Neutral Cobalt−Carbonyl Bond Energy by Combined Threshold Photoelectron Photoion Coincidence and He(I) Photoelectron Spectroscopy

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Ultraviolet photoelectron (PE) spectroscopic experiments were carried out on cyclopentadienyl cobalt dicarbonyl $CpCo(CO)_2$ (**I**) using a pyrolysis inlet system. Above a certain temperature this molecule loses a carbonyl group, resulting in the 16-electron molecule CpCoCO (**II**). By subtracting the PE spectrum of (**I**) from the mixed experimental spectrum, the PES of (**II**) was obtained. Adiabatic and vertical ionization energies (IEs) were also determined. By using a thermodynamic cycle, which included the appearance energy of $CpCoCO^+$ determined in an earlier threshold photoelectron photoion coincidence (TPEPICO) experiment, the dissociation energy of CpCoCO···CO was obtained to be 1.91 ± 0.05 eV. Quantum-chemical calculations were also carried out to help the reassignment of the photoelectron spectrum of (**I**) and to help establish a reliable value of the adiabatic IE of (**II**).

Introduction

Cyclopentadienyl cobalt dicarbonyl, $CpCo(CO)_2$, has attracted much attention in the past few years both because of its catalytic properties and as a precursor in organometallic chemical vapor deposition (CVD) experiments. It is clear that in both processes the first reaction step is a carbonyl loss from the cobalt center. The energetics of this reaction is, therefore, of great importance.

Recently, Vollhardt and co-workers[1] demonstrated the use of $CpCo(CO)_2$ and its derivatives in the stereoselective [2 + 2 + 2] cycloadditions to the benzofuran nucleus in their efforts at a new synthesis of morphinoids. Varela and co-workers[2] synthesized novel spiropyridines by cobalt-catalyzed double co-cyclization of bis-alkynenitriles and alkynes. Diastereomeric cobalt complexes were prepared by Slowinski et al.[3] from chiral phosphine oxide-substituted linear enediynes by stereoselective [2 + 2 + 2] cycloaddition. $CpCo(CO)_2$ can even be used in supercritical water solvent in cyclotrimerization reactions of monosubstituted acetylenes to form substituted benzene derivatives.[4] The high stereoselectivity of the $CpCo(CO)_2$-catalyzed reactions allow synthesis of new classes of compounds with helical chirality.[5]

Cyclopentadienyl cobalt dicarbonyl is also extensively used in organometallic chemical vapor deposition experiments. Recently, a number of papers were published about the formation of epitaxial $CoSi_2$ layers on silicon surfaces.[6−9] In addition, β-CoGa thin layers were formed on GaAs by chemical beam epitaxy using $CpCo(CO)_2$ and $GaEt_3$.[10] Lithium cobalt oxide films can be prepared from $CpCo(CO)_2$ and *t*-BuLi as demonstrated by Kenny and co-workers.[11] As an alternative to physical deposition of metals for chip wiring, chemical deposition of copper−cobalt alloys is possible using $CpCo(CO)_2$ as a precursor.[12]

In all of the above processes, the cobalt−carbonyl bond undergoes fission, which makes this bond energy an important value. A number of experiments have been carried out to study the resulting 16-electron species, CpCoCO, formed from the $CpCo(CO)_2$. In liquefied noble gas solvents, CpCoCO is formed by ultraviolet irradiation.[13,14] In hydrocarbon solvents, one carbonyl ligand is replaced by a solvent molecule in the photochemical experiments.[15−17] The cobalt−carbonyl bond energy was measured in the anion by Sunderlin et al. using energy-resolved collision-induced dissociation.[18]

In a recent paper, we have published bond energy data on the $CpCo(CO)_2^+$ ion.[19] Threshold photoelectron photoion coincidence spectroscopy (TPEPICO) was used to determine the Co−CO bond strength in $CpCo(CO)_2^+$ and $CpCoCO^+$. The bond energies were determined to be 1.53 ± 0.02 eV (148.1 ± 2 kJ/mol) and 1.50 ± 0.01 eV (144.8 ± 1 kJ/mol), respectively. Heats of formation of the $CpCo(CO)_n^+$ ions were also derived by combining our TPEPICO data with a liquid-phase heat of formation[20] and a measurement of the heat of vaporization.[19] No bond energy data of the neutral species was determined, however.

