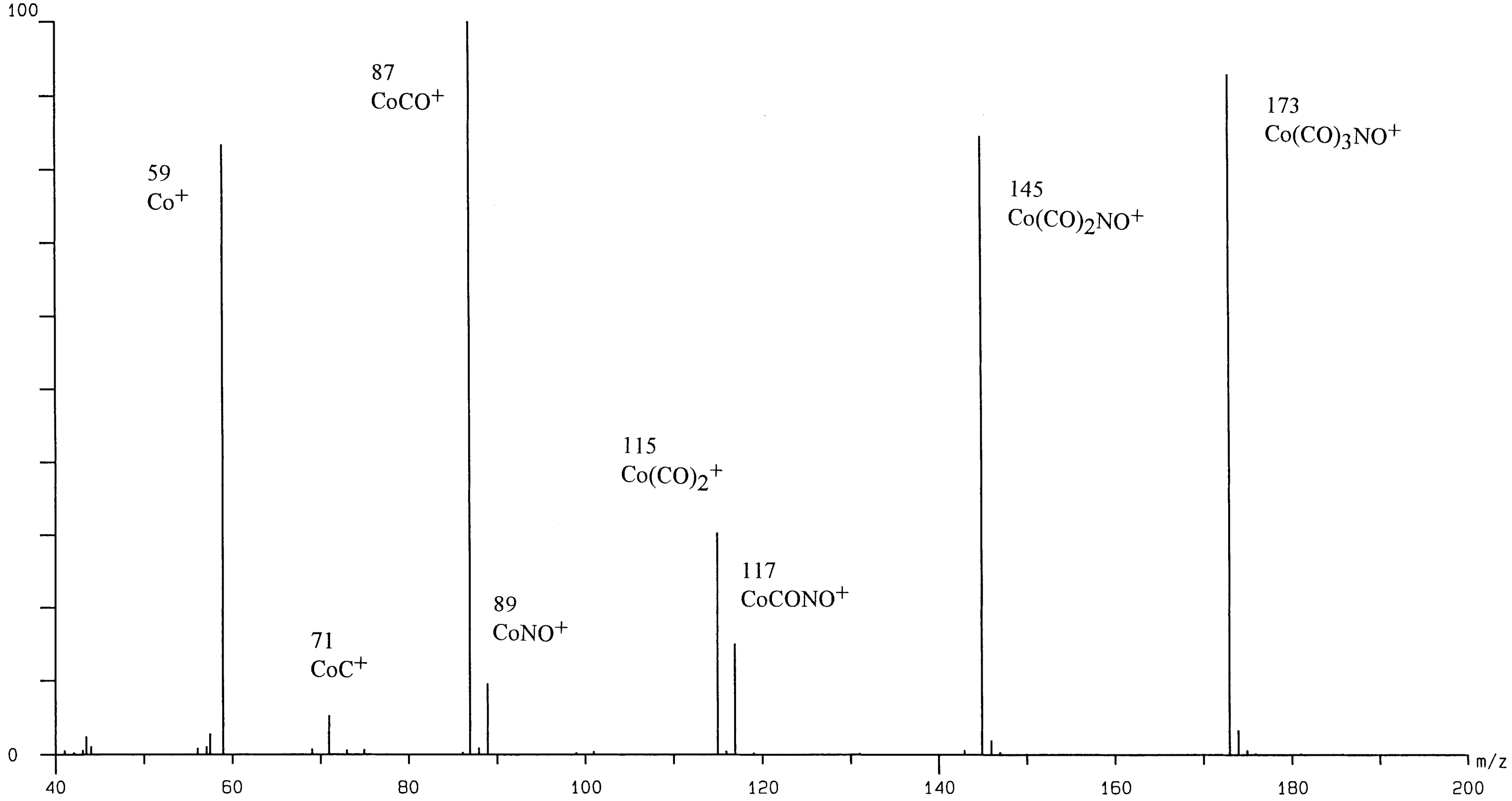

Fig. 1. Mass spectrum of $Co(CO)_3NO$ on electron impact ionization at 70 eV electron energy.

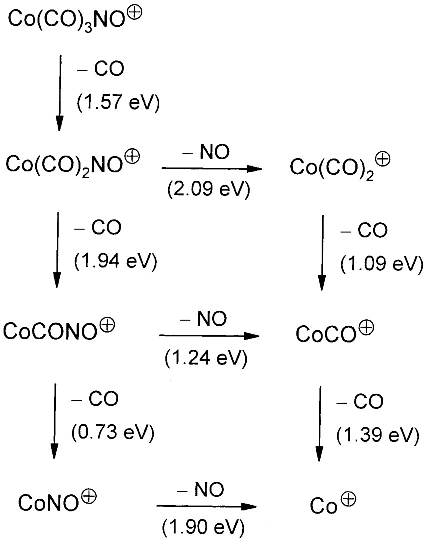

Fig. 2. Metastable ion decay on EI ionization of $Co(CO)_3NO$. Additionally, detached neutral ligands and the corresponding dissociation energies serve for illustration of the thermochemical results of the stable ions.

