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ELECTRONIC STRUCTURE OF TRANSITION METAL COMPOUNDS

XXIII *. THEORETICAL AND SPECTROSCOPIC INVESTIGATIONS OF HETEROLIGAND PENTACARBONYL COMPLEXES OF GROUP VIA TRANSITION METALS

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Summary

The electronic structures of a series of 18 transition metal pentacarbonyl complexes of the general formula $M(CO)_5L$ (M = Cr, Mo, W; L = Me_2XYMe, Me_2XXMe_2; X = P, As; Y = S, Se; Me = CH_3) have been investigated by semiempirical calculations of the CNDO and INDO type and by various spectroscopic studies. Information concerning the ground state of the pentacarbonyl derivatives has been derived from ^1H NMR, ^{31}P NMR and IR data; He(I) photoelectron spectra in the outer valence region have been measured in order to study the nature of the cationic hole-states. Theoretical and experimental data are combined to give a detailed description of the electronic structure of the $M(CO)_5L$ complexes.

(1) Introduction

In connection with our experimental studies on heteroligand pentacarbonyl complexes of VIA transition metal elements [2–6] and with theoretical and photoelectron investigations on polycarbonyl derivatives in the 3*d* series [7–10] we became interested in the electronic structure of the pentacarbonyl complexes of VIA elements (M = Cr, Mo, W) containing ligands of the general types Me_2XXMe_2 and Me_2XYMe, where X and/or Y are atoms of main group V and VI (X = P, As; Y = S, Se) with lone pair orbitals suitable to substitute one carbonyl ligand in

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* For part XXII see ref. 1.

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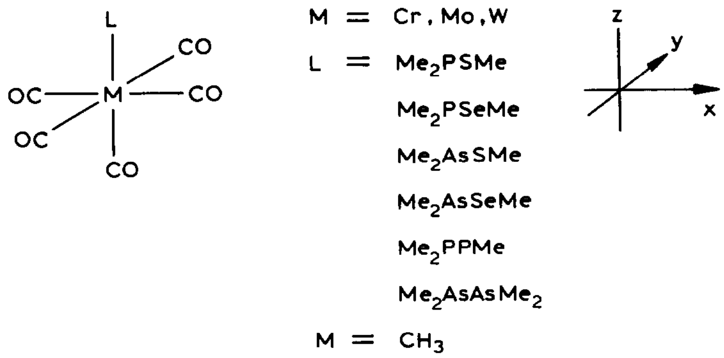

$M(CO)_6$ complexes. In this contribution we present semiempirical CNDO/INDO calculations for the chromium derivatives based on a recently developed ZDO * Hamiltonian and designed to reproduce the results of ab initio calculations of higher quality [11]. In order to throw light on the electronic structure of the pentacarbonyl complexes in the electronic ground state, the results of ^1H NMR, ^{31}P NMR and IR measurements are discussed. Some details of these investigations have been published recently [5,6]; in this paper, however, these results are correlated with semiempirical MO calculations. The nature of the cationic states of the VIA pentacarbonyl derivatives is studied by means of photoelectron (PE) spectroscopy; the experimental data are compared with theoretically determined ionization energies.

The bonding capabilities and the relative importance of σ donor and π acceptor interactions in transition metal carbonyls containing N or P ligands have been previously studied by various techniques. Information about the electronic structure has been deduced on the basis of carbonyl stretching frequencies [4,12–14], ^{31}P and ^{183}W NMR data [15,16], or of He(I)/He(II) PE spectra [17–20] by correlating the ionization energies using Koopmans' theorem [21] ($I_{v,j} = -\varepsilon_j$). Thus either ground state or cationic hole-state properties have been used in describing the electronic structure of $M(CO)_5L$ complexes. To gain a more complete picture of the bonding situation in these compounds we have studied a large number of pentacarbonyl derivatives with different coordination patterns (variation of M (Cr, Mo, W), L (Me_2XXMe_2, Me_2XYMe), and X, Y (P, As, S, Se)), combining spectroscopic information on the ground state and the cationic states with the results of various calculations. The PE spectra and MO results for the free Me_2XYMe ligands were reported recently [22].

(2) Computational details

The CNDO/INDO calculations on the chromium pentacarbonyl derivatives are based on a recently developed ZDO Hamiltonian for transition metal compounds [11]. The MO model was employed for the determination of ionization energies in 3*d* complexes either by relaxational methods (e.g. ΔSCF and transition operator formalism) [7,8,23,24] or by means of many-body calculations taking account of both relaxation and correlation effects during the electron ejection [9,10,25–28]. In

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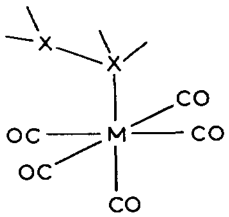
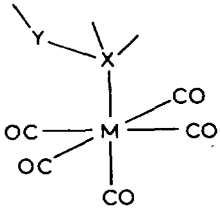
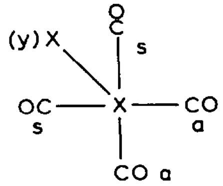
* ZDO, zero differential overlap.

calculations on the Cr complexes with P or S heteroatoms the INDO version of our semiempirical MO procedure was used, while for Cr complexes with As or Se we were restricted to the simpler CNDO variant because the Slater–Condon parameters for the As or Se atom, necessary for the INDO approach, are not available.

The geometrical parameters for the MO calculations were derived from X-ray data for related pentacarbonyl complexes [29,30] and were extrapolated from the bond lengths and bond angles of suitable derivatives of the free ligands [31,32]. We have assumed a *cis* orientation for the methyl groups on X and Y.







x, *y*-plane

s = *syn*

a = *anti*

The XX or XY vector of the Me_2XXMe_2/Me_2XYMe substituents bisects one $CO_{eq}CrCO_{eq}$ angle (see above), leading to two topologically different types of equatorial CO groups, described as *syn* and *anti* ligands, which we interrelated via reflections on the *x*, *z* and *y*, *z* planes. For our discussion we use the irreducible representations of the point group C_{4v} as the perturbation of the Cr 3*d* levels by the uncoordinated X/Y ligand fragment is only of minor importance. Our recent studies [5,6] have shown that in Me_2XYMe complexes always the element of Main Group V (P, As) is coordinated to the transition metal.

