

# Electronic structure of $[\text{CpCoMe}_2\text{SiC}_4\text{H}_4]$ , photoelectron and $\text{MSX}_\alpha$ studies

Marie-Gabrielle Faba, Danielle Gonbeau \*, Geneviève Pfister-Guillouzo

Laboratoire de Physico-Chimie Moléculaire, URA 474, Université de Pau & des Pays de l'Adour, Avenue de l'Université, 64000 PAU, France

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## Abstract

The electronic structure of  $[\text{CpCoMe}_2\text{SiC}_4\text{H}_4]$  is described. Data from UV photoelectron spectroscopy (HeI, HeII) are used in conjunction with  $\text{MSX}_\alpha$  calculations. The agreement of theory and experiment allows us to identify the main interactions occurring in the complex, and suggests particular features of its reactivity.

**Keywords:** Cobalt; Tetramethylsilole; PE spectrum;  $\text{MSX}_\alpha$  calculations

## 1. Introduction

Over the past several years the description of the electronic structure of dienes bonded to transition metals has received special attention [1–3]. Besides investigations of complexes of the type  $[\text{M}(\text{CO})_3\text{L}_2]$ , studies on metal cyclopentadienyl diene complexes have been reported. In particular a photoelectron spectroscopy study [2b] of complexes  $[\text{M}(\eta^5\text{C}_5\text{R}_5)\text{L}_2]$  ( $m = \text{Co}, \text{Rh}, \text{or Ir}$ ) has shown variations in the nature of the first ionization (ionization from an orbital, more or less metal d in character). Therefore, we investigated a new Group 14 ( $\eta^4$ -metallole)cobalt complex in order to analyse the changes induced by the silole. In a previous paper specific characteristics of the silole have been described [4].

The present work involves a study of the electronic structure of the new CpCo–(silole) complex, by combining photoelectron spectroscopy and quantum mechanical calculations ( $\text{MSX}_\alpha$  method [5]).

## 2. Computational and experimental details

The standard version of the method was used for the  $\text{MSX}_\alpha$  calculations. The values of the parameters

are shown in Table 1. As for different metallocenes [6], the cobalt sphere is assumed to be tangential to the ligand spheres. In the case of the ligands, overlapping atomic sphere radii were taken as 88% of the atomic number radii calculated with the molecular superposition program (overlap about 20%). Furthermore, we have not introduced an empty interstitial sphere for the cyclopentadienyl anion. For the  $\alpha$  parameters we have chosen values proposed by Schwarz [7]; for the intersphere and outersphere, a weighted average of the atomic  $\alpha$  has been used.

The calculations were carried out on the non-methylated derivative. The geometrical parameters for the two ligands were chosen on the basis of the data reported in the literature [8] (Fig. 1). For the metal–ligand distance a classical value determined for similar cobalt complexes was adopted. Preliminary calculations

Table 1  
 $\text{MSX}_\alpha$  parameters for  $[\text{CpCoSiC}_4\text{H}_6]$

Atom	Sphere radii (a.u.)	$\alpha$	$l_{\text{max}}$
Co	2.2390	0.71018	2
Si	2.2982	0.72751	1
C <sub>4,16</sub>	1.7660	0.75928	1
C <sub>5,17</sub>	1.7037	0.75928	1
C <sub>10,12,13,20,21</sub>	1.6985	0.75928	1
H <sub>i</sub>	0.8500	0.77725	0
Outersphere	8.6820	0.76459	3

\* Corresponding author.