Table 2
Ionization and appearance energies (IE, AE) on EI ionization of $Co(CO)_3NO$

Ion	m/z	IE, AE (eV)	Literature
$Co(CO)_3NO^+$	173	7.89 ± 0.3	8.8[a], 8.11[b], 8.26[c]
$Co(CO)_2NO^+$	145	9.46 ± 0.3	9.65[d]
$CoCONO^+$	117	11.40 ± 0.3	
$Co(CO)_2^+$	115	11.55 ± 0.3	
$CoNO^+$	89	12.13 ± 0.3	
$CoCO^+$	87	12.64 ± 0.3	
Co^+	59	14.03 ± 0.3	

[a] [15a].
[b] [15b].
[c] [15c].
[d] [15d].

For these individual degradation steps, data from Tables 2 and 3 allow the calculation of bond energies from differences in the appearance energies. The results are summarized in Table 4. Starting from the molecular ion, elimination of the first CO ligand requires 1.57 eV. From the resulting $Co(CO)_2NO^+$ ions, the detachment of CO needs 1.94 eV, whereas the detachment of NO needs 2.09 eV. From $Co(CO)_2^+$ ions the successive elimination of the two remaining CO ligands needs 1.09 and 1.39 eV, respectively. From $CoCONO^+$ ions the elimination of CO needs 0.73 eV whereas the elimination of NO needs 1.24 eV. $CoNO^+$ ions need 1.90 eV to eliminate NO, finally ending in Co^+. Averaging over these various steps,

Table 1
Metastable ion decay of $Co(CO)_3NO$

(a) Daughter ions of a given parent ion

Parent ion	m/z	Daughter ion	m/z
$Co(CO)_3NO^+$	173	$Co(CO)_2NO^+$	145
$Co(CO)_2NO^+$	145	$CoCONO^+$	117
$CoCONO^+$	117	$CoNO^+$	89
$Co(CO)_2^+$	115	$CoCO^+$	87
$CoNO^+$	89	Co^+	59
$CoCO^+$	87	Co^+	59

(b) Parent ions of a given daughter ion

Daughter ion	m/z	Parent ion	m/z
$Co(CO)_2NO^+$	145	$Co(CO)_3NO^+$	173
$CoCONO^+$	117	$Co(CO)_2NO^+$	145
$Co(CO)_2^+$	115	$Co(CO)_2NO^+$	145[a]
$CoNO^+$	89	$CoCONO^+$	117
$CoCO^+$	87	$Co(CO)_2^+$	115
Co^+		$CoNO^+$	89
		$CoCO^+$	87

[a] Very weak signals. Neutral loss spectra at mass 30 (NO) confirm $Co(CO)_2NO^+$ as precursor of $Co(CO)_2^+$.

Table 3
Gas-phase enthalpies of formation ΔH_f°

Species	ΔH_f° (eV)	ΔH_f° (kJ/mol)
Co	4.447	428.4 ± 4
Co^+	12.328[a]	
C_5H_5	2.52	242.4 ± 8[b]
C_3H_3	3.53	340.6 ± 8.4
C_2H_2	2.36	227.4
CO	−1.15	−110.5
NO	0.948	91.3
$Co(CO)_4$	−5.835	−562.1 ± 7.4[c]
Cp_2Co	3.184	306.7[c]
	2.875	277[d]
	3.207	309[d]
Cp_2Ni	3.593	346.1[d]
Ni	4.464	430.1[e]

[a] Using IE(Co) = 7.881 eV [16].
[b] [17]. Recently, a slightly higher value of 261 ± 4 kJ/mol (≡2.71 eV) was suggested [11].
[c] [9].
[d] [18].
[e] [16].

Table 4
Dissociation energies D (A–B) for $Co(CO)_3NO$ as derived from the IE/AE data and enthalpies of formation ΔH_f°

A	B	D (eV)
$Co(CO)_2NO^+$	CO	1.57
$Co(CO)_2{}^+$	NO	2.09
$CoCONO^+$	CO	1.94
$CoCO^+$	CO	1.09
$CoCO^+$	NO	1.24
$CoNO^+$	CO	0.73
Co^+	CO	1.39
Co^+	NO	1.90
Co	NO	1.89
XCo^+	CO	1.34 (mean value)
YCo^+	NO	1.74 (mean value)
For comparison		
$CpNi^+$	NO	1.95[a]
Co	CO	1.42 (mean value, see text)

[a] 188 ± 20 kJ/mol [4].