For the interpretation of the PE spectra of transition metal compounds the validity of Koopmans' theorem cannot be assumed [33]. As a result of strong electronic reorganization in the case of strongly localized metal 3*d* electrons, significant differences between the sequence of the ionization potentials and the one-electron energies in the ground state are often encountered. However, in various publications we have demonstrated that the PE spectra of transition metal complexes can be reproduced with remarkable accuracy by means of a simplified Green's function approach [34] in the computational framework of our ZDO Hamiltonian. These investigations have shown that Koopmans' theorem is a sufficient approximation for ligand ionization processes in the outer valence region [9,10,25–28]; net reorganization energies of about 0.5 eV have been determined for electron ejections from these delocalized orbitals. In the case of ionization events out of MO's with predominant 3*d* amplitudes a close correspondence between the calculated Koopmans' defects and the localization properties of the orbital wave function is observed. In related molecules with comparable MO properties, nearly constant reorganization energies have been determined, these being a function of the 3*d* center and of the coordination pattern of the ligands.

In order to avoid the time-consuming perturbational Green's function calculations for each Cr complex we applied the many-body approach to $Cr(CO)_6$. The self-energy part was approximated by a renormalized model potential [26–28], 14 hole-states and 11 particle states were considered in the perturbational summation. The calculated reorganization energy of the t_{2g} ionizations of $Cr(CO)_6$ ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$), $\Delta I_{t_{2g}}$, was used to correct the one-electron energies of the Cr $3d$ orbitals in the pentacarbonyl complexes. For $\Delta I_{t_{2g}}$ an energy increment of 1.61 eV was calculated; the one-electron energies of the ligand orbitals were corrected by 0.5 eV, a value based on our previous experience. The theoretically determined ionization energies of the pentacarbonyl complexes with Cr are therefore given by the two simple formulae:

Cr $3d$ ionization $\quad -I_{v,j}^{\text{cal}} = \varepsilon_j + \Delta I_{t_{2g}}$

ligand ionization $\quad -I_{v,j}^{\text{cal}} = \varepsilon_j + \Delta I_{\text{ligand}}$

$\Delta I_{t_{2g}} = 1.61$ eV, $\Delta I_{\text{ligand}} = 0.50$ eV

(3) Ground state properties

To rationalize the electronic structure of the free ligands we considered the interaction between the sp^n lone-pair of X and the $p\pi$ orbital at Y leading to a bonding and an antibonding linear combination [22]. In the pentacarbonyl complexes a localized representation for the ligand lone-pairs (sp^n, p_π) is more suitable. The sp^n orbital of the coordinated Me_2X moiety is stabilized due to the $3d_{z^2}/4p_z$ acceptor of the pentacarbonyl fragment, while the uncomplexed XMe_2/YMe lone-pair function is only slightly perturbed in the $M(CO)_5L$ complex. Thus a lone-pair sequence $p\pi/(sp^n)$ uncomplexed on top of the sp^n complexed orbital is to be expected.

The t_{2g} orbitals of an unperturbed octahedron ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$) split into a b_2 linear combination ($3d_{xy}$) and into an e combination ($3d_{xz}$, $3d_{yz}$) if the symmetry is lowered from O_h to C_{4v} (used for the $M(CO)_5L$ complexes) [35]. For the Cr $3d$ orbitals the MO sequence b_2 ($3d_{xy}$) on top of e ($3d_{xz}/3d_{yz}$) must be expected as a result of the reduced acceptor capability of the axial heteroligand compared with the carbonyl group.

The CNDO/INDO orbital energies, ε_i, for the six chromium pentacarbonyl derivatives with the ligands Me_2PSMe, Me_2PSeMe, Me_2AsSMe, $Me_2AsSeMe$, Me_2PPMe_2 and $Me_2AsAsMe_2$ are summarized in Table 1. It is seen that the qualitative expectations are in accordance with the computational findings. The three highest occupied orbitals of the pentacarbonyl complexes are Cr $3d$ linear combinations.

The near degeneracy between two $3d$ functions ($3d_{xz}$ and $3d_{yz}$) shows that the point group C_{4v} is a sufficient approximation to define the irreducible representations of the complex. The energy gap between b_2 ($3d_{xy}$) and e ($3d_{xz}/3d_{yz}$) spans a range between 0.2 and 0.5 eV with the expected sequence. Two exceptions are the Me_2PSMe and Me_2PPMe_2 derivatives where negligible b_2/e splits are predicted. With respect to the t_{2g} set of $Cr(CO)_6$ a destabilization of the Cr $3d$ orbitals in the pentacarbonyl complexes of about 2 eV is predicted. This can be attributed to the enhanced σ donor properties of the heteroligands and their reduced π acceptor capability.

The next MO in the Cr complexes is always the sp^n/p_π combination of the

TABLE 1

ORBITAL ENERGIES (ε_i), MO-TYPE AND Cr 3*d* CONTRIBUTION OF THE HIGHEST OCCUPIED MO's IN THE CHROMIUM PENTACARBONYL LIGAND COMPLEXES ACCORDING TO SEMIEMPIRICAL CNDO/INDO CALCULATIONS. Me = CH_3

