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Gas-phase photoelectron spectroscopic study of (σ-allyl)Mn(CO)$_5$ and (σ-allyl)Re(CO)$_5$

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Abstract

The He(I) photoelectron spectra of (σ-allyl)Mn(CO)$_5$ **(1)** and (σ-allyl)Re(CO)$_5$ **(2)** were recorded and interpreted by means of comparison to the spectra of related compounds and low level ab initio molecular orbital calculations. On the basis of the found correlation a new assignment is proposed for the photoelectron spectrum of (allyl)CpFe(CO)$_2$. The transformation reaction to the π-allyl derivatives was also investigated. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Photoelectron spectroscopy; Allyl complex; Manganese; Rhenium

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1. Introduction

Transition metal complexes with π-bonded species such as η^5-cyclopentadienyl (Cp), different cyclooctatetraene (COT) or η^3-allyl complexes have been studied extensively [1]. σ-Bonded hydride and alkyl compounds were also a subject of thorough photoelectron spectroscopic investigations. Less attention has been paid to complexes with σ-bonded ligands containing unsaturated groups (such as η^1-allyl). This fact however can be understood since no special donor–acceptor effects can be expected because the metal center and the π-bonding seems to be 'isolated' in terms of organic chemistry. In this report, we discuss the electronic structure of (σ-allyl)Mn(CO)$_5$ **(1)** and (σ-allyl)Re(CO)$_5$ **(2)** by means of their He(I) photoelectron spectra. In the case of **(2)**, the He(II) spectrum was also recorded.

To the best of our knowledge, the only σ-allyl complex which has been examined so far by photoelectron spectroscopy is (allyl)CpFe(CO)$_2$ [2]. In their paper Fehlner and co-workers observed a mixing between orbitals of mainly metallic d-character and the olefinic π-orbitals, which can be related to the unusual reactivity of the σ-allyl complexes (e.g. while the reaction of alkyl complexes with acids results in a M–C bond cleavage, that of allyl complexes protonates the complex on the double bond giving an olefin complex [3]).

The photoelectron spectra of RM(CO)$_5$ type species (M = Mn, Re) with a high variety of R groups were investigated by many research groups [4–6]. Although the assignment of these spectra were dubious, the most reliable one is that given by Higginson et al. [6]. The electronic structure of these compounds can be discussed in terms of the formal d^6 configuration of the metal and the local C_{4v} symmetry of the M(CO)$_5$ moiety. There are three occupied d-type (thus mainly metallic) orbitals of b$_2$ and e symmetry, correlating with the t$_{2g}$ orbitals of O$_h$ symmetry of the corresponding hexacarbonyls. There is another low energy occupied orbital of a$_1$ symmetry, which is a ligand-to-metal bond orbital. Additionally, in the case of the Re complexes, the ionization from the e-type orbitals yields two bands separated by ca. 25 meV, due to spin–orbit coupling. Obviously, in the case of the examined (allyl)M(CO)$_5$ complexes, where the overall symmetry is C$_1$, strict symmetry rules do not apply.

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2. Experimental and theoretical methods

2.1. Preparations

The examined compounds were prepared by previously published methods ((σ-allyl)Mn(CO)$_5$ [7], (σ-allyl)Re(CO)$_5$ [8]) under inert atmosphere (N_2) using standard Schlenck technique. The applied solvents were purified under N_2 using Na/benzophenone. The samples were freshly distilled under reduced pressure (ca. 30°C/1 mbar) in the case of **(1)**) or at atmospheric pressure (in a short-path distillation apparatus at 50°C, complex **(2)**) and analyzed by MS and IR spectroscopy before use.

2.2. Photoelectron spectroscopic measurements

The ATOMKI ESA 32 photoelectron spectrometer equipped by two different sample inlet systems for highly volatile and solid samples, a He(I)/He(II) photon source, a seven-membered electrostatic lens system and a hemispherical electron energy analyzer has been described elsewhere [9] in detail.

The spectra were recorded applying constant analyzer voltage (FAT mode; $E_{\text{pass}} = 1$ eV for **(1)** and 2 eV for **(2)** at He(I) and 5 eV for **(2)** at He(II)). Each spectrum was calibrated against the ^2P doublet of Ar. The resolution at the $^3P_{3/2}$ peak of Ar was 25 meV at He(I) and 100 meV at He(II) radiation, respectively. Band intensities were measured by fitting a Shirley-type background and pseudo-Voigt peaks to the spectra.