Table 5
Gas-phase enthalpies of formation of $Co(CO)_3NO$ and fragments

Species	ΔH_f° (eV)	IE (eV)
$Co(CO)_3NO$	−4.20	7.89
$Co(CO)_3NO^+$	3.69	
$Co(CO)_2NO^+$	6.41	
$CoCONO^+$	9.50	
$Co(CO)_2{}^+$	7.55	
$CoNO^+$	11.38	
$CoCO^+$	9.79	

The estimated error is ±0.3 eV. The ionization energy (IE) refers to the corresponding neutral species.

mean dissociation energies of (1.34 ± 0.61) eV for the $(Co–CO)^+$ bond and (1.74 ± 0.35) eV for the $(Co–NO)^+$ bond are obtained. The last result can be compared very well with results for CpNiNO with $D(CpNi–NO)^+ = 1.95$ eV [4] and also for $CpMo(CO)_2NO$ with a $(Mo–NO)^+$ bond energy around 2.5 eV [5]. These energetic aspects are somewhat contradictive to the 70 eV mass spectra with respect to the lower abundance of $CoCONO^+$ compared to $Co(CO)_2{}^+$ ions at m/z 117 and 115, paralleled by the intensities of $CoNO^+$ and $CoCO^+$ ions at m/z 89 and 87, respectively. Although the fragmentation to the corresponding NO containing ions needs less energy, their lower abundance points to a kinetically preferred decomposition of molecular ions along the $Co(CO)_2{}^+$ and $CoCO^+$ route. In some support of this, a very low intensity of metastable ions leading to $Co(CO)_2{}^+$ was found. A kinetic model for this behavior is currently in progress.

An enthalpy of formation of $Co(CO)_3NO$ of (−4.20 ± 0.3) eV is obtained according to reaction (1)

$$Co(CO)_3NO \rightarrow Co^+ + 3CO + NO + e^- \qquad (1)$$

using $AE(Co^+) = (14.03 \pm 0.3)$ eV as reaction enthalpy and formation enthalpies for the products from Table 3. All the derived formation enthalpies are given according to the mass spectrometric convention, which means that the formation enthalpy of the formal particle electron is incorporated into the formation enthalpy of the cation.

Using the formation enthalpy of the parent compound, those of its fragments are calculated and summarized in Table 5.

The following evaluation of the (Co–NO) bond strength in the neutral parent compound is subject to a certain limitation since the used energy for the three (Co–CO) bonds is, in fact, a mean value from the four (Co–CO) bonds in $Co(CO)_4$. The reported mean (Co–CO) bond energy of 1.42 eV from the comprehensive data compilation for organometallic compounds [9] is readily reproduced from the formation enthalpies of $Co(CO)_4$ and CO given in Table 3.

Subtracting the ionization energy $IE(Co) = 7.88$ eV from the enthalpy of reaction (1), a reaction enthalpy (ΔH_r) of 6.15 eV is obtained for

$$Co(CO)_3NO \rightarrow Co + 3CO + NO. \qquad (2)$$

Within the experimental error limit, this is in accordance with a one-photon-dissociation study in the gas-phase which yielded an energy range of (6.40–7.58) eV for the formation of ground state Co according to reaction (2) [10]. Adopting the energy of 1.42 eV for each (Co–CO) bond (see above), a value of 1.89 eV remains for the (Co–NO) bond energy.

3.2. *Cyclopentadienyl-cobalt-dicarbonyl*

A mass spectrum of $CpCo(CO)_2$ is shown in Fig. 3. Molecular ions appear at m/z 180. As seen