Compound	MO	MO-Type	ε_i (eV)	% Cr 3*d*
$Cr(CO)_5Me_2PSMe$	44	$3d_{xy}$	−9.34	54.7
(INDO)	43	$3d_{xz}/3d_{yz}$	−9.36	66.8
	42	$3d_{xz}/3d_{yz}$	−9.37	66.7
	41	S p_π	−11.40	0.3
	40	P(n)(CrP-σ)	−11.74	4.1
$Cr(CO)_5Me_2PSeMe$	44	$3d_{xy}$	−8.96	50.3
(CNDO)	43	$3d_{xz}/3d_{yz}$	−9.43	70.0
	42	$3d_{xz}/3d_{yz}$	−9.44	70.0
	41	Se p_π	−11.19	0.9
	40	P(n)(CrP-σ)	−11.90	2.9
$Cr(CO)_5Me_2AsSMe$	44	$3d_{xy}$	−9.15	52.6
(CNDO)	43	$3d_{xz}/3d_{yz}$	−9.55	70.0
	42	$3d_{xz}/3d_{yz}$	−9.56	70.0
	41	S p_π	−12.00	0.1
	40	As(n)(CrAs-σ)	−12.29	2.5
$Cr(CO)_5Me_2AsSeMe$	44	$3d_{xy}$	−9.10	52.2
(CNDO)	43	$3d_{xz}/3d_{yz}$	−9.50	69.8
	42	$3d_{xz}/3d_{yz}$	−9.50	69.8
	41	Se p_π	−11.37	0.1
	40	As(n)(CrAs-σ)	−12.12	2.6
$Cr(CO)_5Me_2PP'Me_2$	47	$3d_{xz}/3d_{yz}$	−9.31	65.3
(INDO)	46	$3d_{xy}$	−9.33	53.7
	45	$3d_{xz}/3d_{yz}$	−9.34	66.5
	44	P′(n) (uncomplexed)	−11.48	1.7
	43	P(n)(CrP-σ)	−11.99	2.9
$Cr(CO)_5Me_2AsAs'Me_2$	47	$3d_{xy}$	−9.02	52.8
(CNDO)	46	$3d_{xz}/3d_{yz}$	−9.38	69.2
	45	$3d_{xz}/3d_{yz}$	−9.38	69.4
	44	As′(n) (uncomplexed)	−11.56	0.3
	43	As(n)(CrAs-σ)	−11.59	2.6

uncomplexed XMe_2/YMe moiety; the calculated stabilization of the 3*d* coupled lone-pair lies in the range between 0.03 eV (AsAs derivative) and 0.7 eV (PSe, AsSe complexes).

In Table 2 the calculated net charges of the six chromium pentacarbonyl complexes are collected [36]. In the case of the symmetric Me_2XXMe_2 complexes the electron density of the coordinated heteroatoms is slightly reduced as a result of a ligand to metal charge transfer. This increase in positive charge is also encountered in the H atoms of the CH_3 groups of the complexed elements.

Wiberg bond indices [36] are collected in Table 3. The two different ZDO variants (CNDO/INDO) lead to different bond indices for the various metal ligand

TABLE 2

CALCULATED NET CHARGES IN THE SIX DIFFERENT CHROMIUM PENTACARBONYL COMPLEXES ACCORDING TO SEMIEMPIRICAL CNDO/INDO CALCULATIONS

Compound	Cr	C_{ax}	O_{ax}	$\bar{C}_{eq}$ [a]	$\bar{O}_{eq}$	X	X′ (Y)	$\bar{C}_{CH_3}$ (X)	$\bar{H}$ (X)	$\bar{C}_{CH_3}$ [X′(Y)]	$\bar{H}$ [X′(Y)]
$Cr(CO)_5Me_2PSMe$	0.317	0.120	−0.243	0.107	−0.234	0.114	−0.101	−0.254	0.115	−0.138	0.087
$Cr(CO)_5Me_2PSeMe$	0.425	0.064	−0.189	0.047	−0.195	0.120	−0.018	−0.124	0.094	−0.073	0.063
$Cr(CO)_5Me_2AsSMe$	0.367	0.073	−0.187	0.030	−0.181	0.302	−0.151	−0.197	0.081	−0.116	0.075
$Cr(CO)_5Me_2AsSeMe$	0.363	0.072	−0.188	0.030	−0.183	0.290	−0.095	−0.198	0.079	−0.086	0.059
$Cr(CO)_5Me_2PP'Me_2$	0.339	0.117	−0.243	0.102	−0.227	0.055	0.035	−0.262	0.112	−0.272	0.099
$Cr(CO)_5Me_2AsAs'Me_2$	0.370	0.069	−0.191	0.030	−0.188	0.169	0.133	−0.194	0.077	−0.190	0.064

[a] – denotes the averaged net charge.

TABLE 3

WIBERG BOND INDICES OF THE CHROMIUM PENTACARBONYL LIGAND COMPLEXES ACCORDING TO SEMIEMPIRICAL CNDO/INDO CALCULATIONS (For comparison also the bond indices of $Cr(CO)_6$ are given)

Compound	CrC_{ax}	CO_{ax}	CrC_{eq} [a]	CO_{eq} [a]	CrC'_{eq} [b]	CO'_{eq} [b]	CrX	XX/XY
$Cr(CO)_5Me_2PSMe$	0.881	2.071	0.725	2.132	0.733	2.092	0.251	0.949
$Cr(CO)_5Me_2PSeMe$	0.827	2.108	0.681	2.147	0.694	2.099	0.205	0.942
$Cr(CO)_5Me_2AsSMe$	0.852	2.114	0.682	2.146	0.696	2.129	0.358	0.951
$Cr(CO)_5Me_2AsSeMe$	0.851	2.112	0.683	2.143	0.695	2.1265	0.359	0.935
$Cr(CO)_5Me_2PPMe_2$	0.882	2.070	0.729	2.127	0.730	2.113	0.250	1.028
$Cr(CO)_5Me_2AsAsMe_2$	0.856	2.107	0.692	2.132	0.692	2.126	0.362	0.922
$Cr(CO)_6$	0.648	2.201						

[a] Bond indices for the two equatorial CO groups that are syn with respect to the orientation of the XX/XY moiety. [b] Bond indices for the two equatorial CO groups that are anti with respect to the orientation of the heteroligand.

interactions. The INDO approach yields a stronger covalent interaction between the 3*d* center and the carbonyl functions as well as the heteroligand L. But irrespective of the actual computational procedure some general trends can be discerned from the summarized material.

(a) The axial CrC_{ax} index exceeds the coupling strength of the equatorial chromium carbon value. The associated CO indices (CO_{ax}, CO_{eq}) indicate that this is the result of an enhanced metal to ligand charge transfer (π acceptor capability of the carbonyl groups) reducing the bond index of the axial CO bond.