Ionization energies of $CpCo(CO)_2$ have been determined using ultraviolet photoelectron spectroscopy (UPS) by Green and co-workers [21] and Lichtenberger et al.,[22] while Li and co-workers[23] recently published the results of a variable-energy photoelectron spectroscopic study of $CpCo(CO)_2$. The use of variable photon energy is especially useful in the correct assignment of the photoelectron bands, as it is widely accepted that the band intensity significantly increases when the photon energy is changed from 20 to 40 eV if the respective molecular orbital has high d-character. Theoretical ionization energies and MO compositions were also given from Xα-SW calculations. Their published ordering of the photoelectron bands is the following: 16a′, 15a′, 14a′, 10a″,11a″, 13a′, starting with the lowest IE.

Experimental Section

Ultraviolet Photoelectron Spectroscopy (UPS) Measurements. The pyrolysis He(I) photoelectron experiments were

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carried out on an ATOMKI ESA 32 instrument, which has been described elsewhere in detail.[24,25] The spectrometer is equipped with a Leybold-Heraeus UVS 10/35 high-intensity gas discharge photon source. With this lamp in He(I) mode, the typical count rate on the Ar $^2P_{3/2}$ peak was higher than 200 000 cps with a fwhm of 30 meV. The sample was introduced into the ionization chamber via a pyrolysis inlet system. Pyrolysis takes place in a 3-mm-i.d. and 6-mm-o.d. quartz tube surrounded by a tantalum cylinder heated by tungsten wires. The maximum temperature is about 350 °C. Higher temperatures can be achieved by electron bombardment. The temperature of the quartz tube is measured by a thermocouple. Between the end of the heated quartz tube and the ionization spot, the decomposition products need to travel only 1 cm to minimize loss due to deposition on the inlet system surfaces.

Pyrolysis spectra of $CpCo(CO)_2$ were recorded between room temperature and 295 °C. This latter value is subject to a possible error because the temperature profile of the quartz tube is unknown and temperature is measured at only one position. No spectra were recorded above 300 °C, partly because the internal cooling cycle of the inlet system was turned off to avoid condensation of the sample. The spectra were calibrated using argon and nitrogen as internal standards. Maximum error in ionization energies is estimated to be less than 0.03 eV.

Quantum Chemical Calculations. To help the interpretation of the photoelectron spectra, quantum chemical calculations were carried out to calculate ionization energies of both the parent compound, $CpCo(CO)_2$ and the 16-electron species, CpCoCO. Hartree−Fock, MBPT(2),[26] B3LYP,[27] and EOM-CCSD[28] levels were used with the pvdz and pvtz basis sets of Ahlrichs and co-workers.[29] For Hartree−Fock level calculations, both the ΔSCF method and Koopmans' theorem[30] were used. The latter was used for the assignment of the photoelectron spectrum of the parent molecule, $CpCo(CO)_2$, while ΔSCF calculations were carried out to help determine the adiabatic IE of CpCoCO as it will be discussed later in more detail. For the assignment of the photoelectron bands in the spectrum of $CpCo(CO)_2$, only the EOM-CCSD method proved to be useful. The Outer Valence Green's Function method[31] as implemented in the Gaussian 98 program system[32] was also used to obtain precise ionization energies. Although this popular and widely accessible method has been useful in many cases, the renormalized third-order ionization energies computed by this method for these organometallic molecules are completely wrong, ranging in ionization energies from 40 to 100 eV depending on the valence orbital in question. The infinite-order EOM-CCSD method gave accurate ionization energies for the parent molecule, $CpCo(CO)_2$. However, it failed to give reasonable ionization energies of the 16-electron fragment molecule, CpCoCO. This is probably due to the multireference nature of the electronic structure of CpCoCO.

The calculations were carried out on an Origin2000 computer system at the University of North Carolina, Chapel Hill using the ACESII[33] and the Gaussian98 quantum chemical codes.[32]

Results and Discussion

Ionization Energies. *Parent Compound, $CpCo(CO)_2$.* Our room-temperature He(I) photoelectron spectrum of $CpCo(CO)_2$ in Figure 1 is in good agreement with the ones in the literature.[21−23] The first vertical ionization energies published were 7.51, 7.59, and 7.59 eV, respectively, which are quite close to our value of 7.55 eV. A list of the vertical ionization energies is given in Table 1, along with the literature values taken from Li et al.[23]