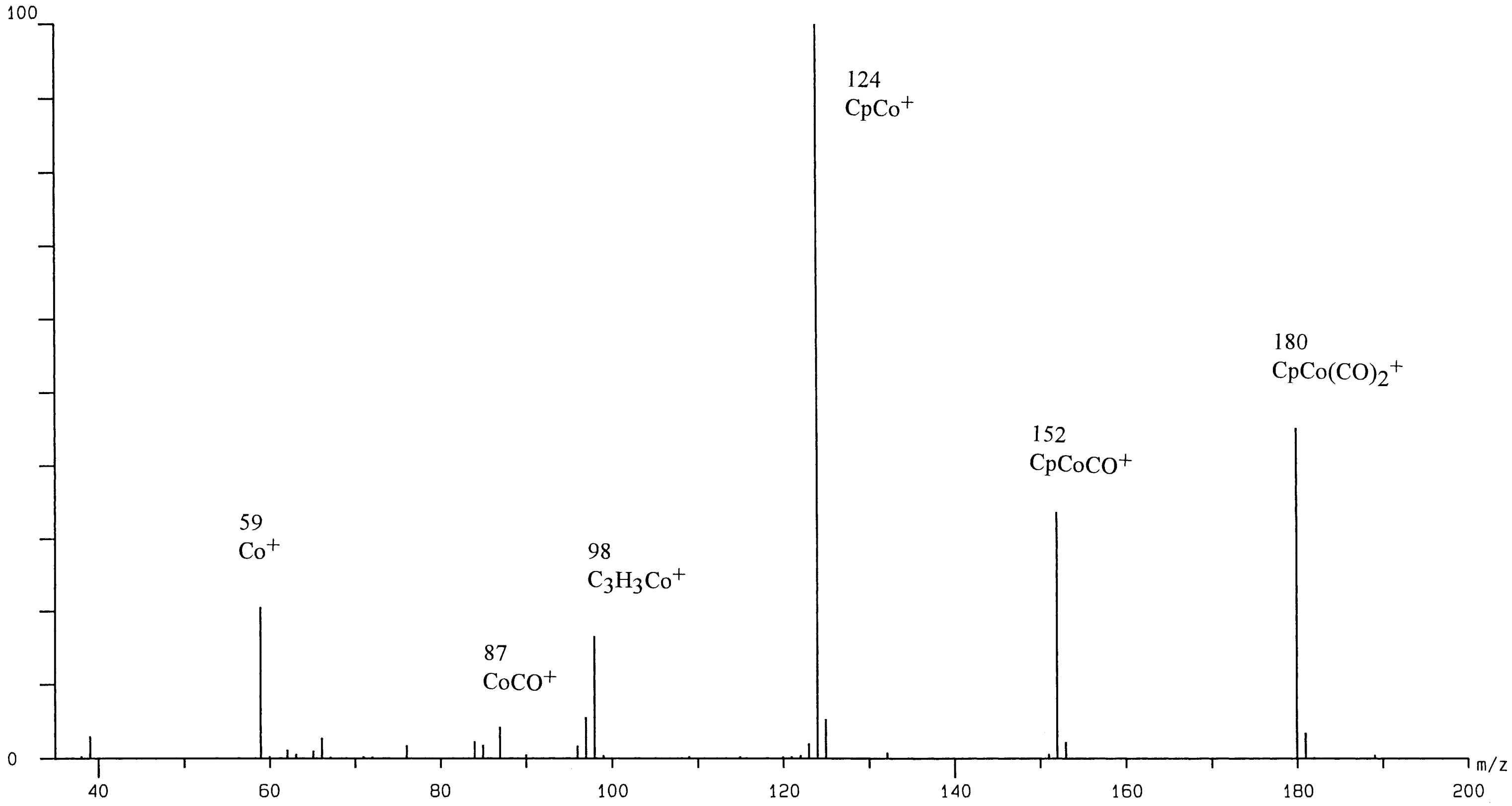

Fig. 3. Mass spectrum of $CpCo(CO)_2$ on electron impact ionization at 70 eV electron energy.

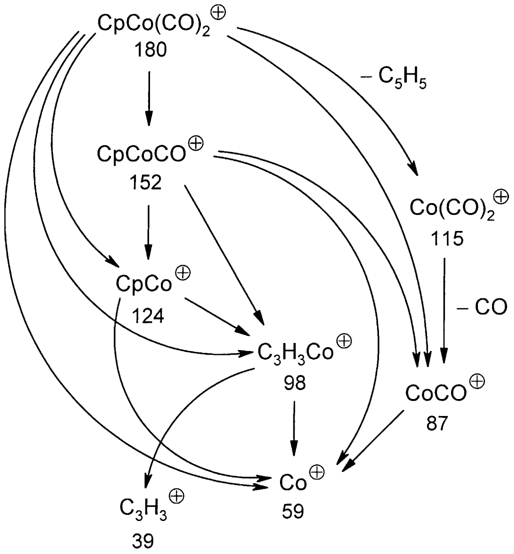

Fig. 4. Metastable ion decay on EI ionization of $CpCo(CO)_2$.

Table 6
Metastable ion decay of $CpCo(CO)_2$

(a) Daughter ions of a given parent ion

Parent ion	*m/z*	Daughter ion	*m/z*
$CpCo(CO)_2^+$	180	$CpCoCO^+$	152
		$CpCo^+$	124
		$C_3H_3Co^+$	98
$CpCoCO^+$	152	$CpCo^+$	124
		$C_3H_3Co^+$	98
		Co^+	59
$CpCo^+$	124	$C_3H_3Co^+$	98
		Co^+	59
$C_3H_3Co^+$	98	Co^+	59
$CoCO^+$	87	Co^+	59

(b) Parent ions of a given daughter ion

Daughter ion	*m/z*	Parent ion	*m/z*
Co^+	59	$CoCO^+$	87
		$C_3H_3Co^+$	98
		$CpCo^+$	124
		$CpCoCO^+$	152
		$CpCo(CO)_2^+$	180
$CoCO^+$	87	$CoCO^+$	115
		$CpCoCO^+$	152
		$CpCo(CO)_2^+$	180
$C_3H_3Co^+$	98	$CpCo^+$	124
		$CpCoCO^+$	152
		$CpCo(CO)_2^+$	180
$CpCo^+$	124	$CpCoCO^+$	152
		$CpCo(CO)_2^+$	180
$CpCoCO^+$	152	$CpCo(CO)_2^+$	180