(b) For the two topologically different types of equatorial CO ligands a predominance of the *anti*-coupling between the 3*d* center and the carbonyl functions is observed. This effect is caused by antibonding XX-σ (XY-σ) admixtures which hinder the covalent interaction for the *syn* ligands.

(c) The bond indices between chromium and the heteroatoms are small compared with the 3*d* carbonyl values. It is of some interest that the X atom of the fourth period (As) leads to a larger covalent interaction with the 3*d* center than the P

TABLE 4

^1H NMR DATA FOR THE $M(CO)_5L$ COMPLEXES AND OF THE FREE LIGANDS[a]

Compound	δ(ligand) (ppm)		δ(complex) (ppm)[b]		$\Delta\delta$ (ppm)[b,c]		Ref.
	Me_2X	XMe_2/ YMe	Me_2X	XMe_2/ YMe	Me_2X	XMe_2/ YMe	
L = Me_2PSMe	1.19	1.98					
Cr			1.23	1.60	0.04	−0.38	
Mo			1.21	1.54	0.02	−0.44	5,6,37
W			1.27	1.41	0.08	−0.57	
L = Me_2PSeMe	1.25	1.82					
Cr			1.28	1.38	0.03	−0.44	
Mo			1.29	1.43	0.04	−0.39	5,6,37
W			1.40	1.37	0.15	−0.45	
L = Me_2AsSMe	1.17	2.05					
Cr			1.21	1.78	0.04	−0.27	
Mo			1.19	1.69	0.02	−0.36	5,6,37
W			1.20	1.64	0.03	−0.41	
L = $Me_2AsSeMe$	1.23	1.90					
Cr			1.24	1.63	0.01	−0.27	
Mo			1.25	1.68	0.02	−0.22	5,6,37
W			1.32	1.57	0.09	−0.33	
L = Me_2PPMe_2	0.92	0.92					
Cr			1.08	0.89	0.16	−0.03	
Mo			1.07	0.82	0.15	−0.10	38
W			1.35	0.91	0.43	−0.01	
L = $Me_2AsAsMe_2$	0.98	0.98					
Cr			1.00	0.83	0.02	−0.15	
Mo			1.03	0.82	0.05	−0.16	39
W			1.13	0.78	0.15	−0.20	

[a] Solvent: C_6D_6 (20%); internal standard: TMS. [b] The first number in each double column (δ(complex), $\Delta\delta$) refers to the coordinated Me_2X group, the second refers to the uncomplexed XMe_2/YMe moiety. [c] $\Delta\delta = \delta(H)_{complex} - \delta(H)_{ligand}$.

donor. A detailed analysis of the orbital wave functions and the AO basis integral of the ZDO-Hamiltonian shows this to be due to the more diffuse As $4s/4p$ orbitals as compared with the $3s/3p$ valence set of P.

(4) ^{1}H-NMR Data

In Table 4 we have listed the ^{1}H shifts of the free ligands (δ(ligand)), the corresponding values for the complexes with Cr, Mo, and W (δ(complex)), and the coordination shifts $\Delta\delta$ of the pentacarbonyl fragments for all 18 possible metal (M) ligand (L) combinations.

The methyl signals of the coordinated Me_2X groups have undergone a lowfield shift, indicating a deshielding of the CH_3 protons due to coordination [5,6,37,38]. This effect is a consequence of the increase in positive charge on the P or As atom by the $M(CO)_5$ group. The calculated net charges for the chromium complexes (Table 2) support this interpretation.

The ^{1}H signals of the uncomplexed XMe_2/YMe moiety of the coordinated ligands are characterized by pronounced highfield shifts in comparison to the free ligands. This effect is explained on the basis of a decoupling of the lone-pair interaction in the XX or XY unit or on the basis of a multicenter $(d–d)\pi$ interaction in M–XX or M–XY fragments, leading to an enhanced electron density on the uncoordinated hetero-atom.

The analysis of the orbital wave functions in the chromium pentacarbonyl derivatives shows that the postulated lone-pair decoupling is reproduced by the model calculations. Furthermore the summarized net charges confirm the enhanced electron density in this ligand fragment. Both effects (decoupling and enhanced electron population) can be rationalized on the basis of $3s/3p$ or $4s/4p$ basis functions of the hetero-centers without explicit consideration of a multicenter $(d–d)\pi$ interaction. The metal ligand (X) coordination leads to a decoupling of the lone-pair interaction; this corresponds to a reduction of the antibonding two-center-four-electron coupling which produces the aforesaid ^{1}H shifts.

(5) ^{31}P NMR Data

Characteristic modifications of the ^{31}P frequencies for the Me_2PSMe and Me_2PSeMe complexes (M = Cr, Mo, W) have been reported [5,6,37]. On coordination most of the ^{31}P resonances undergo a remarkable lowfield shift, which is reduced in the series Cr > Mo > W and S > Se, respectively, and this is in line with previous experience on coordinated phosphanes [4–6,15,37]. An exception, however, is found for $W(CO)_5Me_2PSeMe$ (highfield shift). Detailed investigations have shown that this effect is attributed mainly to the nature of the M–P interaction and to a smaller extent to the SeMe group [37,40]. This conclusion is supported by the comparable δ_c variation in the two series $M(CO)_5Me_2PSMe$ (M = Cr, Mo, W) and $M(CO)_5Me_2PSeMe$ (M = Cr, Mo, W), respectively.