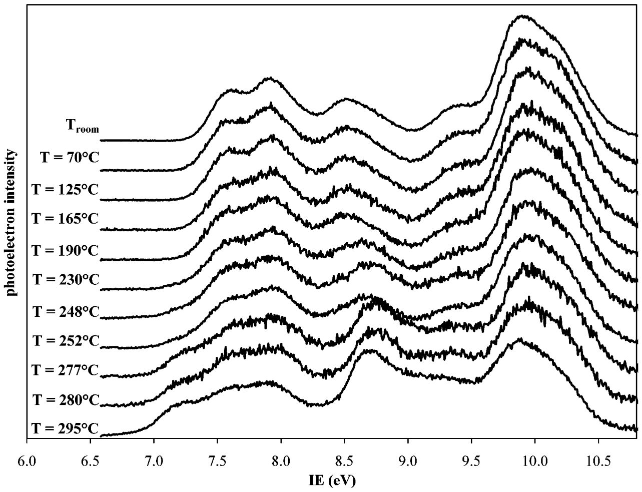

Figure 1. Appearance of the new photoelectron bands due to the formation of CpCoCO in the pyrolysis photoelectron spectra of $CpCo(CO)_2$ between room temperature and 295 °C.

Quantum chemical calculations were performed on $CpCo(CO)_2$ to assist the assignment of the photoelectron bands. Table 1 lists the calculated vertical ionization energies together with their orbital type. In some cases, the IE obtained at the HF level of theory differs from the experimental values by as much as 3−4 eV. The agreement between the experiment and the calculation is much better at the EOM-CCSD level. The difference between the latter and the Koopmans-values is largest for the orbitals 15a′ and 10a″, where the electron-correlation effects seem to be very significant. Also, the order of the molecular orbitals at the HF level is not in line with the results of the higher-level calculations. For this reason a precise assignment of the photoelectron bands of these molecules is very difficult, and is generally not possible without variable energy photoelectron spectra (at least HeI and HeII) and high-level quantum-chemical calculations.

It is also difficult to determine the correct assignment of some of the photoelectron bands to molecular orbitals from the EOM-CCSD calculations alone, because the calculated ionization energy difference between orbitals 13a′ and 11a″ is less than the estimated error of these calculations. To support our assignment, the d-orbital character of the corresponding orbitals was also considered. As mentioned above, Li and co-workers[23] published variable-energy photoelectron spectra of $CpCo(CO)_2$. The relative intensity increase of the valence bands between 20 and 30−40 eV photon energy grows from the first (lowest IE) to the fourth photoelectron band. The fifth and sixth bands strongly overlap, so that it is not possible from their publication to determine whether the left or right side of this band gains intensity. The change in the PES band intensities with increasing photon energy is given by $1 < 2 < 3 < 4 >$ (5 or 6) for PES bands 1, 2, etc. This information can be compared to the calculated d-orbital contributions to the molecular orbitals. From our population analysis calculations, the metal d-orbital involvement in the valence molecular orbitals has the following order: $11a'' < 16a' < 15a' < 10a'' < 14a' < 13a'$. If we use the order of the ionization energies from the EOM-CCSD calculations, the sequence is the following: $16a' < 15a' < 10a'' < 13a' \gg 11a'' < 14a'$. As one can see, this is completely in line with the experimental band intensity data of Li, which provides strong support for our assignment. However, this ordering differs from that reported by Li et al.,[23] a difference that we attribute to their use of lower level quantum-chemical calculations and the large correlation effects in the electronic structure.

TABLE 1: Ionization Energies of $CpCo(CO)_2$

	valence	Koopmans		EOM-CCSD			
expt	orbital	pvdz	pvtz	pvdz	pvtz	orbital type	from ref 23
7.55	16a′	8.586	7.387	7.659	7.821	Cp−Co−CO(π)	7.59 (16a′)
7.92	15a′	12.177	10.431	7.812	8.001	Co	7.94 (15a′)
8.53	10a″	12.896	11.252	8.627	8.801	Cp−Co−CO(π)	8.54 (14a′)
9.35	13a′	14.139	12.969	9.841	10.000	Co−CO(σ)	9.35 (10a″)
9.87	11a″	10.136	8.462	9.942	10.040	Cp−Co	10.00 (11a″)
10.22	14a′	12.030	11.180	10.096	10.259	Cp−Co[−CO(σ)]	10.49 (13a′)