2.3. Quantum chemical calculations

In order to help the interpretation of the spectra (in Koopmans' approximation [10]) ab initio (all-electron HF/3-21G [11] and HF/dz [12]) quantum chemical calculations were performed for complex **(1)**. For this purpose Tx90 [13] program was used with full geometry optimization in natural internal coordinates defined by the INTC [14] program. In order to visualize the molecular orbitals simple semiempirical extended Hückel (EHMO) calculations applying the CACAO [15] program were used at the HF/d*z* geometry.

3. Results and discussion

3.1. Spectrum assignments

The spectra of compounds **(1)** and **(2)** are shown in Figs. 1 and 2, respectively. The tentative assignment of the spectra can be made by simply comparing them to those of related compounds. Our proposed assignments (Table 1)—surprising at first glance—can be confirmed by facts discussed below and by the correlation chart for ionization energies (IE) shown in Fig. 3.

The most important difference between the spectra of the manganese and rhenium compounds is that the e orbital splits in the latter case due to spin–orbit coupling. The reported ζ value for the Re 5d orbitals is 0.26 eV [6]. Thus the difference (0.6 eV) of the first two bands (A and B) in the spectrum of **(2)** cannot be related to this coupling. Even the other pair of bands, C and D, are too far away (0.44 eV). The only reasonable assignment is that B and C correspond to the e^{-1} ionization. The splitting of these bands is 0.3 eV, which is only slightly higher than that measured for the hydride and methyl complex (0.26 and 0.22 eV, respectively). Thus the position of the e bands in the case of the Re compound is assigned, and it seems likely that the ordering of the bands is similar in the case of the manganese complex, too.

The b_2 orbitals are considered to be of the highest metallic character, so they are expected to be at similar position in the different compounds. This can be clearly seen in Fig. 3: in the case of the rhenium complex the difference between the b_2 band positions in various compounds is within the experimental error, and even in the manganese complex is not > 0.2 eV.

The IE difference between the b_2 and e bands are reported to be between 0.3 and 0.5 eV in the related (hidride, alkyl, perfluoroalkyl and acyl) manganese complexes, and between 0.5 and 0.7 eV in the rhenium series [6]. The measured values are 0.41 eV for **(1)** and 0.56 eV for **(2)**, in accordance with these expectations.

Although He(II) data are only available for complex **(2)** the measured intensity data can also support the given assignment. The data show a high uncertainty, however some trends are evident. The highest increase on going from He(I) to He(II) is shown by the b_2 orbital, which is consistent with the expectation that this is the orbital of the highest contribution from the metal d orbitals. The mixed $\pi + a_1$ orbitals do not seem to change.

The most surprising feature of the spectra is an indication of the great mixing between the carbon–metal and the π(C=C) bonds resulting in unexpected band positions. If we did not suppose a mixing, an IE close to 9.7 eV would be expected as this value was measured for 1-butene ('allyl-methane') [16], and the inductive effect of the methyl and M(CO)$_5$ groups should be close to each other. As there is no feature in that region and a new band appears at unreasonably low ionization energy (band A), one must suggest a strong mixing between the corresponding orbitals. This effect is further confirmed by the quantum chemical calculations (see Section 3.2). Obviously, the orbital of higher ionization energy has a higher contribution from the π(C=C) type orbital, while the band at the lower end of the spectrum can be related to an orbital of greater metallic character.