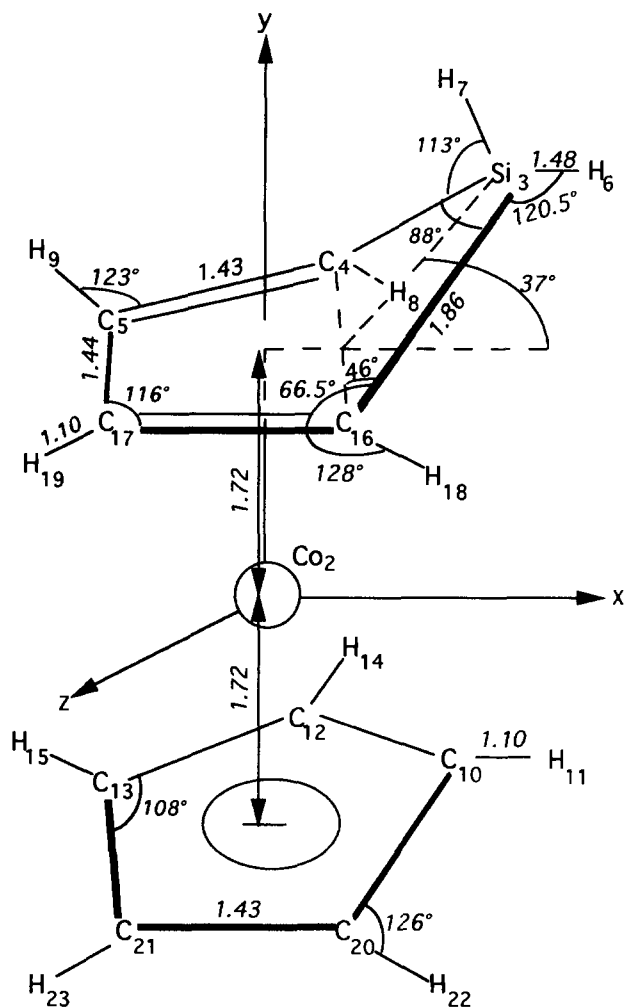


Fig. 1. Geometrical parameters of  $[\text{CpCoSiC}_4\text{H}_6]$ .

by the EHT method (standard parameters) [9] have facilitated the study of different orientations of the two ligands. As the eclipsed conformation appeared slightly

favoured, this conformation was considered for  $\text{MSX}_\alpha$  calculations.

Spectra were recorded on a PES Laboratories 0078 spectrometer equipped with a HeI-HeII source. All spectra were calibrated with the  $^2p_{3/2}$  and  $^2p_{1/2}$  lines of xenon (12.13 eV and 13.43 eV) and argon (15.76 eV and 15.93 eV).

### 3. Photoelectron spectrum of $[\text{CpCoMe}_2\text{SiC}_4\text{H}_4]$

As previously described [4], the photoelectron spectrum of 1,1,3,4-tetramethylsilole exhibits two bands (8.20 eV and 9.80 eV) associated with the ionization of  $\pi 1a_2$  and  $2b_1$  orbitals in  $C_{2v}$  symmetry, respectively. The following two IP (9.85 eV and 10 eV) correspond to the involvement of  $\sigma_{\text{Si-C}}$  orbitals. The IP observed at 11 eV is attributed to the ionization of the totally symmetric  $1b_1 \pi$  orbital. The cyclopentadienyl anion in  $D_{5h}$  symmetry is characterized by two occupied sets of orbitals,  $e''_1$ , correlated with  $a_2$  and  $b_1$  symmetries in  $C_{2v}$ , and  $a''_2$ , correlated with  $b_1$  in  $C_{2v}$ . The photoelectron spectra of different metallocenes [10] show that the IP from the  $e''_1$  orbitals may be expected at about 9.5 eV.

In the complex, the  $\pi$  orbitals of the ligands interact even though the two rings are relatively far apart. However, because of the different energies of these orbitals, a strong localization on one ligand is probable. Nevertheless the bonding or antibonding character of the combination is important for the interactions with cobalt d orbitals. Beside the characteristic ionizations of the ligands, four ionizations associated with metal ( $d^8$  configuration) have to be considered.