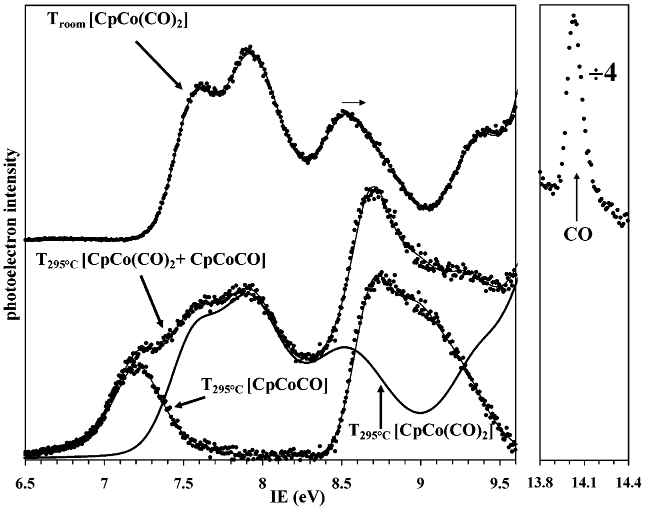

Figure 2. Subtraction of the parent molecule's spectrum from the pyrolysis UPS. In fitting the high-temperature spectrum of $CpCo(CO)_2$ to the experimental data, the position and approximate relative intensities of the bands are fixed, while the fwhms are slightly increased. Experimental noise was not subtracted from the data in obtaining the UPS of CpCoCO as it is shown on the lowermost curve. On the right side, a higher-energy part of the pyrolysis photoelectron spectrum with the emerging carbon monoxide peak is shown.

Pyrolysis Spectra. To measure the UPS of the CpCoCO fragment, the source was heated and successive UPS spectra were collected as a function of the temperature. Although the whole spectrum up to 21 eV was recorded, only the low-energy section relevant to the metal d orbitals is shown in Figure 1. It is evident that new peaks grow in around 7.2 and 8.7 eV. In addition, a strong narrow peak at 14.01 eV, clearly assignable to the ground $1^2\Sigma^+$ state of CO, emerged. This CO peak was very useful in determining at what temperature the dissociation takes place. It was also very important to note that the CO peak and the new bands came up simultaneously confirming that the new bands are due to the 16-electron CpCoCO molecule.

To obtain the photoelectron spectrum of CpCoCO from the pyrolysis spectrum at 295 °C, the spectrum of the parent molecule, $CpCo(CO)_2$, has to be subtracted. Because the peaks associated with the $CpCo(CO)_2$ compound broaden slightly as the temperature is raised (see Figure 1), we chose to fit the room-temperature spectrum with a series of Voigt functions (sum of Gaussian and Lorenzian functions). This fitted spectrum is shown as a solid line through the upper spectrum in Figure 2. The broadened spectra as a function of the temperature in Figure 1 could thus be fitted by adjusting just the width of the constituent Voigt peaks. When the broadened parent molecule peaks are subtracted from the total spectrum at 295 °C, what remains is the photoelectron spectrum of CpCoCO as shown in Figure 2. The upper curve shows the 295 °C spectrum (dots) with the result of the fitting procedure (solid line). The solid line below corresponds to the simulated 295 °C spectrum of the parent molecule. The dots and the solid line show the result of the subtraction leading to the photoelectron spectrum of CpCoCO.

Figure 2 also contains the previously mentioned CO peak obtained at 295 °C. The integrated intensity of this peak is about twice the intensity of the first band in the CpCoCO peak at 7.2 eV. These similar intensities support the claim that the derived UPS spectrum is that of CpCoCO. Indeed it is difficult to imagine that it could be anything but our target compound because the Co−CO bond energy is rather weak so that its rupture is expected long before the breaking of the Cp−Co bond, or the pyrolysis of the Cp ring itself. Finally, we note that the evolution of the UPS in Figure 1 shows only a single compound growing in starting at about 230 °C which means that we are dealing with just a single reaction.

The first four CpCoCO vertical ionization energies are 7.21, 8.68, 8.94, and 9.24 eV. These energies were obtained by fitting the spectrum with a series of pseudo-Voigt peaks. We did not attempt to assign this photoelectron spectrum, as there is not enough information available for a precise assignment. The EOMIP-CCSD method used for the parent molecule did not give accurate enough ionization energies in this case. This is probably due to the multireference nature of the electronic structure of CpCoCO. Multireference configuration interaction (MR-CI) or the size-extensive extensions of MR-CI are probably required to calculate these energies.