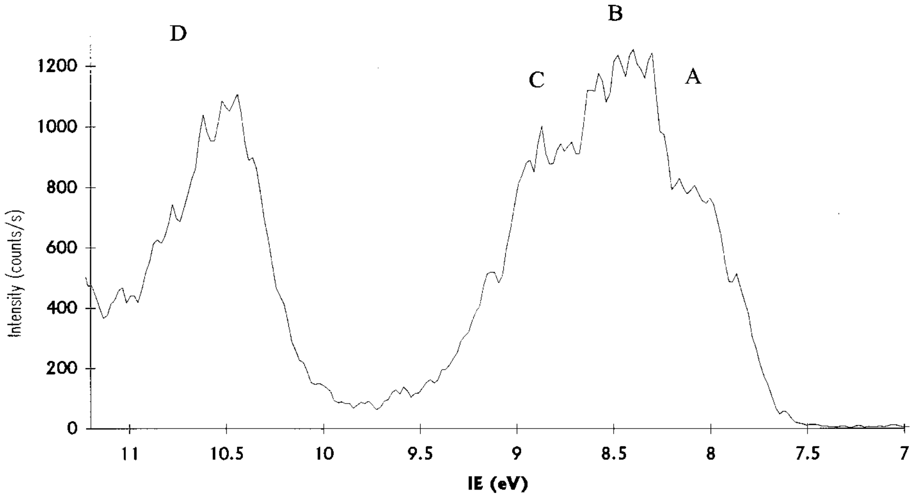

Fig. 1. Low energy region of the He(I) photoelectron spectrum of (allyl)Mn(CO)$_5$.

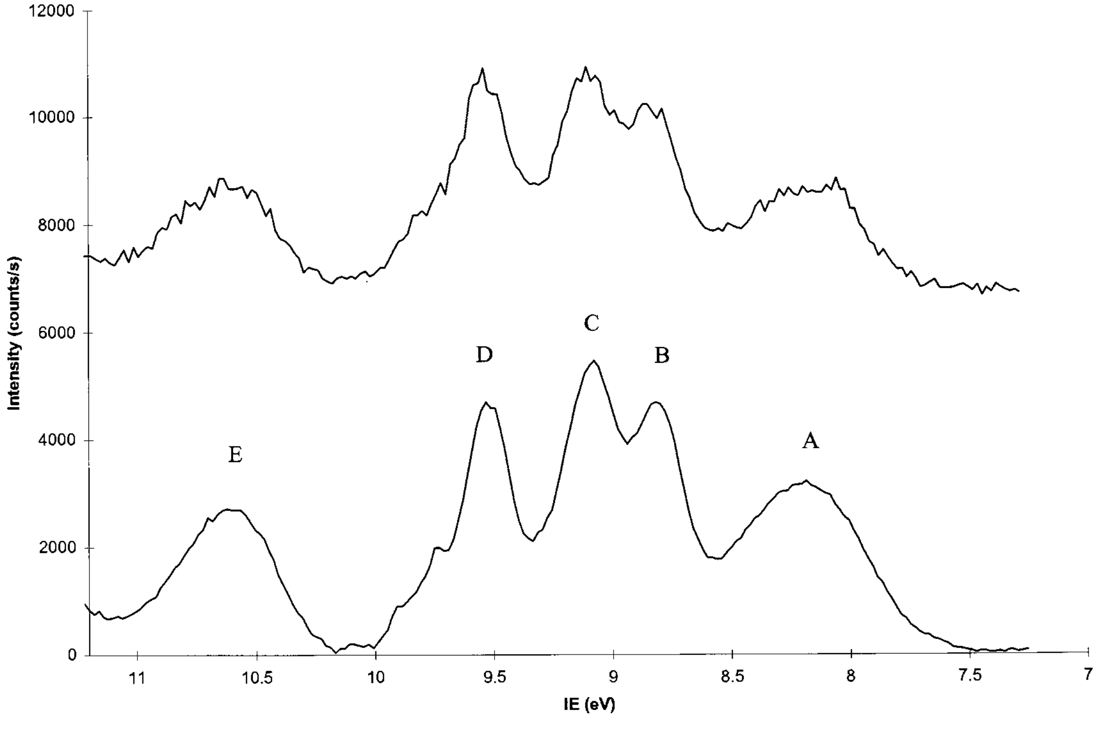

Fig. 2. Low energy part of the He(I) and He(II) photoelectron spectrum of (allyl)Mn(CO)$_5$ (He(II) values × 20 and shifted by 6000 cps).

On these grounds one can suggest a new assignment for the spectrum of (allyl)CpFe(CO)$_2$ [2]. The reported ionization energies are shown in Table 2 together with those of the corresponding methyl complex and the original and modified band-assignments. The first two bands in the spectrum of the methyl compound are correlated to the metal d ionizations. There are two bands in similar position in the allyl spectrum, so it seems to be plausible to assign them in the same way. Again, there is a peak at 9.78 eV which is close to that assigned as π(Cp) in the methyl complex (9.94 eV). The peak at 10.24 eV is close to the $\pi + a_1$ band of the complexes discussed above. The only difference between this scheme and that proposed for the manganese and rhenium complexes, is that virtually there is no ionization at lower energies. However, scrutinizing the spectrum it is evident that another band, appearing as a shoulder, exists at lower ionization energies (~ 7.5 eV). This band has not been assigned in the original paper. Although it should be noted that the bonding in such a complex, containing both allyl and Cp groups, is more complicated than those discussed above.