The photoelectron spectrum of  $[\text{CpCoMe}_2\text{SiC}_4\text{H}_4]$  (Fig. 2) shows a band at 6.55 eV, the intensity of which increases under HeII radiation. A similar, stronger

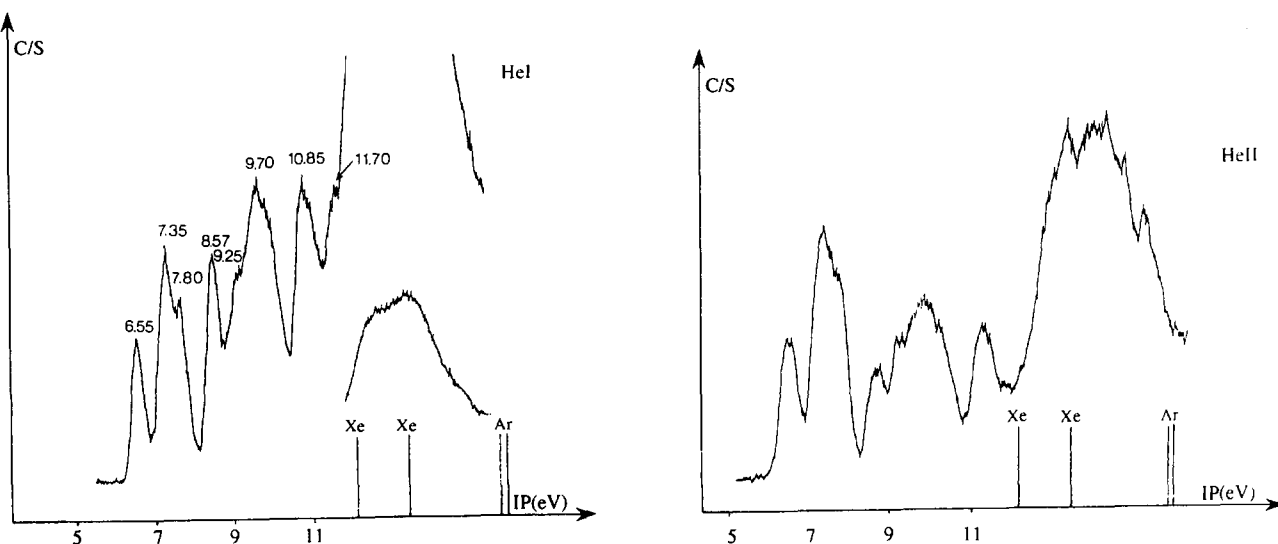


Fig. 2. Photoelectron spectra (HeI/HeII) of  $[\text{CpCoMe}_2\text{SiC}_4\text{H}_4]$ .

increase is observed for the second broad band (7.35 eV, 7.80 eV). This allows us to assign the 6.55 eV IP to the ionization from an orbital delocalized on both the 3d AOs of cobalt and on the ligands. In addition, the IPs at 7.35 eV and 7.80 eV are strongly localized on d orbitals. Similar intensity changes have been observed for complexes  $[M(C_5R_5)L_2]$  when M is Rh or Ir and  $L_2 = (\eta^4\text{-cyclohexa-1,3-diene})$  or  $(\eta^4\text{-buta-1,3-diene})$  [2b]. Intensity differences were noted when M is Co ( $L_2 = (\eta^4\text{-cyclohexa-1,3-diene})$ ), but they were not so large. In addition, the separation between the first IP and the average IP of the three d bands is similar for  $[M(\eta - C_5R_5)L_2]$  (M = Rh or Ir) (approximately 1.2 eV) and for the CpCo silole (approximately 1.3 eV), greater than the value reported for  $[Co(\eta - C_5R_5)L_2]$  (approximately 0.5 eV).

For  $[CpCoMe_2SiC_4H_4]$  no change for the band at 8.57 eV is observed in going from HeI to HeII excitation. This IP is attributed to ionization from an orbital with a large participation of the silole considering its energy. The slight stabilization relative to the 8.20 eV obtained for the silole arises from interactions occurring in the complex.