The extraction of the adiabatic ionization energy from the spectrum in Figure 2 is considerably more difficult than determining the vertical IE. We thought of two possibilities: extrapolation to zero intensity at the first band, or shape-analysis of this band. The latter approach relies on our findings that the width (fwhm) of the first bands of the parent molecule and the CpCoCO fragment are almost identical at the pyrolysis temperature. Also, the calculated composition of the corresponding molecular orbitals is similar, suggesting that the difference between the adiabatic and the vertical IE of $CpCo(CO)_2$—if that is known—can be used to estimate the adiabatic IE of CpCoCO. That is,

$$\mathrm{IE_{ad}}\{\mathrm{CpCoCO}\} \approx \mathrm{IE_v}\{\mathrm{CpCoCO}\} - (\mathrm{IE_v} - \mathrm{IE_{ad}})\{\mathrm{CpCo(CO)_2}\}$$

In the literature, an adiabatic ionization energy value of $CpCo(CO)_2$ can be found in the NIST Chemistry Webbook.[34] Although this value of 7.35 eV is attributed to the publication of Lichtenberger and Calabro,[22] these authors report only the vertical IE of 7.59 eV. The NIST compilation thus simply assigns an adiabatic IE near the base of the first peak. This assignment is similar (and equally arbitrary) to our derived adiabatic IE obtained in an earlier threshold PES experiment.[19] If we use the $\mathrm{IE_v} - \mathrm{IE_{ad}}$ for $CpCo(CO)_2$ in our CO loss fragment, we obtain an adiabatic ionization energy of CpCoCO of 6.97 eV. This number is also consistent with the result of the extrapolation-to-zero method in the CpCoCO spectrum; thus our value for the adiabatic ionization energy of CpCoCO is 6.97 ± 0.05 eV.

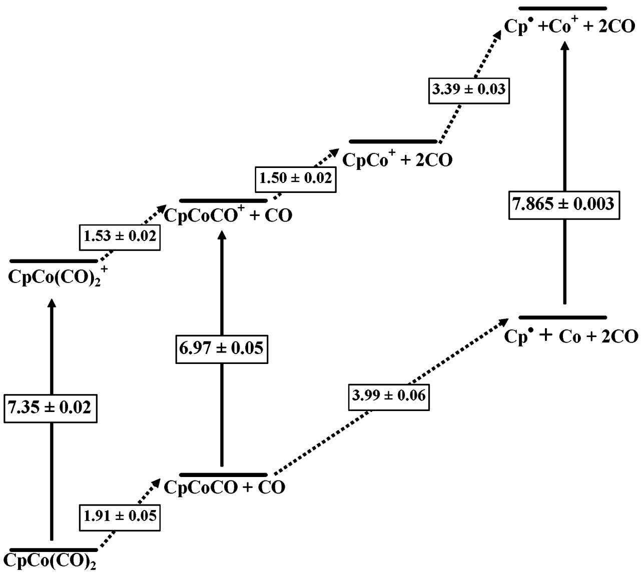

Figure 3. Relative energy diagram of the systems studied. The appearance energies of ionic fragments were determined earlier.[19] Solid arrows show adiabatic ionization energies, dotted arrows correspond to dissociation energies.

We made significant efforts to establish a theoretical value of the adiabatic ionization energy of CpCoCO. One can either calculate directly the adiabatic ionization energy or calculate both the vertical and the adiabatic values, and from the difference of these values, obtain the adiabatic IE using the experimental vertical ionization energy available from the pyrolysis photoelectron spectrum. As calculations show, the first method is not suitable because of the lack of accuracy probably due to strong electron correlation effects. Our best value for the adiabatic IE is 6.88 eV at the MBPT(2)/pvdz level. Both the HF/pvdz (3.01 eV) and the B3LYP/pvdz (6.17 eV) ionization energies are rather far from the value given above, based on experimental data. The difference between the adiabatic and vertical ionization energies was also calculated. This value is 0.551 eV at the HF, 0.572 eV at the MBPT(2), and 0.273 eV at the B3LYP levels using the pvdz basis set. These IE differences obtained at the MBPT(2) or B3LYP levels can be used to estimate the adiabatic ionization energy from the experimental vertical IE. The adiabatic IE obtained from the experimental vertical IE and the MBPT(2) energy difference given above is 6.64 eV. This value is not far from the purely theoretical value of 6.88 eV, but the accuracy is still below the anticipated accuracy of the experimental data as explained above. Furthermore, if one uses the IE difference value at the B3LYP/pvdz level of 0.273 eV, the obtained adiabatic IE is 6.94 eV, which is rather close to the experimental value of 6.97 eV.