(c) Neutral fragments and their parent ions

Fragment	Mass	Parent ion	*m/z*
CO	28	$CoCO^+$	87
		$CpCoCO^+$	152
		$CpCo(CO)_2^+$	180
C_5H_5	65	$CpCo^+$	124
		$CpCoCO^+$	152
		$CpCo(CO)_2^+$	180

from the metastable ion decay (Fig. 4, Table 6), successive eliminations of two CO ligands lead to $CpCoCO^+$ at *m/z* 152, and to $CpCo^+$ at *m/z* 124. $CpCo^+$ ions show either the elimination of the entire Cp ligand or the partial Cp degradation by elimination of C_2H_2 resulting in the formation of $C_3H_3Co^+$ at *m/z* 98. To a smaller extent the degradation of the Cp ligand also occurs by elimination of C_2H_3 or C_2H_4. Finally, Co^+ ions are formed. A second fragmentation pathway from molecular ions is centralized around $CoCO^+$ ions at *m/z* 87. Parent ions from those are either molecular ions, $CpCoCO^+$ ions or $Co(CO)_2^+$ ions at *m/z* 115. In addition, neutral loss spectra show the elimination of C_5H_5 (overall mass 65) from $CpCo(CO)_2^+$ and $CpCoCO^+$ ions and the elimination of CO (mass 28) from $CoCO^+$ yielding Co^+.

Using $AE(Co^+) = (13.47 \pm 0.3)\,eV$ (Table 7), a formation enthalpy of $CpCo(CO)_2$ of $(-0.92 \pm 0.3)\,eV$ is obtained according to reaction (3) and product enthalpy data taken from Table 3.

$$CpCo(CO)_2 \rightarrow Co^+ + Cp + 2CO + e^- \qquad (3)$$

Among the latter, the formation enthalpy of C_5H_5 is still under dispute, but the recently suggested value of $\Delta H_f^\circ = 261 \pm 4\,kcal/mol$ ($\equiv 2.71\,eV$) [11] is, within the experimental error limit, close enough to support that one used here and in our previous studies on related compounds.

From this, the formation enthalpies of some fragments are calculated and summarized in Table 8.

Following these data, the detachment of the first and the second CO ligand from molecular ions requires 1.40 and 1.29 eV, respectively (Table 9). From the

Table 7
Ionization and appearance energies (IE, AE) on EI ionization of $CpCo(CO)_2$

Ion	*m/z*	IE, AE (eV)	Literature[a]
$CpCo(CO)_2{}^+$	180	7.08 ± 0.3	8.3 ± 0.2
$CpCoCO^+$	152	8.48 ± 0.3	10.1 ± 0.2
$CpCo^+$	124	9.77 ± 0.3	11.7 ± 0.2
$C_3H_3Co^+$	98	13.24 ± 0.3	16.8 ± 0.3
$CoCO^+$	87	14.50 ± 0.3	16.5 ± 0.4
Co^+	59	13.47 ± 0.3	16.8 ± 0.3

[a] [19]; EI; used references: O_2 from a small air leak and Hg from the diffusion pump.

Table 8
Gas-phase enthalpies of formation of $CpCo(CO)_2$ and fragments

Species	ΔH_f° (eV)	IE (eV)
$CpCo(CO)_2$	−0.92	7.08
$CpCo(CO)_2{}^+$	6.16	
$CpCoCO^+$	8.71	
CpCo	4.20	6.95
$CpCo^+$	11.15	
$C_3H_3Co^+$	12.26	
For comparison		
Co	4.446	7.881
Co^+	12.328	
Cp_2Co		5.35

The estimated error is ±0.3 eV. Values for neutral fragments are calculated with a mean bond energy of D_m(Co–CO) = 1.42 eV. Ionization energies (IE) refer to the corresponding neutral species.

resulting $CpCo^+$ ion the detachment of the entire Cp ligand needs 3.70 eV.

A formation enthalpy of $C_3H_3Co^+$ ions of 12.26 eV is obtained according to

$$CpCo(CO)_2 \rightarrow C_3H_3Co^+ + C_2H_2 + 2CO + e^- . \qquad (4)$$

Table 9
Dissociation energies *D* (A–B) for $CpCo(CO)_2$ as derived from the IE/AE data and enthalpies of formation ΔH_f°

A	B	*D* (eV)
$CpCoCO^+$	CO	1.40
$CpCo^+$	CO	1.29
Co^+	Cp	3.70
Co^+	C_3H_3	3.60
Co	Cp	2.77
XCo^+	CO	1.35 (mean value)

A dissociation energy $D(Co–C_3H_3)^+$ of 3.60 eV is required for the detachment of this C_3H_3 ligand according to

$$C_3H_3Co^+ \rightarrow Co^+ + C_3H_3 \qquad (5)$$

For an estimation of the (Co–Cp) bond energy in the neutral parent compound, ΔH_f° (CpCo) is calculated according to reaction (6)

$$CpCo(CO)_2 \rightarrow CpCo + 2CO \qquad (6)$$

$$CpCo \rightarrow Co + Cp \qquad (7)$$

where the reaction (6) enthalpy is again approximated by two mean (Co–CO) bond energies of 1.42 eV each. As ionization energy of this fragment, IE(CpCo) = 6.95 eV is obtained, which is reasonably located between IE($CpCo(CO)_2$) and IE(Cp_2Co) (Table 8). According to reaction (7) a bond energy *D*(Co–Cp) = 2.77 eV is obtained.