In view of the previous observations concerning the ligands (IP silole: 9.85 eV, 10 eV; IP cyclopentadienyl anion: ca. 9.5 eV) the broad band 9.25 eV–9.70 eV is associated with the characteristic ionizations of silole and cyclopentadienyl. According to the intensity variations during the HeI/HeII transition we propose that there is a noticeable participation of d orbitals in the low energy range, and that in the middle part of the broad band, there is a significant participation of the  $b_1$  orbitals of silole strongly localized on silicon (a decrease of intensity is observed under HeII radiation).

The band at 10.85 eV is attributed to more than one IP. In the light of intensity variations, we think that we have ionizations from  $b_1$  silole orbitals.

#### 4. Ground state electronic structure

(a) For this formally  $d^8$  compound the HOMO at  $-7.23$  eV is delocalized on cobalt, silole and cyclopentadienyl (Table 2). The contour plots in the  $xoy$  plane (bisecting plane of the two cycles containing the cobalt atom) and those in  $xoz$  parallel planes, suggest the " $b_1$ " nature of this orbital (Fig. 3). In addition, the participation of silole results from the interaction of the  $d_{xy}(\text{Co})$  orbital with the first  $b_1^*$  virtual orbital of silole. However, the orbital at  $-8.37$  eV is  $d_{x^2-y^2}$  localised on Co. The next orbital at  $-8.76$  eV is characteristic of ligands ( $a_2$  sil.,  $a_2$  cycl.). The orbitals at  $-8.80$  eV and  $-8.84$  eV, are principally  $d_{xz}$  (Co) and  $d_{z^2}$  (Co). However, in the former case, an interaction with the bonding combination of  $a_2$  ligands orbitals appears, whereas in the latter case, a slight

Table 2  
CpCoSiC<sub>4</sub>H<sub>6</sub> MSX<sub>α</sub> calculation

Orbital	Energy (eV)	Charge distribution (%)								
		Co	Si	C <sub>4</sub>	C <sub>5</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>13</sub>	int	out
20 a'	-5.11	27	0	22	16	3	2	4	25	0
12 a''	-5.65	49	0	12	5	0	12	5	16	0
19 a'	-7.23	35	1	13	3	7	1	12	27	0
18 a'	-8.37	91	0	0	0	0	0	0	7	0
11 a''	-8.76	27	2	17	8	0	12	8	25	0
10 a''	-8.80	66	0	9	0	0	10	1	15	0
17 a'	-8.84	83	0	3	1	0	1	2	9	0
16 a'	-9.63	38	2	2	1	15	4	16	21	0
9 a''	-10.05	42	1	14	4	0	14	6	17	0
15 a'	-10.22	5	22	3	20	0	0	1	34	0
14 a'	-11.47	3	19	16	15	2	3	2	30	1
8 a''	-11.64	3	22	39	8	0	1	0	21	0
13 a'	-12.05	4	18	12	13	3	6	9	26	1

interaction with  $b_1$  orbitals occurs. At lower energies, we observe two MOs at  $-9.63$  eV and  $-10.05$  eV of predominant ligand character (of  $b_1$  and  $a_2$  symmetries, respectively), but with a significant  $d_{Co}$  participation. Finally at  $-10.22$  eV, a  $b_1$  combination appears with a major localization on the silole. Beyond  $-11$  eV, orbitals with  $\sigma$  character are present.

Analysis of the virtual orbitals indicates a LUMO predominantly  $3d_{yz}$  Co, but with participation of the two ligands. The second virtual orbital is highly localized on silole.