Table 1
Measured vertical ionization energies (eV) and intensities (relative to the first (A) band) of **(1)** and **(2)** and related compounds

Compound	$a_1+\pi$	e	b_2	a_1	π+al	σ(C–C, C–H)	Ref.
$(\sigma\text{-allyl})Mn(CO)_5$	8.14	8.54	8.95		10.56	11–13	This work
	A	B	C		D		
$CH_3Mn(CO)_5$	—	8.65	9.12	9.49	—	11–13	[5]
$HMn(CO)_5$	—	8.85	9.14	10.55	—	—	[5]
$(\sigma\text{-allyl})Re(CO)_5$	8.23	8.83; 9.13	9.54		10.66	11–13	This work
	A	B; C	D		E		
He(I) intensity:	(100)	(80; 80)	(60)		(60)		
He(II) intensity:	(100)	(90; 70)	(80)		(60)		
$CH_3Re(CO)_5$		8.71; 8.93	9.51			11.5–13.5	[6]
$HRe(CO)_5$		8.89; 9.15	9.51	10.47			[6]

3.2. Theoretical results

The results of the geometry optimization are shown in Table 3, with some gas-phase electron diffraction data of the related compound, $(CH_3)Mn(CO)_5$. As is evident from the data, the agreement between the theoretical and experimental data is satisfactory, although the reliability of such a low level calculation for transition metal compounds is doubtful.

The calculated Hartree–Fock orbital energies are shown in Table 4, together with the simple extended Hückel (EHMO) results and the experimental ionization energies. According to the population analysis based on the ab initio results, the metal–orbital contributions to the 1st and 5th highest occupied MO's are remarkable ($\sim$25%), although their main character is allylic, while the 2nd–4th MO's are definitely of metallic character. As an example, one of the affected MO's is shown in Fig. 4. These results are fully consistent with the assignment given above, although the energy differences between the calculated MO energies and those of the experimental ionization energies do not agree. The non-validity of the Koopmans' approximation in transition metal complexes is a known fact and can probably be attributed to the high relaxation effects [17].

3.3. Rearrangement reaction

As has been known for decades [3,7,18], certain transition metal–carbonyl allyl complexes can lose a CO ligand giving a π-allyl complex. In the case of **(1)** this reaction has been reported to be initiated by both heating and UV-light, while for **(2)** only the UV-induced reaction has been found. We also tried to follow the thermally-induced CO-loss reaction of **(1)** and **(2)** applying a pyrolyzer directly connected to the photoelectron spectrometer. In the case of the manganese