In conclusion, quantum-chemical calculations at these levels of theory are not able to give reliable estimates of the adiabatic ionization energy. Because of this, the experimental value derived above is used in the thermochemical calculations.

Thermochemistry. The previous threshold photoelectron photoion coincidence (TPEPICO) study reported both the ionization energy of $CpCo(CO)_2$ (7.35 ± 0.02 eV) and the dissociative ionization to the $CpCoCO^+ + CO$ products (8.88 ± 0.02 eV).[19] The difference between these two energies is the first CO loss bond energy (1.53 eV) for the ion. Having now measured the ionization energy of the CpCoCO fragment, we are in a position to determine the neutral bond energy for the first CO loss process. As shown in Figure 3, this bond energy of 1.91 ± 0.05 eV is just the difference between the 0 K appearance energy for $CpCoCO^+ + CO$ and the ionization energy of CpCoCO. The error limit is determined mainly by the uncertainty in the adiabatic ionization energy obtained in this study. Figure 3 also includes the second CO loss and Cp loss bond energies in the ion as well as the sum of these bond energies in the neutral molecule. This diagram is constructed using the 0 K thermochemical information shown in Table 2.

TABLE 2: Auxiliary and Derived Thermochemical Values (kJ/mol)

molecule	$\Delta_f H°_{298}$	$\Delta_f H°_0$	$H°_{298} - H°_0$
$CpCo(CO)_2$ (l)	−169 ± 10[a]		
$CpCo(CO)_2$ (g)	−117 ± 10[b]	−99 ± 10[b]	24.18[b]
CpCoCO (g)	184 ± 10	199 ± 10	21.67[c]
CO (g)	−110.5[d]	−113.8[d]	8.665[d]
$Cp^•$	262 ± 4[e]	274 ± 4[e]	14.3[e]
Co	426.7 ± 1[f]	425.1 ± 1[f]	4.77[f]
Co^+ [g]	1185.4 ± 1[f]	1183.9 ± 1[f]	6.30[f]

[a] Chipperfield et al.[20] [b] Sztáray and Baer.[19] [c] Determined in this study from DFT calculations of the vibrational frequencies. [d] Wagman et al.[38] [e] Roy et al.[35] and Kiefer et al.[36] [f] Chase et al.[39] [g] Consistent with the Rosenstock convention, the heat capacity of the electron was treated as 0.0 kJ/mol at all temperatures.

The energies in Figure 3 are based on the measured heat of formation of $CpCo(CO)_2$(liquid),[20] our previously measured heat of vaporization of this compound,[19] and a new value for the heat of formation of the cyclopentadienyl compound.[35,36] The only measurement of the $Cp-Co^+$ bond energy was reported in 1985 by Jacobsen and Freiser, who found a value of 3.69 ± 0.40 eV.[37] On the basis of the measured bond energies and the known heats of formation in Table 2, we find this value to be 3.39 ± 0.03 eV. The other interesting aspect of Figure 3 is the sum of the second CO and Cp bond energies. In the ionic compounds, this is 4.89 eV, whereas in the neutral compound it is 3.99 eV. The measurement of the CpCo ionization energy would provide the final piece of information need to determine all of the neutral bond energies.

Conclusions

It has been demonstrated in this work that threshold photoelectron photoion coincidence spectroscopy combined with pyrolysis He(I) photoelectron spectroscopy can be an effective tool to determine the neutral bond energy in an organometallic complex. Cyclopentadienyl cobalt dicarbonyl is a fortunate case in some ways. First, its vapor pressure is sufficiently high that it can be measured at room temperature, therefore the pyrolysis inlet apparatus is simple. Second, as demonstrated in the TPEPICO experiments and quantum-chemical calculations published earlier,[19] the carbonyl loss leads to a fragment molecule, which is fairly stable, and does not lose another carbonyl group almost immediately as it is the case with $CpMn(CO)_3$ or $MeCpMn(CO)_3$. Third, the HOMO of the 16-electron complex is destabilized with respect to the parent 18-electron molecule; thus, the first band of the CpCoCO appears below any $CpCo(CO)_2$ bands, so the most important value, its first ionization energy, can be obtained with good signal-to-noise.

Further combined TPEPICO-UPS experiments are planned on a number of organometallic complexes to derive reliable neutral thermochemistry data, which is still quite sparse in this field.

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