(b) These results enable us to construct a diagram of

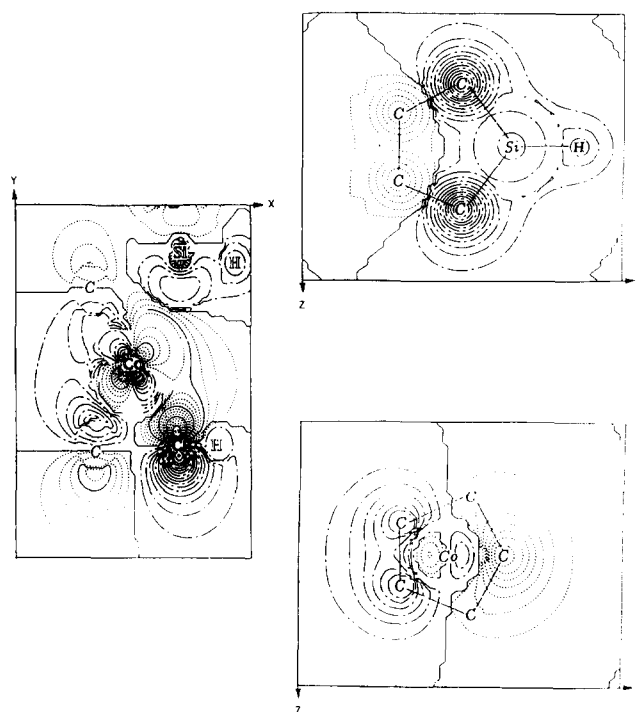


Fig. 3. Wave function contours of the 19 a' orbital (the full letters correspond to the atoms projected onto the sheet plane and the others to atoms actually present in this plane).

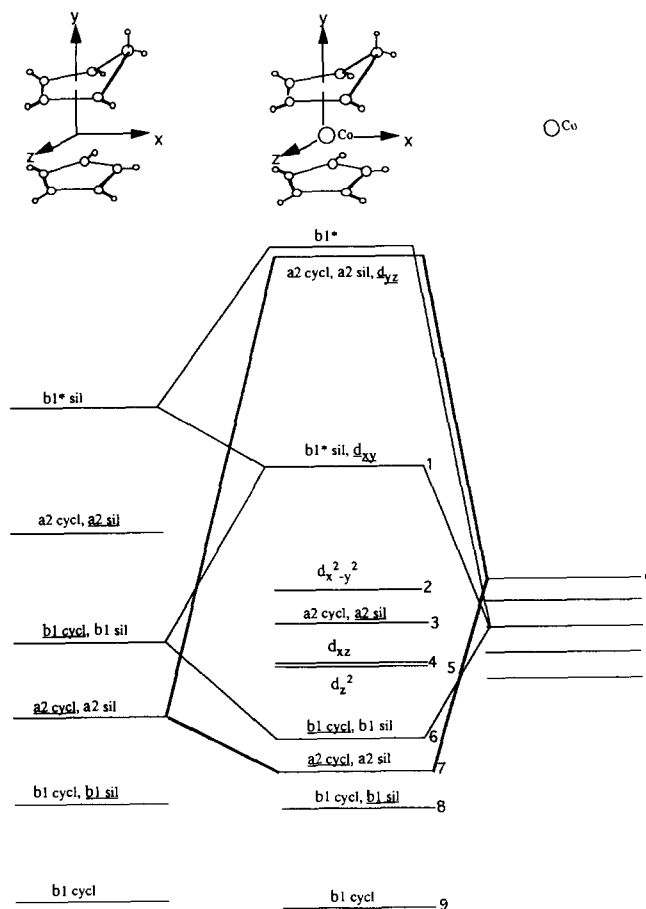


Fig. 4.  $[\text{CpCoSiC}_4\text{H}_6]$ : main interaction diagram in  $\text{MSX}_\alpha$  (the numbered levels correspond to the occupied MO).

the most important interactions (Fig. 4). In this complex, the main interactions occur between the  $\pi$  orbitals of the ligands and the  $d_{yz}$ ,  $d_{xy}$  orbitals of the cobalt atom. For easier discussion, the original symmetry of the ligands was used.

The first main interaction concerns the  $d_{yz}$  orbital and the  $a_2$  combination with a pronounced cyclopentadienyl character. The second important interaction involves three orbitals, the  $d_{xy}$  cobalt orbital, the  $b_1$  combination with cyclopentadienyl character, and the first  $b_1^*$  virtual orbital of the two ligands system (primarily localized on silole).