(6) Carbonyl Stretching Frequencies in the CO Valence Region

The IR spectra of the $M(CO)_5L$ complexes can be rationalized on the basis of an idealized C_{4v} geometry around the transition metal center leading to 3 IR-active CO

TABLE 5

CO FREQUENCIES $\nu(\mathrm{cm}^{-1})^a$ AND VALENCE FORCE CONSTANTS k (10^2 Nm^{-1}) OF THE Me_2XYMe COMPLEXES WITH Cr AND Mo AS nd (n = 3, 4) CENTER (Solvent cyclohexane)

Compound	$\nu(A_1^2)$	$\nu(B_1)$	$\nu(A_1^1)$	$\nu(E)$	k_1	k_2	k_i
$Cr(CO)_5Me_2PSMe$	2070 m	1989 m	1959 s	1947 vs	15.72	15.90	0.30
$Cr(CO)_5Me_2PSeMe$	2071 m	1987 w	1960 s	1949 vs	15.73	15.93	0.29
$Cr(CO)_5Me_2AsSMe$	2067 m	1989 w	1957 s	1947 vs	15.78	15.89	0.29
$Cr(CO)_5Me_2AsSeMe$	2073 w	1988 vw	1959 s	1952 vs	15.70	15.97	0.29
$Mo(CO)_5Me_2PSMe$	2078 m	1992 m	1961 s	1954 vs	15.75	16.02	0.30
$Mo(CO)_5Me_2PSeMe$	2080 m	1994 w	1962 s	1955 vs	15.76	16.04	0.30
$Mo(CO)_5Me_2AsSMe$	2080 m	1994 w	1963 s	1959 vs	15.76	16.09	0.30
$Mo(CO)_5Me_2AsSeMe$	2078 m	1994 w	1961 s	1956 vs	15.74	16.04	0.30

[a] Intensities: s, strong; vs, very strong; m, middle; w, weak; vw, very weak.

frequencies of the irreducible representations A_1^1, A_1^2 and E [41]. The A_1^1 vibration corresponds to the *trans* (axial) CO group, A_1^2 symbolizes the symmetric vibration of the four equatorial CO ligands while E represents the degenerate antisymmetric counterpart. For the CO frequencies the following relation is fulfilled: $\nu(A_1^2) > \nu(A_1^1) > \nu(E)$.

As representative IR data for the pentacarbonyl complexes the CO frequencies of the $M(CO)_5Me_2PSMe$ and $M(CO)_5Me_2PSeMe$ (M = Cr, Mo) derivatives are listed in Table 5. The force constants (k_1: *trans* CO ligand; k_2: *cis* CO ligands) and the interaction constant k_i were determined on the basis of the simplified Cotton–Kraihanzel force field [41].

The force constant of the *cis* (equatorial) CO ligands exceeds the k_1 value associated with the axial *trans* carbonyl function. This difference has often been attributed to a significant $(d\text{–}d)\pi$ interaction in the transition metal P or As bond [12,13]. The Wiberg indices of Table 3 on the other hand clearly reveal that this gradation of the carbonyl force constants can be rationalized without assuming $(d\text{–}d)\pi$ coupling. It was mentioned in section 3, above that the axial CrC Wiberg indices are larger than the equatorial ones, while the opposite is true for the associated CO indices. This can be explained in terms of dramatically reduced acceptor capabilities of the hetero fragments L leading to an increased charge transfer to the *trans* carbonyl ligand. This charge reorganization, of course, results in a strengthened transition metal carbon bond and a reduced CO bond order. In this section and in section 4 it has been shown that various experimental observations can be rationalized without the assumption of a $(d\text{–}d)\pi$ interaction; redistribution of the electronic charges in the pentacarbonyl compounds leads to a straightforward explanation of ^1H NMR shifts and of the magnitude of carbonyl force constants. It must be mentioned, however, that this does not mean that $(d\text{–}d)\pi$ interactions have no significance, as we do not know to what extent the $3d$ or $4d$ orbitals of P or As are involved in the exact wave function of the electronic ground state. To answer this question detailed ab initio studies with large bases are necessary.

(7) PE Spectra

The first vertical ionization potentials, $I_{v,j}$ of the 18 pentacarbonyl complexes are summarized in Table 6. As representatives we have shown six PE spectra in Fig. 1.