These data allow an evaluation of the peculiar fragmentation to $CoCO^+$ at *m/z* 87 which comprises the detachment of the first CO ligand and (overall) of the Cp ligand from molecular ions. Clearly, the least energetic and dominant fragmentation pathway from molecular ions is a detachment of two CO ligands which needs only 2.69 eV. Although no explicit dissociation energy is available for the detachment of Cp from $CpCoCO^+$ ions, it is evident that Cp is bound much more strongly to the metal entity than the second CO ligand with an expected bond energy of at least 3.70 eV for entire Cp compared to 1.29 eV for CO.

As options, the formation of $CoCO^+$ ions according to reactions (8) and (9) is analyzed.

$$CpCo(CO)_2 \rightarrow CoCO^+ + C_5H_5 + CO + e^- \qquad (8)$$

$$CpCo(CO)_2 \rightarrow CoCO^+ + C_3H_3 + C_2H_2 + CO + e^- \qquad (9)$$

Adopting ΔH_f° ($CoCO^+$) from Table 5 options for reaction enthalpies of 12.08 or 15.45 eV are expected for reaction (8) or (9), respectively. The experimentally found AE($CoCO^+$) of 14.50 eV is in some favor of reaction (9), but, at present, the most likely explanation is a formation analog to reaction (8) with product(s) carrying excess energy. Nevertheless, although $CoCO^+$ ions are not too abundant in the 70 eV mass spectra, the fragmentation to these ions is evidence for a competitive second decomposition mechanism from molecular ions. It is conceivable, that a dissociative repulsive channel is accessible at higher excitation energies.

The present results allow some insight into the bonding conditions of cobalt to NO by a comparison of the energy for the detachment of Cp (as a five electron ligand) and the sum of the energies for the detachment of NO (a three electron ligand) and CO (a two electron ligand). A reaction enthalpy of 3.70 eV is obtained for

$$CpCo^+ \rightarrow Co^+ + Cp, \qquad (10)$$

whereas a significant smaller enthalpy of 2.63 eV is obtained for

$$CoCONO^+ \rightarrow Co^+ + CO + NO. \qquad (11)$$

From this, in cations, the cobalt to NO binding tends to a similar behavior as cobalt to CO, whereas the cobalt to Cp binding points to a more pronounced participation of electrostatic effects.

3.3. *Biscyclopentadienyl-cobalt*

This compound, as a metallocene prototype, has received some more experimental attraction than the two other title compounds. In contrast to the 18 electron systems in $Co(CO)_3NO$ and $CpCo(CO)_2$, Cp_2Co is a 19 electron system with a $^2E_{1g}$ ($e_{2g}^4 a_{1g}^2 e_{1g}^1$) ground state carrying an electron in the antibonding e_{1g} molecular orbital [12]. Therefore, the first ionization energy corresponds to the removal of this antibonding electron to yield the $^2A_{1g}$ ion state and it's value is expected to be relatively low compared to other cyclopentadienyl sandwich compounds. In fact, on photoelectron spectroscopy, a first IE of 5.56 eV was obtained, but the assignment has been reported to be less certain than for other sandwich compounds [12]. In old mass spectrometric works on EI ionization of several cyclopentadienyl metal compounds, IEs of (6.2 ± 0.3) eV [13] and (5.7 ± 0.2) eV [14] were published.

Table 10
Ionization and appearance energies (IE, AE) on EI ionization of Cp_2Co

Ion	*m/z*	IE, AE (eV)	Literature
Cp_2Co^+	189	5.35 ± 0.3	5.56[a], 6.21[b]
$CpCo^+$	124	10.21 ± 0.3	14.00[b]
Co^+	59	14.19 ± 0.3	14.66[b]

[a] [12]; photoelectron spectroscopy.
[b] [20]; EI; used reference: xenon.

Relevant results on photoelectron spectroscopy and on EI ionization are added to Table 10. Additionally, Table 3 contains some formation enthalpies, obtained by combustion calorimetry.

A mass spectrum is depicted in Fig. 5. Molecular ions appear at *m/z* 189. Confirmed by the metastable ion decay (Fig. 6, Table 11), their fragmentation is governed by detachment of Cp to $CpCo^+$ at *m/z* 124 or directly to Co^+. $CpCo^+$ ions eliminate either Cp, yielding Co^+, or C_2H_2 with a formation of $C_3H_3Co^+$ at *m/z* 98. From the latter, Co^+ is formed by detachment of C_3H_3.