This last interaction leads to three orbitals, a very high energy one with a strong  $b_1^*$  character, an intermediate one (HOMO of the complex) localized on  $d_{xy}$  Co with a significant  $b_1^*$  participation, and a lower energy one that involves the  $b_1$  cyclopentadienyl orbital in slight interaction with  $d_{xy}$  Co orbital.

Beside these two main interactions, other less important ones can be distinguished. As a consequence of an interaction with  $d_{yz}$  Co and  $d_{xz}$  Co orbitals, stabilization of the  $a_2$  orbitals combination localized on silole is observed. However, the  $b_1$  orbital combination

with silole character and high localization on silicon remains almost unchanged. In addition, very slight interactions with ligands are observed in the complex for  $d_{z^2}$  Co and  $d_{x^2-y^2}$  Co.

(c) We tried to estimate the charges of the cobalt atom in the complex. Studies on several organometallic compounds [11] show that the intersphere charge can be attributed to the ligands. In the case of cobalt, this leads to the configuration  $3d^{8.20}$ ,  $4s^{0.29}$ ,  $4p^{0.51}$ , which corresponds to a  $0.51 e^-$  transfer from the 2p orbitals of the ring atoms towards the 4p orbitals of cobalt, and to a  $0.29 e^-$  occupation for the 4s orbital of cobalt.

The evaluation of the population of the  $d_{xy}$  which participates in the  $19 a'$ ,  $16 a'$ ,  $15 a'$  and  $14 a'$  orbitals enables us to estimate an overall metal-to-ligand transfer of  $1.44 e^-$ . Conversely the interaction of the  $d_{yz}$  virtual AO of cobalt with the  $a_2$  orbitals of silole and cyclopentadienyl induces a ligand-to-metal transfer of  $2.44 e^-$  (according to a formal occupation  $3d^8$  ( $\text{Co}^+$ )). Although these evaluations are only suggestive, the ligand-to-metal transfer appears to be greater than the metal-to-ligand, leading to a neutral cobalt. Similar observations have been reported for related complexes [12,13]. Charge distribution data obtained with  $\text{MSX}_\alpha$  method predict accumulation of charge on the central metal greater than that evaluated by LCAO calculations. In addition, for  $[\text{Cp}_2\text{Co}]$  (with a formal  $3d^7$  Co i.e.  $\text{Co}^{2+}$ ) a value of  $+0.4$  has been deduced from X absorption spectrum [14].

## 5. Ionization potentials: Experimental and theoretical comparison

The results in Table 3 show values too high for the whole spectrum. Although the experimental data con-

Table 3  
Calculated ionization potentials (IP calc.) of  $[\text{CpCoSiC}_4\text{H}_6]$  and experimental vertical ionization potentials (IP exp.) of  $[\text{CpCoMe}_2\text{SiC}_4\text{H}_4]$

Ionic state	Charge distribution (%)										IP calc. (eV)	IP exp. (eV)
	Co	Si	C <sub>4</sub>	C <sub>5</sub>	C <sub>10</sub>	C <sub>12</sub>	C <sub>13</sub>	int	out			
19 A'	33	1	12	2	8	1	13	26	0		9.30	6.55
18 A'	91	0	0	0	0	0	0	7	0		10.63	
10 A''	88	0	1	1	0	2	0	7	0		11.04	7.35
17 A'	85	0	2	1	0	1	2	8	0		11.08	7.80
11 A''	5	1	25	7	0	20	8	31	0		10.78	8.57
16 A'	36	4	2	1	14	4	14	22	0		11.74	
15 A'	10	21	3	18	1	0	2	31	0		12.16	9.25
9 A''	44	2	14	4	0	13	6	15	0		12.19	9.70
14 A'	3	18	17	16	2	3	2	28	1		13.44	
8 A''	3	21	40	8	0	1	0	21	0		13.66	10.85
13 A'	5	19	12	13	2	6	8	26	1		14.03	

cern the dimethylated derivative with IP values lower than those of the non-substituted system, the important difference obtained here is a result of the calculation conditions used. In  $MSX_{\alpha}$  similar shifts have already been observed. The values of these shifts are variable and mainly depend on the overlaps of the chosen spheres. We are not seeking a quantitative agreement, but a comparison between the experimental assignments and the nature of the calculated IPs, so no additional calculations were carried out.