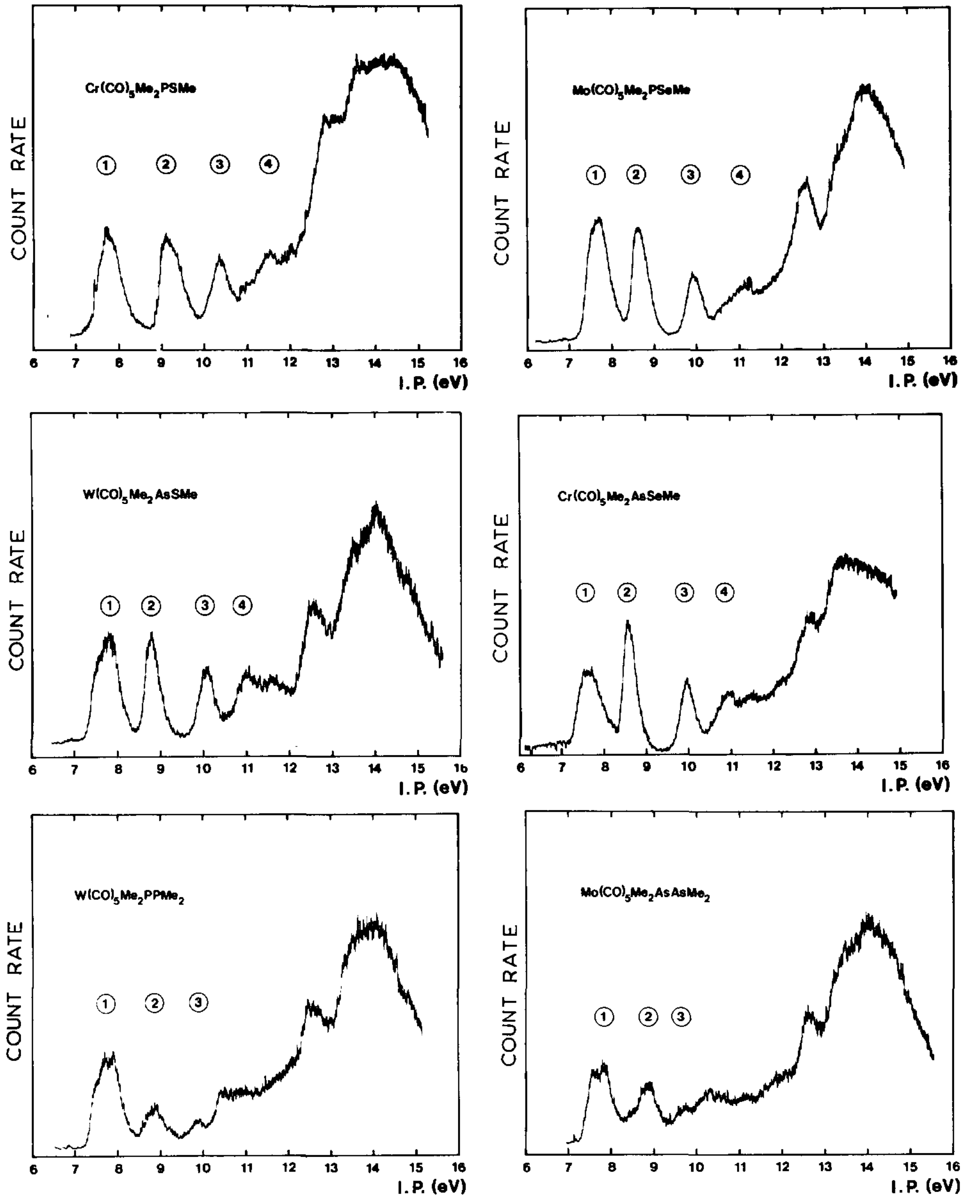


Fig. 1. He(I) PE spectra of Cr(CO)$_5$Me$_2$PSMe, Mo(CO)$_5$Me$_2$PSeMe, W(CO)$_5$Me$_2$AsSMe, Cr(CO)$_5$Me$_2$-AsSeMe, W(CO)$_5$Me$_2$PPMe$_2$, Mo(CO)$_5$Me$_2$AsAsMe$_2$.

In Fig. 2 we have correlated the first PE bands in the series Cr(CO)$_5$L (L = Me$_2$PSMe, Me$_2$PSeMe, Me$_2$AsSMe, Me$_2$AsSeMe, Me$_2$PPMe$_2$ and Me$_2$AsAsMe$_2$) and in Fig. 3 the first PE bands in the series M(CO)$_5$L (L = Me$_2$PSMe, Me$_2$PSeMe, Me$_2$PPMe$_2$) with M = Cr, Mo and W have been compared. To interpret the PE spectra empirically we refer to the first ionization energies for the unperturbed

TABLE 6

MEASURED VERTICAL IONIZATION POTENTIALS, $I_{v,j}^{exp}$, OF THE 18 TRANSITION METAL PENTACARBONYL COMPLEXES (All values in eV, sh, shoulder)

Compound	$I_{v,j}^{exp}$						
$Cr(CO)_5Me_2PSMe$	7.7			9.1	10.2_5	11.5	12.0
$Cr(CO)_5Me_2PSeMe$	7.6_5			8.8	10.1	11.2	
$Cr(CO)_5Me_2AsSMe$	7.6			8.9	10.1	11.1	11.8
$Cr(CO)_5Me_2AsSeMe$	7.7			8.6	10.0	11.0	11.6
$Cr(CO)_5Me_2PPMe_2$	7.7			8.8	9.8		
$Cr(CO)_5Me_2AsAsMe_2$	7.8			8.9	9.8		
$Mo(CO)_5Me_2PSMe$	7.8			8.9_5	10.2_5	11.5	12.1
$Mo(CO)_5Me_2PSeMe$	7.7			8.8	10.0	11.1	
$Mo(CO)_5Me_2AsSMe$	7.8	8.2_5(sh)		8.8	10.0	11.1	11.7
$Mo(CO)_5Me_2AsSeMe$	7.7	8.0 (sh)		8.6	10.0	11.0	11.6
$Mo(CO)_5Me_2PPMe_2$	7.7	7.9		8.9	9.9		
$Mo(CO)_5Me_2AsAsMe_2$	7.55	7.8		8.8	9.7		
$W(CO)_5Me_2PSMe$	7.9			9.1	10.3	11.4	
$W(CO)_5Me_2PSeMe$	7.9			8.7_5	10.2	11.2	
$W(CO)_5Me_2AsSMe$	7.6 (sh)	7.8		8.8	10.1	11.1	11.6
$W(CO)_5Me_2AsSeMe$	7.6	7.9		8.7	10.1	11.1	11.6
$W(CO)_5Me_2PPMe_2$	7.4 (sh)	7.7	7.9	8.8	9.9		
$W(CO)_5Me_2AsAsMe_2$	7.41	7.65	7.9	8.8	9.6		

hexacarbonyl complexes ($Cr(CO)_6$, 8.40 eV, $Mo(CO)_6$ 8.50 eV, and $W(CO)_6$ 8.56 eV) [17,42]: and the first ionization potentials of the free ligands which have been reported recently [22,43,44].

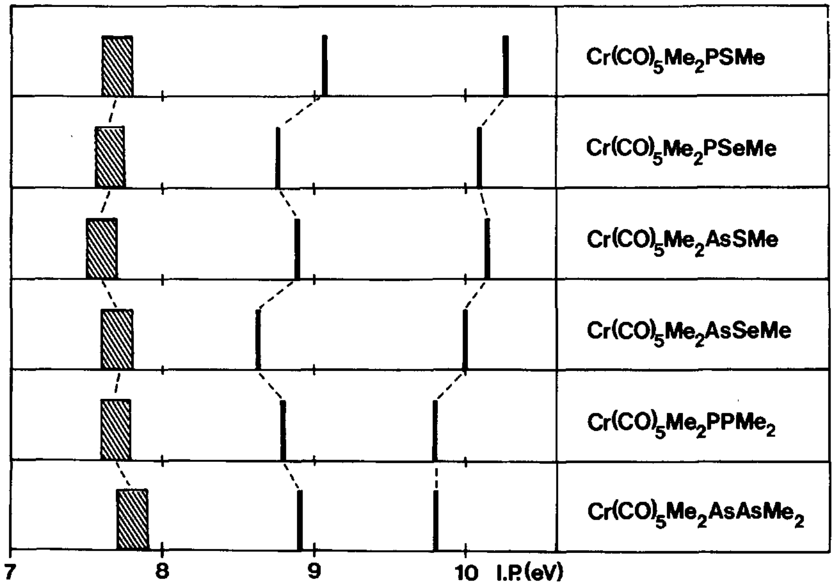


Fig. 2. Correlation between the first bands of the He(I) PE spectra of $Cr(CO)_5L$ with the ligands $L = Me_2PSMe$, Me_2PSeMe, Me_2AsSMe, $Me_2AsSeMe$, Me_2PPMe_2 and $Me_2AsAsMe_2$.