Using $AE(Co^+) = (14.19 \pm 0.3)$ eV and data from Table 3, a formation enthalpy of (3.18 ± 0.3) eV of Cp_2Co is obtained according to reaction (12) (see Table 12).

$$Cp_2Co \rightarrow Co^+ + 2Cp + e^- \qquad (12)$$

This result is corroborated by thermochemical data (Table 3). Furthermore, within the experimental error

Table 11
Metastable ion decay of Cp_2Co

(a) Daughter ions of a given parent ion

Parent ion	*m/z*	Daughter ion	*m/z*
Cp_2Co^+	189	$CpCo^+$	124
		Co^+	59
$CpCo^+$	124	$C_3H_3Co^+$	98
		Co^+	59

(b) Parent ion of a given daughter ion

Daughter ion	*m/z*	Parent ion	*m/z*
$CpCo^+$	124	Cp_2Co^+	189
Co^+	59	Cp_2Co^+	189
		$CpCo^+$	124

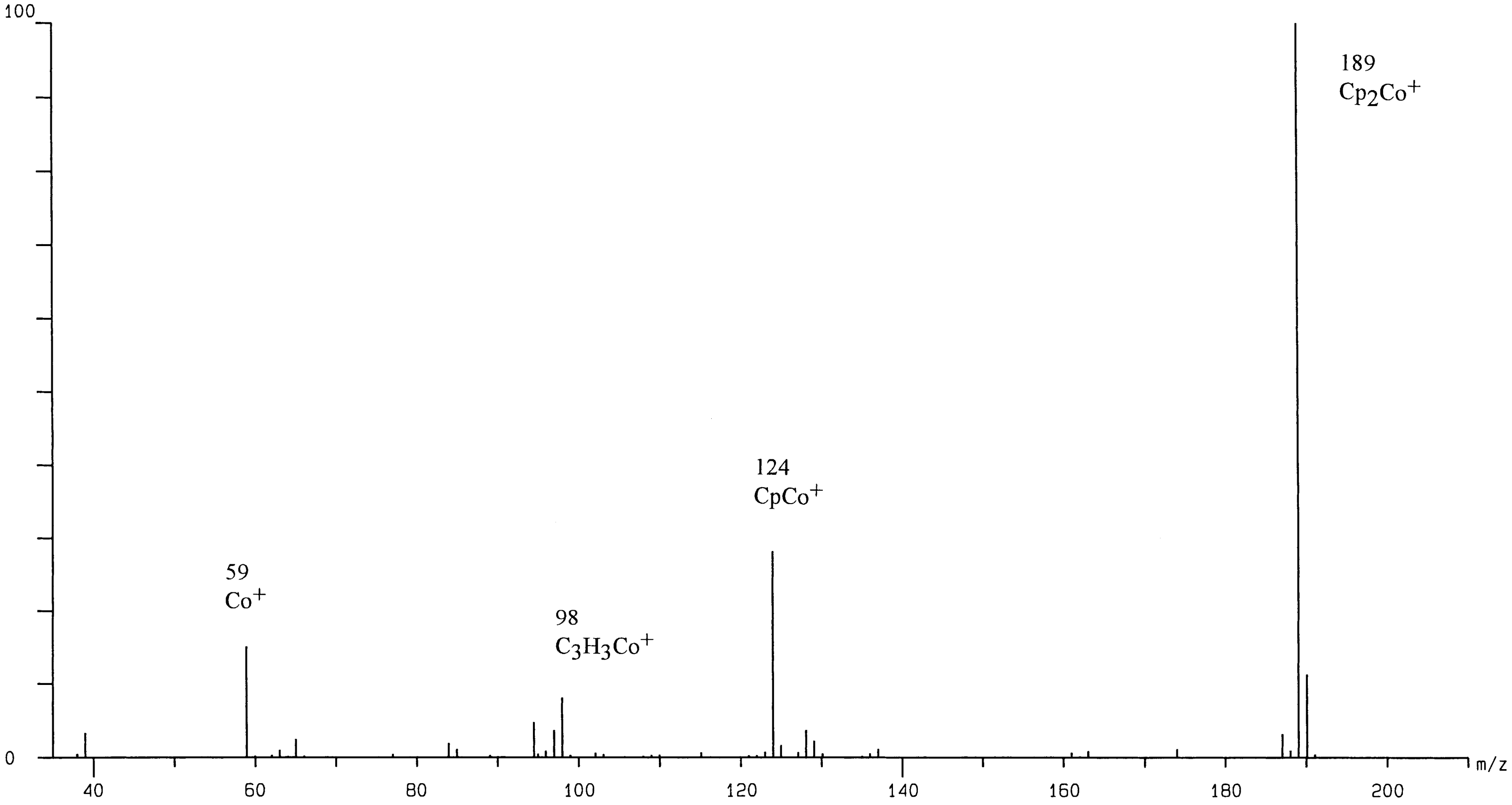

Fig. 5. Mass spectrum of Cp_2Co on electron impact ionization at 70 eV electron energy.