According to the results obtained, the first IP at 9.31 eV is associated with ionization from an orbital delocalized on the cobalt and the two ligands (i.e. with  $d_{xy}$  Co and  $b_1^*$  silole character). This is consistent with the moderate intensity increase observed for the IP at 6.55 eV during the HeI/HeII transition. This result is consistent with the one obtained for complexes  $[Co(\eta - C_5R_5)L_2]$ . Indeed, the  $b_1^*$  orbital of silole is lower in energy than the LUMO of L diene ( $\eta^4$ -cyclohexa-1,3 diene) and the interaction is more successful for the CpCo–silole complex. In this case, the interaction is as important as in complexes  $[M(\eta - C_5R_5)L_2]$  when M is Rh or Ir.

For the second broad band between 7.35 eV and 7.80 eV, the experimental assignment is particularly straightforward as strong intensity variations have been observed. This is consistent with the three calculated IPs at 10.63 eV, 11.04 eV and 11.08 eV associated with high d character MOs.

The band at 8.57 eV has been attributed to an ionization involving silole because of its energy and its low sensitivity to irradiation change. As this is in contrast to the nature of the calculated IP at 11.74 eV (36% d Co), this band must be associated with the calculated IP at 10.78 eV.

The band between 9.25 eV and 9.70 eV corresponds to three IPs, calculated at 11.74 eV, 12.16 eV and 12.19 eV. The intensity variations when going from HeI to HeII excitation are consistent with the first and last significant d orbitals contributions. This is the result of the two main interactions characteristic of the system, interaction of the  $b_1$  and  $a_2$  orbitals of the two cycles with the  $d_{xy}$  and  $d_{yz}$  of cobalt. In the same way, for the IP calculated at 12.16 eV, an important contribution of silole appears consistent with the intensity decrease observed in the central part of the band.

Finally, the broad band at 10.85 eV characterized by a clear intensity decrease (during HeI/HeII transition) is attributed to three IPs calculated at 13.44 eV, 13.66 eV and 14.03 eV. They are associated with orbitals strongly localized on silole.

On the whole, the results of  $MSX_{\alpha}$  analysis are consistent with the experimental assignments. The only failure concerns the IP associated with the symmetric combination of  $a_2$  ligands orbitals strongly localized on silole. It is difficult to decide whether this discrepancy

arises from a wrongly calculated value for this IP, or from IPs attributed to d orbitals which are too high.

## 6. Conclusion

We have investigated the electronic structure of  $[CpCoMe_2SiC_4H_4]$  using photoelectron spectroscopy and  $MSX_{\alpha}$  calculations. Two main ligand–metal and metal–ligand interactions have been inferred. Estimation of the associated transfers shows a ligand-to-metal transfer greater than the metal-to-ligand. The experimental and theoretical agreement for the lowest IP at 6.55 eV allows us to infer that the HOMO is delocalized on both the silole and the d orbitals of the cobalt. This result is consistent with those previously obtained for complexes  $[M(\eta - C_5R_5)L_2]$  (M = Co, Rh, or Ir) [2b]. As a consequence, electrophilic attack on  $[CpCoMe_2SiC_4H_4]$  should occur on the silole, more specifically at the  $C_{\alpha}$  atoms.

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In the early stages of this work a collaboration with Prof. E. Colomer was initiated. It was unfortunately cut short by his death in 1990.

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