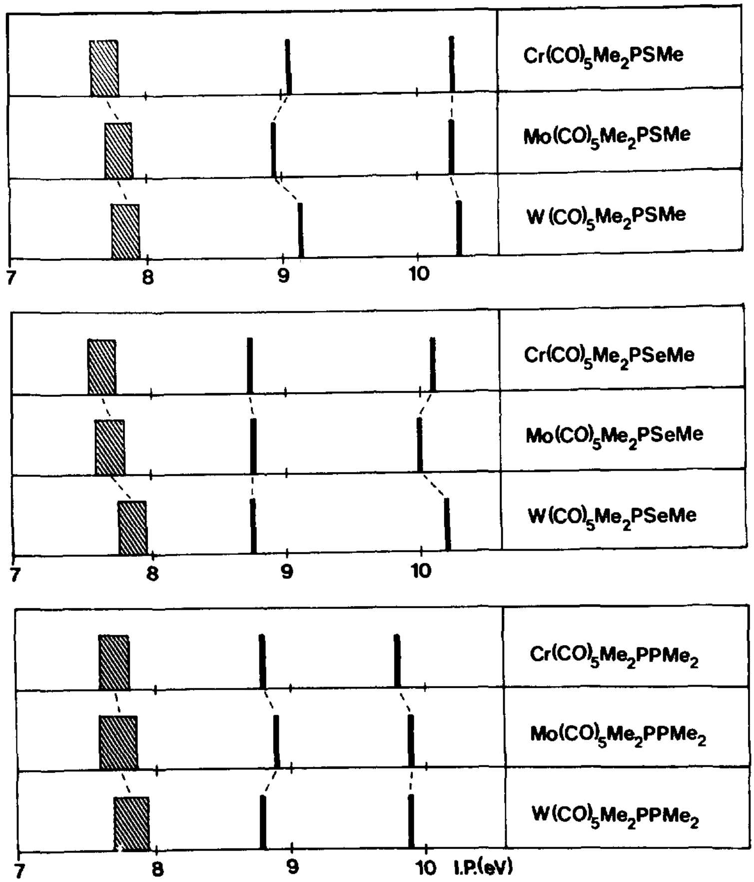


Fig. 3. Correlation between the first bands of the He(I) PE spectra in the series $M(CO)_5L$ (L = Me_2PSMe, Me_2PSeMe, Me_2PPMe_2) with M = Cr, Mo and W.

The PE spectra of the pentacarbonyl complexes have band structures that are always comparable for a common class of molecules. For the Cr derivatives a single maximum between 7.6–7.8 eV is observed which must be assigned to the three Cr $3d$ ($3d_{xy}$, $3d_{xz}$, $3d_{yz}$) ionization events. Compared to those of $Cr(CO)_6$, the nearly degenerate IP's are lowered by 0.8–0.6 eV. In the case of the unsymmetric Me_2XYMe ligands two well resolved band maxima are observed on the high energy side of the Cr $3d$ ionization processes. The first maximum is found between 8.6 and 9.05 eV and the second between 10.0 and 10.25 eV. It is clear that these two IP's are to be assigned to the p_π lone-pair of the YMe moiety and to the sp^n hybrid of the coordinated heteroatom. According to the theoretical analysis in section 3, the first ligand band corresponds to the p_π linear combination of the free lone-pair center and the second to the stabilized coordinated Me_2X unit. Typical sp^n and p_π ionization energies of ligand fragments are [45,46]: p_π: $(CH_3)_2S$ 8.71 eV, $(CH_3)_2Se$ 8.40 eV; sp^n: $(CH_3)_3P$ 8.60 eV, $(CH_3)_3As$ 8.65 eV.

The p_π lone-pair is stabilized by about 0.3 eV due to complexation of the ligand

L; the sp^n hybrid on the coordinated atom, however, is stabilized by more than 1.5 eV. These differences impressively demonstrate that the simplified MO model with (nearly) uncoupled lone-pairs is a sufficient approximation to rationalize the electronic structure of the transition metal pentacarbonyl complexes.

In most of the Me_2XYMe derivatives two additional maxima on the low energy side of the overlapping carbonyl bands can be detected. These ionization events can be assigned to the XX-σ orbital or to XC/YC-σ linear combinations [22]. In the two symmetric Me_2XXMe_2 complexes (X = P, As) broad ligand bands are detected that are not well resolved. Comparison with the PE spectra of the free ligands [43,44] suggests that different conformers (Me_2XXMe_2 orientation) are also present in the

TABLE 7

COMPARISON BETWEEN THE MEASURED VERTICAL IONIZATION POTENTIALS ($I_{v,j}^{exp}$) OF THE CHROMIUM COMPLEXES AND THEORETICALLY DEDUCED IONIZATION ENERGIES ($I_{v,j}^{cal}$)