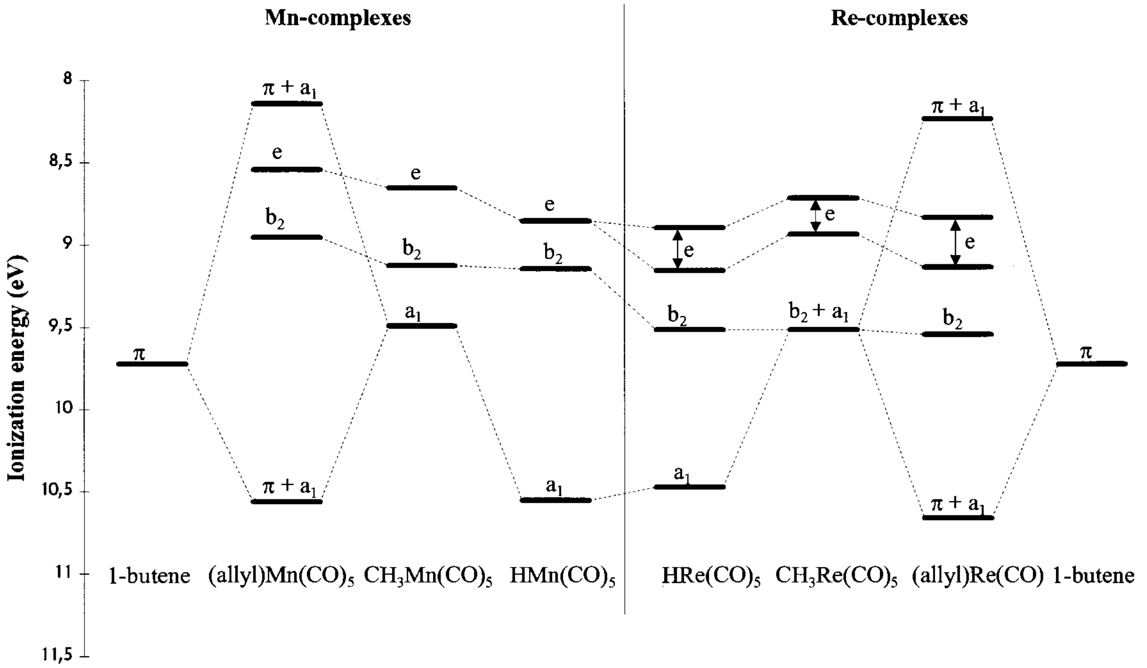

Fig. 3. Correlation chart for the low ionization energies of $RMn(CO)_5$ and $RRe(CO)_5$ complexes (R = H, CH_3, allyl).

Table 2
Ionization energies and assignments of $RCpFe(CO)_2$ [2] ($R = CH_3$, allyl)

$R = CH_3$		Fe 3d 7.91	Fe 3d 8.56	σ(Fe–C) 9.21	π(Cp)+Fe 9.94
R = allyl	~7.5(shoulder)	7.97	8.54	9.78	10.24
Original assignment		Fe 3d	σ(Fe–C)	π(C=C)	π(Cp)+Fe
Proposed assignment	$\pi+\sigma$(Fe–C)	Fe 3d	Fe 3d	π(Cp)+Fe	σ(Fe–C)+π

Table 3
Equilibrium bond lengths of (**1**) at HF/3-21G and HF/dz level of theory and experimental geometrical parameters of $CH_3Mn(CO)_5$ (data in pm)

	$r(Mn-C_{allyl/methyl})$	$r(Mn-C_{CO})_{ax.}$	$r(Mn-C_{CO})_{equ.}$	r(C–O)	Ref.
HF/3-21G	226.3	195.7	195.7	112.7	This work
HF/dz	229.5	201.6	195.7	112.9	This work
$CH_3Mn(CO)_5$	218.5	186.0	182.0 (fixed)	114.1	[20]

Table 4
Highest occupied orbital energies of (**1**)

Main character	M–C, C=C	Mn d	Mn d	Mn d	M–C, C=C
ε (eV) EHMO	−12.44	−12.85	−12.86	−12.99	−13.59
ε (eV) HF/3-21G	−8.01	−10.04	−10.19	−10.30	−11.14
ε (eV) HF/dz	−7.53	−10.70	−10.76	−10.81	−10.93
Experimental IE	8.14	8.54	8.54	8.95	10.56

complex, we observed a definite change to the corresponding π-complex, (π-allyl)$Mn(CO)_4$ on heating. The spectrum obtained at 170°C, together with that of the π-complex, is shown in Fig. 5. The single, sharp band at 14 eV, and the pattern between 16 and 18 eV, come from the spectrum of the evolving free CO. The spectra are very similar apart from the band broadening due to thermal effects and the bands of the unreacted σ-complex. This is a clear indication of the $\sigma \rightarrow \pi$ rearrangement. To the best of our knowledge, this is the first gas-phase report on the preparation of (π-allyl)$Mn(CO)_4$. No other reaction product ((σ-allyl)$Mn(CO)_4$ or (allyl)$Mn(CO)_3$ that are proposed earlier [19]) can be proved on these grounds.