Table 12
Gas-phase enthalpies of formation of Cp_2Co and fragments

Species	ΔH_f° (eV)	IE (eV)
Cp_2Co	3.18	5.35
Cp_2Co^+	8.53	
CpCo	4.20[a]	6.67
$CpCo^+$	10.87	

The estimated error is ±0.3 eV. Ionization energies (IE) refer to the corresponding neutral species.
[a] Result for $CpCo(CO)_2$.

Table 13
Dissociation energies D (A–B) for Cp_2Co as derived from the IE/AE data and enthalpies of formation ΔH_f°

A	B	D (eV)
CpCo	Cp	3.54
Co	Cp	2.77
$CpCo^+$	Cp	4.86
Co^+	Cp	3.98
XCo	Cp	3.15 (mean value)
XCo^+	Cp	4.42 (mean value)
For comparison		
Ni	Cp	2.97 (mean value for Cp_2Ni)[a]
Ni^+	Cp	3.47 (mean value for Cp_2Ni^+)[b]
Ni^+	Cp	3.98[c]
CpFe	Cp	3.95[d]
Fe	Cp	(3.00–3.82)[e]
$CpFe^+$	Cp	4.61[e]
Fe^+	Cp	4.04[e]

[a] Calculated with ΔH_f° values from Table 3.
[b] [21].
[c] [4,22]
[d] [23].
[e] [1a].

limit, it is in line with a calculation according to

$$Cp_2Co \rightarrow CpCo^+ + Cp \qquad (13)$$

adopting ΔH_f° ($CpCo^+$) from the $CpCo(CO)_2$ results.

From this, in neutral Cp_2Co a mean bond energy D_m(Co–Cp) of 3.15 eV is obtained according to

$$Cp_2Co \rightarrow Co + 2Cp. \qquad (14)$$

The two sequential (Co–Cp) dissociation energies in neutral Cp_2Co can be estimated by adopting ΔH_f° (CpCo) from Table 8. The elimination of the first and the second Cp ligand needs 3.54 and 2.77 eV, respectively (Table 13). Derived directly from the IE/AE data, the corresponding sequential dissociation energies in the cation are 4.86 and 3.98 eV (Table 13). From this, a mean value of $D_m(\text{Co–Cp})^+ = 4.42$ eV is obtained. Evidently, in the neutral and in the cationic species, the detachment of the first ligand needs more energy than that of the second. The increase in the bond energies on going from the neutral parent compound to the corresponding cation in part reflects the increased stability of the latter after removal of the antibonding e_{1g} electron on ionization. Furthermore, participating Coulomb effects on the bond energies can be estimated from the comparison with the 20 electron system Cp_2Ni with a $^3A_{2g}$ ($e_{2g}^4a_{1g}^2e_{1g}^2$) ground state, where the removal of an e_{1g} electron leads to an $^2E_{1g}$ ion state [12]. Thus, the electron system in Cp_2Ni^+ corresponds to that in ground state Cp_2Co. Similarly, Cp_2Fe is isoelectronic to Cp_2Co^+. The data in Table 13 exhibit a minor influence of the mere electron configuration on the corresponding dissociation energies for these systems. As the major effect, however, a strong increase in the mean dissociation energies for the two Cp ligands is seen on going from the neutral to the cationic species.

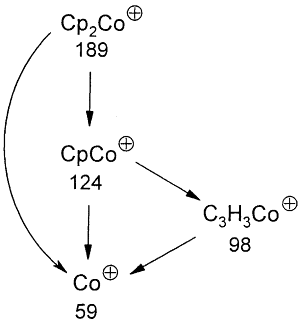

Fig. 6. Metastable ion decay on EI ionization of Cp_2Co.

Although data for the sequential Cp dissociation energies in nickelocene are not available, the detailed results for ferrocene and cobaltocene point to the fact that the strongest increase comes from the first Cp ligand, accompanied by a less pronounced increase from the second Cp ligand.

4. Conclusions

The comparison of results for the different title compounds, where always two carry a common type of ligand, shows that inherently consistent results are obtained within the experimental error limit of ±0.3 eV. This is evidence that dissociation energies tend to be specific for the type of bond rather than for the type of complex. Therefore, the following averaged values can be given: $\Delta H_f^\circ\ (\mathrm{CpCo}^+) = 11.01\,\mathrm{eV}$, $\mathrm{IE(CpCo)} = 6.81\,\mathrm{eV}$, $D(\mathrm{Co{-}Cp})^+ = 3.84\,\mathrm{eV}$, $D_\mathrm{m}(\mathrm{Co{-}CO})^+ = 1.35\,\mathrm{eV}$.

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