Compound	MO	Assignment	$I_{v,j}^{cal}$	$I_{v,j}^{exp}$
$Cr(CO)_5Me_2PSMe$	44	Cr $3d_{xy}$	7.73	7.7
	43	Cr $3d_{xz}/3d_{yz}$	7.75	
	42	Cr $3d_{xz}/3d_{yz}$	7.76	
	41	S p_π	10.90	9.1
	40	P(*n*)(CrP-σ)	11.24	10.2_5
$Cr(CO)_5Me_2PSeMe$	44	Cr $3d_{xy}$	7.35	7.7
	43	Cr $3d_{xz}/3d_{yz}$	7.82	
	42	Cr $3d_{xz}/3d_{yz}$	7.83	
	41	Se p_π	10.69	8.8
	40	P(*n*)(CrP-σ)	11.40	10.1
$Cr(CO)_5Me_2AsSMe$	44	Cr $3d_{xy}$	7.54	7.6
	43	Cr $3d_{xz}/3d_{yz}$	7.94	
	42	Cr $3d_{xz}/3d_{yz}$	7.95	
	41	S p_π	11.50	8.9
	40	As(*n*)(CrAs-σ)	11.79	10.1
$Cr(CO)_5Me_2AsSeMe$	44	Cr $3d_{xy}$	7.49	7.7
	43	Cr $3d_{xz}/3d_{yz}$	7.89	
	42	Cr $3d_{xz}/3d_{yz}$	7.89	
	41	Se p_π	10.87	8.6
	40	As(*n*)(CrAs-σ)	11.62	10.0
$Cr(CO)_5Me_2PP'Me_2$	47	Cr $3d_{xz}/3d_{yz}$	7.70	7.7
	46	Cr $3d_{xy}$	7.72	
	45	Cr $3d_{xz}/3d_{yz}$	7.73	
	44	P′(*n*)(uncomplexed)	10.87	8.8
	43	P(*n*)(CrP-σ)	11.67	9.8
$Cr(CO)_5Me_2AsAs'Me_2$	47	Cr $3d_{xy}$	7.41	7.8
	46	Cr $3d_{xz}/3d_{yz}$	7.77	
	45	Cr $3d_{xz}/3d_{yz}$	7.77	
	44	As'_n(uncomplexed)	11.06	8.9
	43	As(*n*)(CrAs-σ)	11.49	9.8

$3d$ complexes (the same bandshape, however, is observed with the symmetric Mo and W species). The theoretically determined ionization energies $I_{v,j}^{\mathrm{cal}}$ for the six Cr complexes are listed in Table 7.

The experimental PE spectra are satisfactorily reproduced by the theoretical approach outlined in section 2. The energy range of the Cr $3d$ ionization processes is predicted with high accuracy; the deviations between theory and experiment are less than 0.3 eV. The predicted ionization potentials for the ligand orbitals are too high. In some cases p_π/sp^n gaps are predicted that are smaller than the measured lone-pair separation. These deviations may be the result of small imbalances in the atomic core energies in the computational procedure or can be ascribed to deviations of the real geometry from the assumed idealized structures. The slight asymmetry of the Cr $3d$ band in the six pentacarbonyl derivatives is in line with the predicted b_2/e separation of the $3d$ functions in the pentacarbonyl complexes. The splitting patterns of the ligand ionization processes in the molybdenum and tungsten pentacarbonyls are similar to that of the Cr derivatives; significant differences are found in the case of the transition metal ionization events. The $4d$ splitting pattern of the $Mo(CO)_5Me_2PYMe$ (Y = S, Se) complexes is comparable to that of the $3d$ bands in the Cr compounds, only one maximum being detected. In the two unsymmetric As complexes high energy shoulders are found. Furthermore the $4d$ band is perturbed in the two symmetric Me_2XXMe_2 derivatives, where two distinct maxima are found. In both pentacarbonyl compounds there is an energy gap of about 0.25 eV between the two centers of gravity. This separation of the various transition metal d ionization energies is enhanced still more in the W derivatives. On the other hand only one maximum is detected in the Me_2PXMe (X = S, Se) complexes where P is coordinated to the $5d$ center. The bandshape is highly unsymmetric in the As complexes; a pronounced low energy shoulder is found for the AsS system and two maxima for the AsSe complex. Three maxima are encountered in the symmetric Me_2XXMe_2 pentacarbonyls; in the P derivative two maxima are separated from a low energy shoulder, while three distinct maxima are separated in the first profile of the $Me_2AsAsMe_2$ complex.

These results clearly indicate that the splitting pattern of the nd ($n = 3,4,5$) ionization processes is influenced by variation of the transition metal center (Cr → Mo → W) as well as by changing the coordinated heteroatom (P, As) or the ligand type (Me_2XYMe, Me_2XXMe_2). The gap between the band maxima increases with increasing atomic number of the transition metal or the coordinated ligand atom, and can so be correlated to increasingly diffuse AO basis functions leading to a larger covalent interaction. In the case of the Me_2XXMe_2 ligands we assume that larger deviations from the idealized C_{4v} symmetry (e.g. mixture of different conformers) result in stronger perturbations of the orbital symmetry. Increase in the differences between transition metal ionization processes with increasing atomic number have been detected in our laboratory in PE studies on the bis-π-allyl complexes of Ni, Pt and Pd [23]. In the light of the foregoing discussion and of the data for the whole variety of pentacarbonyl derivatives studied in this paper, it is highly questionable that separated band maxima in $W(CO)_5L$ complexes have their origin in spin–orbit coupling of the transition metal center [19,20]. We believe that the different maxima of the $4d$ and $5d$ ionization events in the Mo and W complexes originate in an increased metal ligand overlap, leading to a more pronounced separation of the complex MO's with predominant transition metal amplitudes. Of course it is impossible to give an unambiguous assignment of the various "transition metal" maxima due to the lack of exact MO calculations for the Mo and W complexes.

(8) Conclusion

The electronic structures of VIA pentacarbonyl complexes have been studied by semiempirical MO calculations and by various spectroscopy techniques (^1H NMR and ^{31}P NMR, IR and PE). It has been demonstrated that their electronic structure can be rationalized by means of simple MO models. Comparison between experimental data and theoretical results has shown that most of the observed phenomena can be explained without the assumption of a pronounced $(d\text{–}d)\pi$ interaction between the transition metal center and the heteroligands. On the basis of our experience, the investigation of excited state properties (e.g. UV spectra) seems likely to be more promising for revealing multicenter $(d\text{–}d)\pi$ couplings.

(9) Experimental

The syntheses of the 18 transition metal pentacarbonyl complexes have been described in the literature [5,6,37–39]. The samples were purified by means of distillation or sublimation, and their purities checked by NMR, IR and mass spectroscopy.
The He(I) spectra were recorded on a PS 18 spectrometer at Perkin–Elmer Ltd. (Beaconsfield, England), and were calibrated with Argon and Xenon. A resolution of about 20 meV of the Ar/Xe lines was obtained.

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