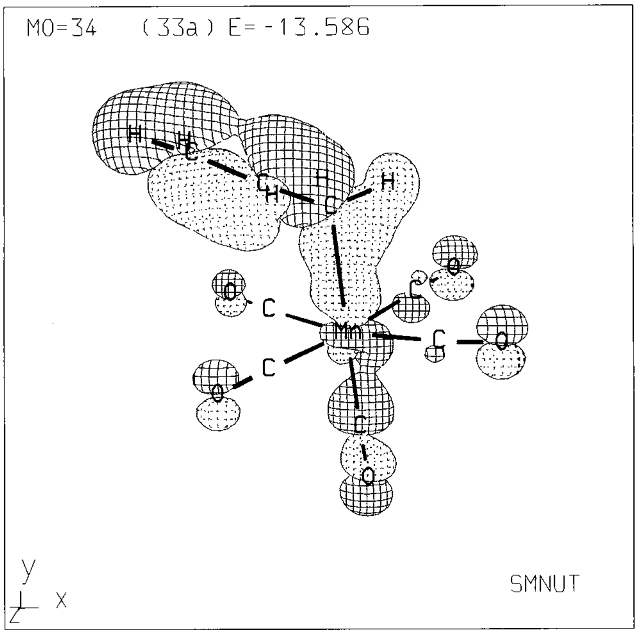

Fig. 4. CACAO plot of the 5th highest occupied MO of (1).

In the case of the Re complex, no π-complex formation could be detected, although the CO loss was evident at pyrolyzer temperatures > 130°C. The only change in the low energy part of the spectrum was that the bands of (**2**) gradually disappeared. The difference in the behavior of (**1**) and (**2**) is consistent with the findings reported in [8]. They, potentially, can show that the dissociation energy of a further CO is higher than the first one in the case of (**1**) and it is lower in the case of (**2**). Thus (**2**) can probably undergo a CVD (chemical vapor deposition)-like process, resulting in a metal or metal-oxide-carbide cover on the pyrolyzer wall rather than a well-defined unimolecular reaction.

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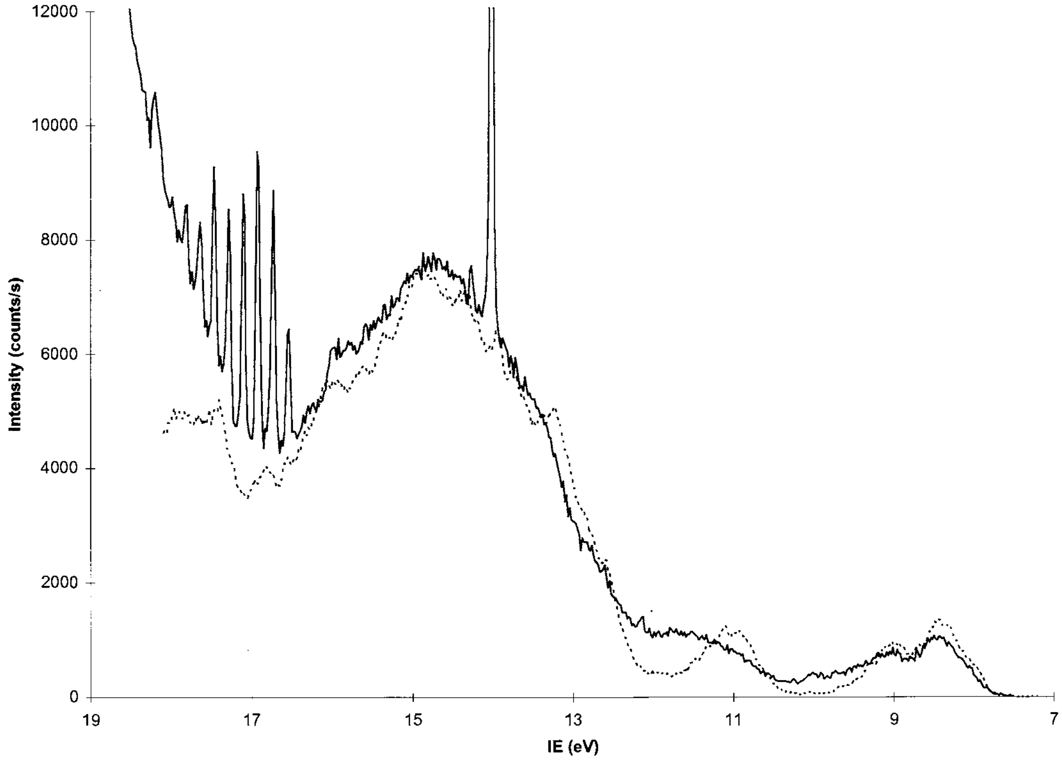

Fig. 5. Spectrum of (**1**) at 170°C vapor-temperature (solid line) and the spectrum of (π-allyl)Mn$(CO)_4$ (dotted line).

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